PROCEEDINGS OF THE
SEVENTEENTH TECHNICAL
SEMINAR ON CHEMICAL SPILLS

COMPTE RENDU: 17e COLLOQUE
TECHNIQUE SUR LES DÉVERSEMENTS
DE PRODUITS CHIMIQUES

JUNE 12 AND 13, 2000
VANCOUVER, BRITISH COLUMBIA
CANADA

LES 12 ET 13 JUIN 2000
VANCOUVER, COLOMBIE-BRITANNIQUE
CANADA

Canada

PROCEEDINGS

Seventeenth Technical Seminar
on Chemical Spills

June 12 and 13, 2000
Coast Plaza Suite Hotel
Vancouver, British Columbia
Canada

Seminar sponsored by

Environmental Protection
Service
Environmental Technology
Advancement Directorate
Environment Canada

COMPTE RENDU

Dix-septième colloque technique
sur les déversements de produits
chimiques

les 12 et 13 juin 2000
Hôtel Coast Plaza Suite
Vancouver, Colombie-Britannique
Canada

Colloque commandité par le

Service de la protection de
l'environnement
Direction générale pour
l'avancement des technologies
environnementales
Environnement Canada

NOTICE

The papers in these Proceedings are published as submitted by the authors. Any statements or views presented here are those of the authors. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Inquiries related to the technical content of papers in this seminar should be directed to the author(s).

Inquiries related to the **Technical Seminar on Chemical Spills**, in general, should be directed to:

Emergencies Science Division
Environment Canada
3439 River Road
Ottawa, Ontario, Canada
K1A 0H3
Phone: (613) 998-9622
Fax: (613) 991-9485
www.etcentre.org/conferences/index.html

Cover Photograph
Derailed tank cars containing sulphuric acid, near Temagami, Ontario.
March 14, 2000

Photo courtesy of: Transport Canada, Ontario Region

AVIS

Les textes contenus dans le présent document sont publiés tels qu'ils sont présentés par les auteurs. Les déclarations et opinions apparaissant dans ce document sont celles des auteurs. La mention de marques de commerce ou de produits commercialisés ne constitue ni une approbation ni une recommandation d'emploi.

Toute demande d'information relative au contenu technique des textes devrait être faite directement auprès des auteurs concernés.

Les demandes relatives au **Colloque technique sur les déversements de produits chimiques** devraient être adressées à:

Division des urgences - science
Environnement Canada
3439, chemin River
Ottawa, Ontario, Canada
K1A 0H3
Tél: (613) 998-9622
Fax: (613) 991-9485
www.etcentre.org/conferences/index.html

Photographie de la couverture
Wagons-citerne déraillés contenant de l'acide sulphurique, près de Temagami, Ontario.
14 mars, 2000.

Courtoise de: Transports Canada, Région de l'Ontario

TABLE OF CONTENTS
TABLE DES MATIÈRES

PAGE

Countermeasures Technology
Techniques d'intervention

Fate and Effects
Sort et effets

PAGE

Monitoring and Analysis
Surveillance et analyse

Safety and Logistics
Sécurité et logistique

PAGE

The Evaluation of Technologies for the Remediation of Contaminated Sediments

D.Cooper, D. Velicogna, K. Volchek, M.Punt
SAIC Canada
Gloucester, Ontario, Canada
david.cooper@saic.com

V. Sharivker
Reactive Energy LLC
Gloucester, Ontario, Canada

Abstract

Many of the commonly available soil remediation processes have limitations with respect to the types of soils and contaminants for which they are amenable. Typically, no one treatment process can clean up a contaminated soil, because of the variability in the contaminants and the soil types found. As well, many of the commonly used remediation processes, such as conventional bioremediation or soil vapour extraction, cannot treat soils containing recalcitrant contaminants (such as chlorinated compounds, PDBs, dioxins and furans) or those having high clay contents.

SAIC Canada has performed several laboratory-, bench-, and field-scale evaluations whereby multiple treatment processes were combined in order to adequately remediate a contaminated site. This paper will discuss the evaluation of a suite of bench scale processes which were used to remediate soil sediments, and present details of the optimizations of selected technologies to develop a possible treatment train.

1.0 Introduction

Several attempts to remediate the selected sediments have failed in the past, in part due to technologies which could not handle the unique mix of contaminants and the nature of the soil and sediment matrix. This project looked at a suite of technologies and determined their performance impact. The primary objective of this study was to document the results of bench scale testing using a suite of technologies to determine their effectiveness at segregating or destroying contaminants in the sampled sediment.

The study generally followed the following steps:

- Sediment Analysis: A plan was implemented to obtain samples of the sediment and analyse those samples for heavy metals, PAHs, MOG and PCBs.
- Technology Selection: An analysis of the sediment identified both organic and inorganic contamination which may be amenable to treatment by different technologies. Technologies were selected based upon their successful treatment of similar soils or contaminants, or by new and promising technology which should theoretically have a positive impact on the remediation of the soil. The chosen technologies included:

- Soils Washing (Enhanced)
- Chemical Leaching
- Microwave Assisted Process
- Two-Phase Partitioning Bioreactor
- Organic Destruction Process
- Advanced Oxidation Process
- Microwave Activated Cracking
- Supercritical Fluid Extraction

2.0 SAIC Testing Facility

Testing took place at the Science Applications International Corporation (SAIC) research facility, located in Environment Canada's Environmental Technology Centre located in Gloucester, Ontario near Ottawa's International Airport.

2.1 Testing Analysis and Results

Contaminants which were analysed included: heavy metals (HM), mineral oil and grease (MOG), polyaromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs). Samples taken were carefully labelled and stored in a fridge. Analyses were carried out by SAIC Canada and Seprotech Laboratories.

3.0 Equipment Descriptions

3.1 Soil Washing

Soil washing (SW) is a process which removes contaminants by either solubilising them in a washing solution or separating them along with finest size fractions of the soil. SW is a generic term that includes both physical washing (conventional soil washing) and chemical leaching (soil leaching). It has been extensively used in site remediation practices in Europe where techniques involve both washing and leaching. In North America its application is mainly limited to washing but leaching is also becoming more common.

SW can be used not only as stand-alone process but also as a pre-treatment step followed by a physicochemical treatment of soil fines. In this case, SW is sometimes called wet classification. Soil washing was studied in this project with respect to its evaluation as pre-treatment technique (wet classification), as a remediation technique enhanced with solvents and surfactants, and as a remediation technique enhanced with acid.

3.1.1 Experimental Method - Wet Classification

The goal of this subtask was to separate a soil sample into several particle size fractions. The fractions would be analyzed for heavy metals and mineral oil and grease (MOG). Based on analytical results, it would become known whether soil can be concentrated into a smaller volume by means of mechanical separation.

Testing took place through a variety of steps which included sieving the soil sample and analyzing the resulting fractions.

Results of the wet classification are provided in Table 1. It is obvious that the sample consists mainly of fines: almost 95% of the total mass is represented by

particles with a size less than 150 microns. At the same time, particles larger than 1 mm make less than 3% of the total mass.

Table 1 Results of Wet Soil Classification

Particle size fraction (mm)	Weight percentage	Concentration of constituents (ppm)										
		As	Cr	Cu	Fe	Pb	Mo	Mn	Ni	Sn	Zn	MOG
>4	0.87	<5	14	29	21,600	40	<1	168	5	<20	61	62,000
1 to 4	1.95	30	50	67	39,600	89	<1	474	21	20	103	22,900
0.425 to 1	1.07	<5	96	202	109,000	200	25	964	56	48	186	41,100
0.15 to 0.425	1.51	<5	170	273	182,000	231	42	1,780	104	150	305	22,000
0.075 to 0.15	6.65	50	249	623	405,000	310	46	3,540	195	63	284	170,000
0.038 to 0.075	24.13	<5	260	575	520,000	218	87	4,070	192	68	185	4,000
<0.038	63.82	80	300	790	523,000	408	38	4,410	237	35	360	3,190
Bulk soil	100.00	55	277	692	489,903	339	59	4,070	213	48	739	15,617

Sample A Initial weight: 2.89 kg (wet), 1.95 kg (dry)

The distribution of heavy metals was found to be as expected, i.e. as the particle size diminished, the contaminant concentration was found to increase. From Table 1, fractions with particle sizes 1 mm and larger contained most of the heavy metals in concentrations below environmental limits.

The distribution of MOG in fractions did not follow the same trend. This was likely due to the fact that petroleum hydrocarbons, whose concentrations were characterized by MOG, were present as free products. In wet classification, significant amount of those free products were retained by sieves which resulted in their higher apparent concentrations in larger size fractions.

Overall, SW should be considered as a useful tool in identifying the distribution of contaminants, especially heavy metals, in different soil fractions. At the same time, it will likely be impractical to use it as a pre-treatment step at full scale for theses sediments. Relatively "clean" fractions represent less than 3% of the soil's weight and the use of wet separation to retrieve these 3% will not be economical.

3.1.2 Enhanced Washing

It has been reported that the effectiveness of physical washing of petroleum-contaminated soils can be enhanced by using a hot water, surfactant, a solvent of a combination thereof. A series of tests were carried out to estimate the effect of those factors on the removal of contaminants. Soil samples were analyzed for MOG only as metals removal was not expected..

Testing took place through a variety of steps;

- Combine a soil sample and water to make a 15% slurry (w/w).
- Place the slurry into the bucket of the flotation machine. Conduct the test at an ambient temperature.
- Start agitation.
- Start aeration.

- Collect the froth for 1 hour.
- Filter the froth and determine its weight.
- Filter the solid residues in the bucket and determine their weight.
- Repeat procedures 1 through 7 using the following conditions:
- 80°C, no additives;
- 80°C, 1g/L surfactant added;
- 80°C, 10% isopropyl alcohol and 1g/L surfactant added; and
- 80°C, 10% isopropyl alcohol and 1g/L surfactant added.
- Submit samples to the lab for MOG analyses.

Results of the enhanced washing are provided in Table 2. The use of hot water, surfactants and solvents alone or in a combination was not effective in removing petroleum hydrocarbons. This is likely due to the presence of hydrocarbons primarily as heavy products. More vigorous conditions, such as higher temperatures and stronger solvents are likely required to enhance the removal.

Table 2 The Effect of Surfactant and Solvent Washing

Sample Description	Sample mass (g)	Beaker mass (g)	MOG (%)	MOG % Removal
Unprocessed Sample A	11.41	54.3771	7.20	
Filter cake (80 C)	11.42	50.7110	6.06	16%
Float (80 C)	12.67	57.4306	6.82	
Filtrate (80 C)	200.00	56.3214	0.02	
Filter cake (80 C, 1g/L surf.)	11.28	58.3088	6.32	12%
Float (80 C, 1g/L surf.)	10.80	57.4191	5.52	
Filtrate (80 C, 1g/L surf.)	200.00	54.2584	0.27	
Filter cake (80 C, 10% (v/v) ISA)	12.16	57.9018	6.88	4%
Float (80 C, 10% (v/v) ISA)	11.39	49.6665	6.16	
Filtrate (80 C, 10% (v/v) ISA)	200.00	48.5699	0.22	
Filter cake (80 C, 1 g/L surf.,10% (v/v) ISA)	14.14	49.7922	6.07	16%
Float (80 C, 1 g/L surf.,10% (v/v) ISA)	6.39	50.7817	10.30	
Filtrate (80 C, 1 g/L surf.,10% (v/v) ISA)	200.00	49.8511	0.18	
Filter cake (20 C)	12.74	51.7744	6.38	11%
Float (20 C)	11.23	52.3689	7.38	
Filtrate (20 C)	200.00	53.1765	0.00	

3.1.3 Chemical Leaching

Organic acids were reportedly used to simultaneously remove both inorganic and organic contaminants. This effect could be achieved due to a "dual" nature of an organic acid that is both an acid capable of dissolving metals and an organic solvent capable of solubilizing organic compounds. Three low molecular weight acids were selected for evaluation tests: formic (FA), acetic (AA) and propionic (PA). In addition, acetic anhydride was for a comparative study. Acetic anhydride was also reported to be effective in removing both metals and non-metals in certain conditions.

Tests were carried out at elevated temperatures to maximize a possible removal of contaminants. This was achieved by boiling soil slurries using a reflux condenser. In some experiments, distillation was done with a distillate recovery. It

was expected that this distillate would contain water, so reducing the water content in the slurry would increase its hydrophobicity. A higher hydrophobicity would enhance the removal of organic contaminants.

Table 3 illustrates results of leaching using the three acids specified above. There is no clear indication that would suggest the most and the least effective acid. For example, FA was much more effective in removing arsenic then the two other acids. At the same time, it was the least effective in removing nickel. Lead concentration was reduced by 25-32% using AA and FA and only by 6-7% using PA. Among all metals, nickel, zinc, and lead had the highest removal rates reaching 32-34%. Copper removal was the lowest not exceeding 2.4%.

It is assumed that acids have different affinities towards each metal. This assumption requires an experimental verification; however, it appears to be possible to predict now which acid would be more effective in removing a specific metal.

Table 4 shows results of metals removal using acetic acid and acetic anhydride. In both cases, the slurry was boiled and, in case of acetic acid, dewatered. Results of these series of tests are somewhat consistent with data in Table 3. Lead removal was highest whereas copper removal was the lowest.

Metal removals in Tables 3 and 4 appear to be low; however, the results should be compared to removals under TCLP conditions. Even though metal concentrations may appear to be high, they may be strongly bound to the soil matrix thus being hardly leachable. Those bound metals are much less hazardous than free unbound metal ions. Once PAH removal results become available, a final judgement may be made on the effectiveness of the above leaching technique.

Table 3 Metal Removal Using Acetic (AA), Formic (FA), and Propionic (PA) Acids

Conditions	As			Cr			Cu		
	[liquid]	[soil]	% removal	[liquid]	[soil]	% removal	[liquid]	[soil]	% removal
Feed Soil Sample	5.5	136.8		4.4	109.7		16.2	403.0	
60°C; 2 hrs	0.4	8.5	6	0.8	16.2	15	0.1	1.5	0
100°C; 2 hrs	0.1	2.0	2	1.0	20.0	18	0.1	1.6	0
Boiling; 2 hrs	0.1	2.1	2	0.9	18.5	17	0.1	2.1	1
60°C; 2 hrs	1.1	26.7	20	0.6	14.6	13	0.3	7.8	2
100°C; 2 hrs	1.2	27.5	20	0.5	10.8	10	0.4	9.9	2
60°C; 2 hrs	0.2	4.2	3	0.7	15.3	14	0.2	4.8	1
100°C; 2 hrs	0.1	2.4	2	0.8	20.0	18	0.2	5.5	1
	Fe			Pb			Mn		
	[liquid]	[soil]	% removal	[liquid]	[soil]	% removal	[liquid]	[soil]	% removal
Feed Soil Sample	4,440	110,448		12.5	310.9		57.9	1440.3	
60°C; 2 hrs	611	13,056	12	4.3	91.9	30	6.3	135.5	9
100°C; 2 hrs	614	12,280	11	5.0	100.0	32	8.2	164.8	11
Boiling; 2 hrs	562	11,708	11	4.5	93.8	30	7.5	156.7	11
60°C; 2 hrs	496	12,039	11	3.3	80.1	26	13.5	327.7	23
100°C; 2 hrs	803	18,417	17	4.2	96.3	31	16.0	367.0	26
60°C; 2 hrs	637	13,326	12	1.1	23.0	7	15.0	313.8	22
100°C; 2 hrs	644	15,481	14	0.8	19.2	6	17.3	415.9	29

...Table 3 cont'

	Ni			Zn		
	[liquid]	[soil]	% removal	[liquid]	[soil]	% removal
Feed Soil Sample	5.07	126.12		10.10	251.24	
60°C; 2 hrs	1.91	40.81	32	1.78	38.03	15
100°C; 2 hrs	2.18	43.60	35	2.93	58.60	23
Boiling; 2 hrs	1.97	41.04	33	2.73	56.88	23
60°C; 2 hrs	0.26	6.31	5	1.14	27.67	11
100°C; 2 hrs	0.54	12.39	10	1.38	31.65	13
60°C; 2 hrs	1.61	33.68	27	1.82	38.08	15
100°C; 2 hrs	1.63	39.18	31	2.82	67.79	27

Table 4 Acetic Anhydride and Acetic Acid Washing

Sample ID SW...	Decription	Pb conc [ppm]	Pb % removal	Fe conc [ppm]	Fe % removal	Zn conc [ppm]	Zn % removal	Hg conc [ppm]	Hg % removal
AN-101	Feed Soil Sample	311		110,448		251		499	
Acetic Anhydride									
AN-102	After 1 hr boiling	157	49%	92,483	16%	203	19%	442	11%
AN-102A		9		424		31		<MDL	
AN-103	After boiling and distillate recovery	165	47%	89,792	19%	223	11%	454	9%
AN-103A		6		180		68		<MDL	
AN-104	After boiling, distillate recovery	232	25%	63,380	43%	308	0%	425	15%
AN-104A	and boiling the non-aqueous slurry	10		290		85		<MDL	
Acetic Acid									
AN-105	After 2 hr boiling	154	50%	86,693	22%	201	20%	396	21%
AN-105A		134		20,904		194		<MDL	
AN-106	After 6 hr boiling	148	52%	89,234	19%	232	8%	370	26%
AN-106A		136		17,420		209		<MDL	

Suffix "A" corresponds to a liquid filtrate of a related solid sample

3.2 Evaluation of the Microwave-Assisted Process

The Microwave-Assisted Process (MAP) technology uses microwaves to enhance the extraction of target compounds from a wide range of materials. Past research has shown that microwave-enhanced extraction of contaminants from soil is an effective sample preparation method for the analysis of contaminated soils. The

key to the technology is the use of solvents that are relatively transparent to microwaves compared to the matrix from which the target compound is being extracted. When the solvent/material mixture is exposed to microwaves, heating occurs only in localised microwave-absorbing areas within the material. The resulting pockets of high temperatures and pressure force the target compounds from the matrix into the solvent, which remains relatively cool. Microwave-enhanced solvent extraction has been shown to require far less energy than conventional solvent-extraction techniques because neither extensive mixing nor heating of the complete slurry is required.

3.2.1 Experimental Method

Two set of tests were performed using a bench-scale MAP unit and two sediment samples. For each set of tests three separate feed samples were taken for analysis of the initial soil. Three additional samples were accurately weighed on pre-weighed aluminium weighing dishes and placed in the fume hood. They were re-weighed after 48 hours to determine the average moisture content of the soil.

Samples of the moist soil were extracted using a Prolabo Soxwave laboratory microwave extraction unit. The procedure used for these tests will be as follows:

- Approximately ten grams of soil were accurately weighed in an extraction vessel and 30 mL of a selected solvent or solvent mixture were added to the vessel.
- The extraction vessel was placed into the microwave extraction chamber.
- The extraction unit was run for a selected exposure time at a selected power level.
- At the end of the exposure time, the extraction vessel was removed from the unit.
- The contents was filtered into a round-bottom flask through a fine porosity filter paper (Whatman #50) in a glass funnel.
- When solvent stopped draining from the filter paper, the filter paper containing the soil residue was carefully placed in a 50 mL beaker and covered with foil. These samples were sent for analysis.
- The contaminated solvent collected in the round bottom flasks was transferred to sealed containers for archiving.

Table 5 summarises the test conditions run during the two test sets. Each test condition was run in triplicate for QA/QC purposes. Run 1 was performed using the first sample designated "A" sediment, while Run 2 was performed using a combination of sediments designated "A", "B" and "C". Tests 1-1, 1-2 and 2-1 were control samples that use the same procedure as above but without exposing the soil/solvent mixture to microwave. The PCB and PAH results for all the runs performed are presented in Tables 6.

Table 5 Summary of MAP Experiments Performed

Run # /Test #	Solvent	Power (W)	Time (s)	Comments
1-1	hexane/acetone (9:1 by vol)	0	60	let stand for 60 seconds (no microwave)
1-2	hexane/acetone (9:1 by vol)	0	60	shaken for 60 s
1-3	hexane/acetone (9:1 by vol)	30	30	microwave extraction
1-4	hexane/acetone (9:1 by vol)	30	60	microwave extraction
2-1	hexane/acetone (9:1 by vol)	0	60	let stand for 60 seconds (no microwave)
2-2	hexane/acetone (9:1 by vol)	60	60	microwave extraction

Table 6 PAH Results for MAP Extraction Runs

Run # /Test #	Solvent	Power (W)	Time (s)		PAH
1-0	feed sample	-	-	Average (ppm)	1670
1-1	hexane/acetone	0	60	Average (ppm) % Removal	1232 26%
1-2	hexane/acetone	shake	60	Average (ppm) % Removal	525.4 69%
1-3	hexane/acetone	30	30	Average (ppm) % Removal	994.6 40%
1-4	hexane/acetone	30	60	Average (ppm) % Removal	423.8 75%
2-0	feed sample	-	-	Average (ppm)	2611
2-1	hexane/acetone	0	60	Average (ppm) % Removal	1483. 43.2%
2-2	hexane/acetone	60	60	Average (ppm) % Removal	1387 46.9%

The results shown in Table 6 show that the PAH removal using a 30 second microwave extraction test (#1-3) was higher than the control sample but lower than the control with shaking. However, the 60 second microwave extraction test (#1-4) was higher than both controls, although not much higher than the control with shaking. When the power was increased in Run #2 to 60 W, the increase in the removal efficiency over the control was not significant (less than 4% increase over the control).

The above results show that for this particular soil the effect of microwave on PAH removal was insignificant. Despite the fact that the MAP technique has shown promise for the removal of PAHs from fine soils, it is possible that because of the

high fines fraction in the soil the contaminants were so strongly bound that the amount of microwave energy used was not enough to extract the contaminants. The moisture content of the soil for Run #1 was less than the moisture content of the soil used for Run #2 (25% versus 33%) which could have also accounted for the lower removals during Run #2. With a higher moisture content, more energy is required to heat the water in the soil and, therefore, despite the increase in power in Run #2, there still may not have been enough energy for significant extraction to occur.

For the process to be feasible, it is necessary that a significant improvement in results be obtained when the microwave is used, which would likely require increasing the power or the extraction time. Further tests would be required to test higher power and exposure times. However, this would only be feasible if the levels tested would be economically viable on the large-scale. This will require an evaluation of the energy requirements on the laboratory-scale and then a scale-up to the large-scale.

3.3 Coupling of MAP with the Two-Phase Partitioning Bioreactor

As a contaminant removal technology, the MAP technique will extract contaminants from soil and create a contaminated solvent stream. Normally, the solvent/contaminant mixture would then be distilled to recover clean solvent to recycle to the process. A concentrated contaminant stream would be left behind that would need to be disposed of. In most cases, the cost of destroying or landfilling this relatively small volume of contaminants would be less than the cost of destroying or landfilling the complete volume of soil. However, other methods of dealing with the contaminants after they are extracted by MAP have also been investigated. One of these methods is the Two-Phase Partitioning Bioreactor (TPPB).

The TPPB is a unique bioreactor system developed by a group of researchers at Queen's University. TPPB combines solvent extraction and bioremediation for the treatment of mixed organic wastes and soil contaminated with organic compounds. This process can overcome one of the main challenges of conventional bioreactor processes - controlling the contaminant level in the bioreactor to ensure that the concentration is high enough to sustain microbe growth while not being so high as to become toxic to the microbes. The key to this technology is that the microbes are only fed as much contaminant as they can handle.

The TPPB process begins with an extraction step where solvents are used to dissolve organic contaminants. The solvent mixture, being immiscible in water, is then "floated" on top of the aqueous-phase in a bioreactor. Because organic contaminants contained in the solvent are partially miscible in water, a certain amount of the contaminant will transfer from the solvent to the aqueous phase until equilibrium occurs. At the same time the microbes in the aqueous phase breakdown the dissolved contaminants. This, in turn, shifts the solubility equilibrium and, as a result, the contaminants continue to transfer from the solvent to the aqueous phase at the same rate that the microbes are consuming them. In the end, after all the compounds have been broken down, the solvent can be recycled back to the extraction stage.

The advantages of this "self-feeding" system include:

- A complicated mechanical feeding system with a controller is unnecessary;

- The microbes are fed only the amount of contaminant that they can degrade at a particular time, therefore, they do not starve as a result of lack of food and they are not killed by an over-abundance of food; and,
- The system can handle can process wastes and contaminated materials that have very high concentrations.

SAIC Canada has been working on an Environment Canada study investigating the application of TPPB technology for soil remediation purposes. This work involves the evaluation of methods to improve the efficiency of the solvent extraction step of the process and the design of the basic components of a bench-scale system that combines the solvent extraction step with the bioreactor step into a continuous flow process. It was felt that, for recalcitrant contaminants, the MAP process may be a feasible extraction method to couple with the TPPB and therefore, as part of this work, an evaluation was performed to select solvents that could be acceptable for both the MAP and TPPB technologies. Unfortunately time constraints prevented the proper testing of the TPPB with the sediment.

The solvent selection was performed by Queen's University using their Extractant Screening Program (ESP) Database (Bruce and Daugulis, 1991). This preliminary search was performed specifically for PCB extraction as these contaminants are one of the greatest concerns in the soil. The database was first used to rank solvent on their ability, based on mass partition coefficient, to extract PCBs. The solvents ranking high on this list had the following characteristics:

- they were all organic solvents (which should come as no surprise given the very hydrophobic nature of PCBs).
- many were aromatic and/or halogenated compounds (which is understandable because generally chemical compounds are dissolved by solvents having similar structures).

From this list a number of compounds that were acceptable for the MAP and TPPB operating conditions were selected using the following additional criteria:

- General criteria:
  - low cost
  - high availability
  - low toxicity
- TPPB criteria:
  - Low aqueous solubility – The solvent must be immiscible in water to aid in its separation from the aqueous phase and to reduce solvent loss to the aqueous phase.
  - High solvent distribution coefficient – The contaminant of interest must be preferentially dissolved in the solvent as opposed to the aqueous phase, such that only a small amount of contaminant is transferred to the aqueous phase at a time.
  - Biocompatible – The solvent must not be toxic to the microbes used in the bioreactor. It has been determined that the biocompatibility of a solvent increases as the log of the octanol/water coefficient (log P) of that compound increases. For this search only solvents with a log P of greater than 3 were included.

- Low Biodegradability – The solvent must not be biodegraded by the microbes used in the bioreactor.
- MAP criteria:
  - low dielectric constant (i.e., less than 5).

Using these additional criteria many aromatic and halogenated compounds were excluded from the preliminary list. After placing all these constraints on the database, a list of possible solvents that would be suitable for both MAP and TPPB for the removal and destruction of PCBs was developed. Cyclohexane was one of the compounds on this final list. For this reason, as well as its availability, it was used as one of the solvents for the tests. Further laboratory work is recommended to determine which of these solvents are most effective for this combined process.

3.4 Supercritical Fluid Extraction.

Supercritical fluid extraction is a solvent extraction technique. This fluid is usually a gas, such as CO_2 or propane, but water has also been used. The fluid is pressurized and heated past its supercritical point which results in the fluid possessing the extraction properties of a liquid, yet the sample penetration properties of a gas. In this project CO_2 was selected as the solvent. In order to achieve a supercritical state, the CO_2 was held at temperatures above 31.1°C and pressurized above 1070.4 psi.

A lab scale unit (ISCO SFX2- 10) was used for the experiments. It has the capacity to run up to 10mL samples. A photograph of this unit is presented in Figure 1. A typical run would have the following parameters. These parameters were derived from a program to extract hydrocarbons from shale:

- Ten grams of soil is pressurized to 3000 psi and held static for 15 minutes.
- Then the sample is dynamically extracted for 20 minutes at 3000 psi. The flow rate during this phase was approximately 0.7 ml/min.
- The pressure is released and the sample cartridge is removed from the oven to cool. After cooling, the treated sample is sent to the laboratory for analysis.

Two extraction temperatures were performed in duplicate, 60°C and 100°C using soil designated Sample A.

The parameters monitored were PCBs and PAHs and are presented in Table 7. The only variable used in this preliminary investigation was temperature. The process was run in duplicate at 60°C and 100°C.

Table 7 Results of SFE Runs

Sample	PCB [mg/kg]	PCB removal	PAH [mg/kg]	PAH removal
Feed	525.5		308.8	
60a	447.9	15%	113.4	63%
60b	504.3	4%	82.4	73%
100a	484.6	7%	396.1	-28%
100b	504.7	4%	126.6	59%

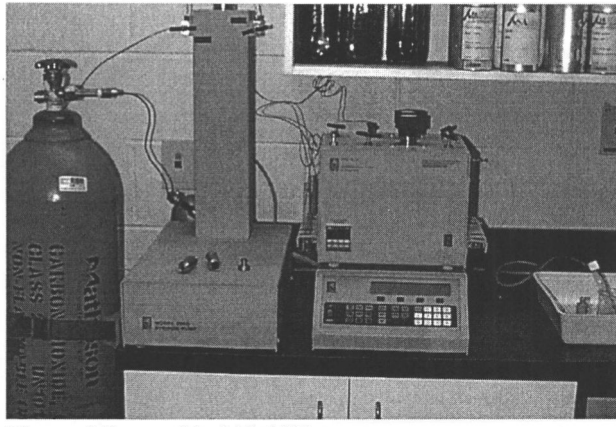


Figure 1 Supercritical Fluid Extractor

The results table show very low removals for PCBs. This is probably due to the physical properties of PCBs. The addition of a modifier will greatly enhance the extraction of PCBs. One such modifier would be methanol. Methanol could be added either to the CO2 stream, or directly to the sample. Modifiers increase the efficiency of the solvent for certain contaminants.

The removal of PAH is better than that for PCBs. It was anticipated that the higher temperature run would have increased the percentage removal. This was not the case. The addition of a modifier, as discussed above, may also have a beneficial effect on the extraction of PAH. Much more work is required in order to properly evaluate the effectiveness of supercritical fluid extraction as a remediation technology.

The supercritical extraction of the soil was promising only for the removal of PAH at the parameters tested. It is anticipated that the addition of a modifier may help extract both the PAH and the PCB. This should be verified by further experiments. Variables which should be investigated could include the use of modifiers, and other solvents, such as butane.

3.5 Organic Destruction Process

The Organic Destruction Process (ODP) process is an enhanced desorption technique. It is a thermal process which is designed to remove chlorinated compounds from contaminated soil. These chlorinated compounds include, but are not limited to polychlorinated biphenyls (PCBs), dioxins and furans. The effect of this technique on polycyclic aromatic hydrocarbons (PAH) was also investigated. The general procedure involves placing the contaminated soil into the reactor with the addition of water and the proper reagents. The reactor is then heated so that all of the moisture is driven off. During the heating stage, any vapours emitted are condensed. The condensate is collected and subsequently treated by Advanced Oxidation Process (AOP). It is anticipated that the halogenated compounds (PCBs, dioxins and furans in this case) are either destroyed, or transferred to the condensate. Some additional variables which were investigated include the effect of iron, pressure, pH, and the

effectiveness of using AOP for the treatment of the condensate. These variables were tested using a bench scale reactor.

3.5.1 ODP Reactor

A bench scale reactor was designed to process 2 Kilograms of soil in a batch mode. A photograph of the reactor is shown in Figure 2. In essence, this reactor is a modified pressure cooker. The pressure inside the reactor is regulated with a check valve set to release at 20 PSI. A second valve, which is a safety relief, is set to release at 50 PSI. The reactor was equipped with a manual valve so that the system could be vented. A pressure gauge records the internal pressure, as well as a thermal couple to monitor temperature. A stirrer is incorporated to ensure even mixing. Heat is applied using a 9KW-propane burner. The exhaust from both the check valve and the release valve are connected to a condenser. The off gasses are condensed and collected at this point. The condensate is then treated in a 450 watt AOP unit (model 7830 by Ace Glass).

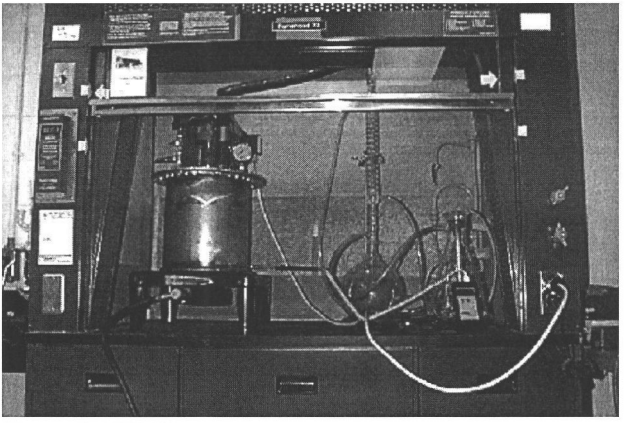


Figure 2 ODP Reactor

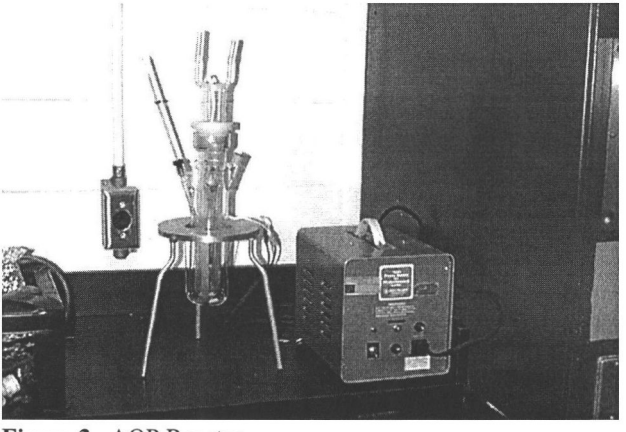


Figure 3 AOP Reactor

The soils used in the bench scale tests were the sediments designated "Sample A" with the system being run using the parameters listed in Table 8.

Table 8 ODP Run Parameters

Run	pH	Pressure	Iron by Weight	Max Temp
1	neutral	20	No	223
2	neutral	Atm	No	386
3	2	20	No	319
4	neutral	20	10%	312
5	neutral	Atm	10%	321

The parameters examined in this set of experiments were pressure, pH, and iron addition. The pressure was set at either atmospheric or 20 psig. The pH was either neutral or at a pH of 2. The effect of iron was also investigated, at 0% addition of iron, or at 10% iron by weight. The iron added was in the form of iron powder at 99% purity. The resulting condensate was also investigated for ease of destruction by AOP.

As can be seen in Table 9, the best removal of PCBs was in run 3 -- acidic conditions, at 20 psi and with no additional iron. The addition of iron resulted in an increase in the removal of PCBs from the system without the additional acid.

The best reduction in PAH occurs with the addition of iron, at 20 psi, and under neutral conditions. The addition of iron was beneficial to the PAH removal process.

Table 9 Results of ODP Runs

Sample	PCB [ug/g]	PCB removal	PAH [ug/g]	PAH removal
PRE1	469		147	
POST1 (pH= 7, P=20, no Fe)	213	55%	94	36%
CON1	5		30	
PRE2	582		162	
POST2 (pH=7, P=atm, no Fe)	241	59%	71	56%
CON2	9		162	
POST3 (pH= 2, P=20, no Fe)	9	98%	113	27%
CON3	7		169	
POST4 (pH=7, P=20, 10% Fe)	55	89%	5	97%
POST5 (pH=7, P=atm, 10% Fe)	133	75%	33	79%

Pre = initial soil, Post = treated soil, Con = condensate

3.5.2 AOP Reactor

The Advanced Oxidation Process (AOP) uses ultraviolet light and an oxidant to mineralize organic contaminants in water. In this study, only UV light was used at various pH levels. The results show no reduction for PCBs or PAH from the feed. This could be due to the lack of oxidant. It is recommended to consider the use of H_2O_2 as an oxidant for the next set of trials.

Table 10 AOP Results

Sample	PCB [ug/g]	PAH [ug/g]
IN1	0.09	2.19
IN4	0.08	2.33
Out (Neutral)	0.07	1.54
Out (Acid)	0.06	3.11
Out (Basic)	0.06	5.12

In= initial condensate, Out = treated condensate

The ODP process showed a positive reduction of contaminants in the soil in all cases. The best reduction for PCBs (98%) occurred when the soil was acidic, with no addition of iron and under pressure. Conversely, these same conditions resulted in the poorest removal of PAH from the soil. The best reduction in the concentration of PAH occurred under pressure, with the addition of iron, at a neutral pH. However under these same conditions, the amount of PCB reduction were still high at 90%. The addition of iron has a beneficial effect for both the PCB and the PAH. Further work should be carried out to determine the mechanism by which iron enhances the reduction of these contaminants. In all of the tests the amount of contaminant decreased, regardless of the variables used. The use of AOP may still be used as a treatment step for the condensate if the system were to be optimized. Additional study should be conducted before AOP is ruled out. What is required for future work is the elucidation of the reduction mechanism for this process. Once that is known, then the optimization of the system parameters will be more evident.

The process was originally designed to reduce the amount of chlorinated compounds in the soil, but the findings of this research show that this process may be applicable to a wider variety of contaminants than originally thought.

3.6 Microwave Activated Cracking of Soil Samples

Microwave Activated Cracking is a destructive technology which uses microwave energy in conjunction with activators and catalysts to break down organic compounds in soil. A series of bench scale tests were performed to determine the effect of different variables on the efficiency of destruction.

The primary equipment used for this series of experiments included the following:

- Reactor - 13 cm reactor operating at a frequency of 2.45 GHz (see Fig.1).
- Feeding device - hydraulic ram with a diameter of 10 cm and a length of 30 cm (see Fig.1).
- A sensitizer, special catalysts, additives including sodium hydroxide pellets and potassium hydroxide pellets, and nitrogen gas were the main consumables.
- All testing was performed using soil designated as "Sample A".

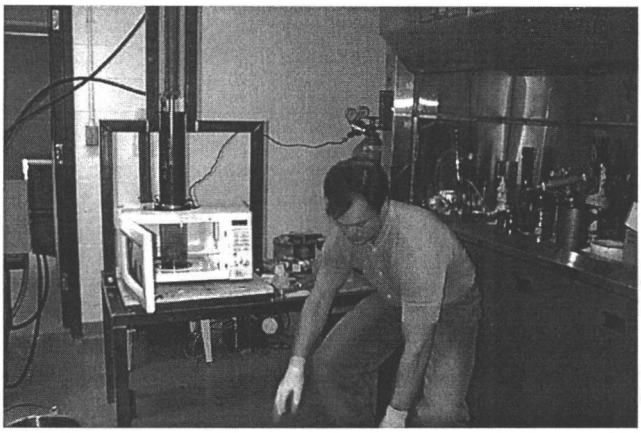


Figure 4 Microwave Cracking Apparatus

The throughput varied over the course of the experiment between 0.1 to 0.5 kg/hr. The feed rate was adjusted using two variables: flow speed of the material in the hydraulic ram and the effective cross section of the extrusion disk. The cross section was determine by the effective volume of the processed material in the reactor and the residence time.

The residence time was calculated based on the mass feed rate and the effective cross section of the extruded material using the following formula:

$$\tau = \frac{\rho \sigma L}{F}$$

where τ is the residence time, ρ is the material density, g/cm3; σ is the cross section of the extruded strands of material mixed with a sensitizer/catalyst, cm2; L is the length of the reactor, cm; F is the mass feed rate, g/s. The cross section was controlled to provide the required residence time which was designated as 10 minutes.

It was difficult to control the power output of the highly modified domestic microwave oven. Power is calculated by averaging a duty cycle over time. This is not acceptable for the current experiments on microwave cracking due to the substantial variations in the absorbed power and the resulting development of high temperatures within the reactor. The reaction temperature was determined by a combination of factors including the feed rate, effective cross section of the extruded material, and the concentration of sensitizer and additives. The sensitizer, catalyst and additives concentrations are presented in Tables 11-15. These values were selected based on previous experiments with hydrocarbons. The data obtained with the 2.45 GHz reactor will be useful in the pilot tests with the 915 MHz reactor since the load and production rates of the pilot reactor are expected to be at least 80 to 120 times greater than with the 2.45 GHz reactor.

Solid residue, which was collected in the bottom container of the microwave reactor, was analyzed for total petroleum hydrocarbons (TPH), polynuclear aromatic hydrocarbons (PAH), polychlorinated biphenyls (PCB), pentachlorophenol (PCP), mineral oil and grease (MOG).

The following experimental compositions under the microwave irradiation were used during this study:

Sample 1: Plain soil from Sample A
Sample 2: Sample A + 1% KOH
Sample 3: Sample A + 1%NaOH +1%KOH + 1%Activated Carbon
Sample 4: Sample A + 5% Activated Carbon + 1% Fe
Sample 5: Sample A + 1%KOH + 5% C/NiO*
* Activated carbon impregnated with a solution of $Ni(NO_3)_2$

The results of the experiments are presented in Tables 11-15.

Table 11 Microwave Cracking – MOG results

Sample	Initial sample	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
MOG (mg/kg)	4,061	<MDL*	<MDL	<MDL	<MDL	<MDL

*MDL – method detection limit

Table 12 Microwave Cracking – TPH results

Sample	Initial sample	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
TPH (mg/kg)	ND	13	12	3,062	60	2,841

Table 13 Microwave Cracking – PAH results

Analyte	Initial sample	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
Naphtalene	25.1	13.5	10.5	<dl	15.6	11.2
Acenaphthylene	13.0	8.2	0.0	<dl	12.0	0.0
Acennaphthene	23.2	10.6	0.0	<dl	14.4	0.0
Fluorene	6.9	2.9	2.5	<dl	4.3	1.5
Phenanthrene	4.0	2.5	1.6	<dl	0.0	0.7
Anthracene	2.9	1.7	1.1	<dl	2.0	0.7
Pyrene	1.9	1.2	8.6	<dl	0.9	14.5
Chrysene (93%)	8.2	4.9	3.2	<dl	5.7	1.8
Benzo(a)anthracene	7.5	4.4	2.9	<dl	5.2	1.1
Benzo(k)fluoranthene	6.7	4.1	2.1	<dl	4.4	1.4
Dibenzo(a,h)anthracene	12.0	6.2	2.9	<dl	9.7	0.0
Indeno(1,2,3-cd)pyrene	7.2	2.0	0.0	<dl	3.1	0.0
Total PAHs	118.6	62.2	35.4	<dl	77.3	32.9

Table 14 Microwave Cracking – PCB results

Sample	Initial sample	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
PCBs (mg/kg)	0.41	0.07	0.19	0.68	0.31	0.41

Table 15 Microwave Cracking – PCP results

Sample	Initial sample	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5
PCP, mg/kg	ND*	128	ND	580	ND	596

*ND – not detected

It is clear from MOG analysis that the process of the destruction of polymers has occurred under the conditions of the microwave irradiation. No mineral oil and grease were detected in the soil samples after treatment (Table 11). At the same time the formation of the petroleum hydrocarbons was observed under the microwave irradiation, especially with reactive compositions, which include hydroxides (Samples 3&5, Table 12).

The best reactive composition for the destruction of the polynuclear aromatic compounds under those experimental conditions includes sodium and potassium hydroxides and activated carbon (Sample 3, Table 13). Simple microwave treatment of the plain soil provides 47% of PAH removal. The use of the activated additives in the reactive mixture caused up to 70% removal of the polynuclear aromatic hydrocarbons. Some of the PAHs, such as Acenaphthylene, Acennaphthene, Dibenzo(a,h)anthracene, Indeno(1,2,3-cd)pyrene seemed to be removed completely from treated samples by microwave irradiation with reactive mixtures which included hydroxides (Samples 2,3 and 5, Table 13).

It was demonstrated that microwave irradiation of the samples has the ability to provide the removal and destruction of PCBs (Sample 1, Table 14). At the same time the formation of the polychlorinated biphenyl and pentachlorophenol was observed in some cases in presence of the activated additives (Tables 14 and 15). It is expected that the presence of alkali metals in the dissolved form (which is inert under the microwave conditions) would provide better results for the chlorinated compounds (such as Na-based dechlorination). It was demonstrated by this study that microwave induced catalytic technology has potential for the treatment of the Sediment Sample A by decomposition of PAHs and formation of TPH., and the catalytic reactions activated by microwave have potential for destruction and removal chlorinated compounds from the treated samples, such as PCB and PCP.

4.0 Conclusions and Recommendations

The results obtained with this series of testing has reinforced the difficult nature of dealing this type of contamination. The high portion of fines which make up the sediment sample limits the effectiveness of many separation techniques, although the target compounds are known to be problematic in these instances. Typical screening techniques which would separate the contaminated fines from the

rest of the bulk soil would prove ineffective with the soil samples under consideration.

Technologies which dealt with the segregation of contamination such as Enhanced Soil Washing, Chemical Leaching, and Supercritial Fluid Extraction all showed some signs of success in dealing with specific organic and metallic compounds. The destructive technologies, MAP, ODP, and Microwave Cracking, were also demonstrated with varying degrees of success. Some of these technologies show promise in dealing with this type of matrix, and further study under additional operating conditions are recommended and planned. The results from the bench scale study will be applied to the scale-up of technologies to the pilot scale.

5.0 References

Bruce, L. J. and A. J. Daugulis., "Solvent Selection Strategies for Extractive Biocatylists", *Biotechnol. Prog.*, Vol. 1, No. 2, pp. 116 – 124, 1991.

Letellier, M., Budzinski, H., Garrigues, P. and Wise S. "Focused Microwave-assisted Extraction of Polycyclic Aromatic Hydrocarbons in Open Cell from Reference Materials (Sediment, Soil, Air Particulates)" *Spectroscopy, Vol.* 13, pp. 71-80, 1996.

Li, K., Bélanger, J. M. R., Lompart, M., Turpin, R. D., Singhvi, R. and Paré, J. R. J. "An Evaluation of Rapid Solid Samples Extraction Using the Microwave-assisted Extraction Process (Maptm) under Closed-vessel Conditions", *Spectroscopy, Vol.* 13, pp.1-13., 1996.

Lopez-Avila, V., Benedicto, J., Charan, C., Young, R. and Beckert, W. F. "Determination of Pcbs in Soils/sediments by MAE and GC/FID", *Elisa. Env. Sci. & Tech.*, Vol. 29(10), pp. 2709-2712, 1995a.

Lopez-Avila, V., Young, R., Benedicto, J., Ho, P., and Kim, R. "Extraction of Organic Pollutants from Solid Samples Using Microwave Energy", *Analytical Chemistry* 67(13), pp. 2096-2102, 1995b.

Onuska, F. I. and Terry, K. A. "Extraction of Pesticides from Sediments Using a Microwave Technique" *Chromatographia.* 36, pp. 91-94, 1993.

Paré, J. R. J., Sigouin, M. and Lapointe, J., *U.S. Patent 5,002,784.* (various international counterparts), 1991.

Paré, J. R. J., U.S. Patent 5,338,557. (various international counterparts), 1994.

Paré, J. R. J., Bélanger, J. M. R. and Stafford. S. S. "Microwave-assisted Process (MAP™): A New Tool for the Analytical Laboratory", *Trends in Analytical Chemistry*, Vol. 13(4), pp. 176-184, 1994.

Paré, J. R. J., *U.S. Patent 5,337,426.* (various international counterparts), 1995a.

Paré, J. R. J., *U.S. Patent 5,458,897.* (various international counterparts), 1995b.

Paré, J. R. J., *U.S. Patent 5,519,947.* (various international counterparts), 1996.

Punt, M., *Microwave-enhanced Extraction of Organic Contaminants from Soil*, M.Sc. Thesis. McGill University, Montreal, Quebec, May 1997.

Novel Technology for Simultaneous Removal of Mixed Contaminants from Solid Waste

S. Cathum, R. Smits, K. Volchek and M. Punt
Environmental Technologies Program
SAIC Canada
Ottawa, Ontario, CANADA

Abstract

A novel methodology incorporating chelation and solvent extraction has been developed to remove simultaneously heavy metals and organic contaminants from a real contaminated solid waste. The method combines solvent extraction and soil leaching in a one-step process, thus allowing an effective recovery of mixed contaminants. The metals are reacted with a chelating agent, and the resulting metal complexes and the organic contaminants are both extracted simultaneously from the contaminated soil with an organic solvent. Experimental results have indicated that Cu, Fe, Pb, Zn, PAHs and PCBs can be removed efficiently from the soil. The reagents used in the process are recyclable and can be reused for further chelation solvent extraction.

1.0 Introduction

The removal of contaminants from mixed contaminated sites has been the focus of efforts to restore the quality of the environment and protect the human health from the adverse effect of hazardous substances. Reports from U.S.A. indicate that mixed contaminated sites make up about 37% of all contaminated sites for which information was available in 1991 (Kovalick, 1991). It is expected that the mixed contamination problem in Canada would be in the same range.

Mixed contaminant sites pose a problem because they normally cannot be effectively treated using a single commercially available process. This is due to the fact that the remediation strategies used for organic contamination are very different from those used for metal contamination. Studies have demonstrated that the combination of solvent extraction with selective complexing agents is effective for recovery of heavy metals (Sparks and Meadus, 1994; McCarthy, 1994; Misra and Mehta, 1995; Meckes et al, 1997; Rovira, et al, 1998; Alguacil and Cobo, 1998; Almela, et al, 1998; Kyuchoukov, et al, 1998; and Srinivasan, et al, 1998; John, et al, 1999; Sarkar and Dhadke, 1999).

Solvent extraction combined with a chelating agent is widely used in the U.S.A., Great Britain, Peru, Chile and a number of African countries, for copper recovery. The process involves separation of heavy metals from aqueous solution with the aid of an immiscible solvent, also called diluent (Srinivasan et al, 1998). A chelant is added to the aqueous solution to complex the metals, thereby rendering the metal miscible in the organic solvent. The metal free aqueous solution, which is called raffinate, is disposed of, recycled, or further treated. In order to recover the chelant, the organic solvent is contacted with strip liquor, whose job is to cleave the bond between the metal and the chelant, thus releasing the metal into the strip solution and the chelant into the solvent. When the metal has been stripped, the organic solvent and the chelant can be recycled for repeated usage either directly or after some treatment for impurities removal. There are several ways to cope with the

metal laden stripping medium (Sarkar and Dhadke, 1999). Regeneration options include acid stripping, electrodeposition, metal reduction or formation of insoluble salts. In addition to the chelant and solvent, the applicable solvent formulation may also contain a third component, called modifier, added to prevent precipitation (Pearl and Wood, 1993). Modifiers are varieties of chemical compounds, and the best example for them is the long chain alcohols.

Solvent extraction technologies use organic chemicals as solvents to extract organic contaminants as opposed to soil washing, which generally uses water or water with wash improving additives, such as, acids and surfactants (Murphy et al, 1993; Griffiths, 1995). Commercial scale units are in operation but hitherto there is no clear solvent extraction technology leader because of the mixed contamination, solvent employed, type of equipment used, or mode of operation. The final determination of the lowest cost/best performance alternative will be, in some cases, more site specific than process dominated.

In 1980, the US Comprehensive Environmental Response Compensation and Liability Act was passed by the congress to provide a mechanism that would ensure hazardous waste sites be cleaned up (Meckes et al, 1996). Since that time over 35,000 hazardous sites have been identified in the United States alone. Most of these sites have been found to contain mixed contaminants, such as, heavy metals, VOCs, TPHs, PAHs, PCBs, and PCDDs/PCDFs. The USEPA has concluded that these sites are hazardous to the environment and human health and must be cleaned up. Since then, different remediation technologies have been used to remediate the sites. Some figures of merit to consider are given in Table 1.

Table 1 Technology Cost comparisons (Du Teaux, 1997; FRTR, 1997)[1]

Technology	**Cost per tonne ($Cdn)**
Slurry Biodegradation	$85 to $265
Solvent Extraction	$130 to $640
Thermal Desorption	$40 to $775
Incineration	$2400 to $9600
In situ Electokinetics	$20 to $60
Soil Washing	$190 to $640
Stabilization/Solidification	$60 to $375
Vitrification	$220 to $2900

The proposed process employs chelation and solvent extraction, hence the name "CHELASOL", to extract mixed contaminants. The process is a nondestructive remediation method operating under normal atmospheric conditions. It allows removal of mixed contaminants without deteriorating naturally occurring humus matter through a combination of soil washing and solvent extraction technologies in a one-step process without risking the performance of each technology. The method requires no pressure or incineration. The heavy metals are chelated, and both of the

1. The values from these references were converted using the following factors: $U.S.= 1.45 $Cdn, 1 tonne = 1.1 ton, 1 tonne = 1 yd^3, 1 tonne = 0.77 m^3 (assuming a soil bulk density = 1.3 kg/L).

chelated metals and the organic contaminants are extracted simultaneously from contaminated soil and water with an organic solvent.

The main objective of this work is to demonstrate the simultaneous removal of mixed contaminants from an actual contaminated site using chelation solvent extraction (CHELASOL) and develop a simplified process flow diagram that can be applied to site remediation.

2.0 Experimental Section

2.1 Pretreatment of contaminated soil for laboratory study

A soil from an actual site contaminated with heavy metals, PCBs and polycyclic aromatic hydrocarbons was prepared as follows:

- Air-dry about 1 kg soil for 24 hours.
- Size down the soil using 2 mm sieve.
- Weigh 5 g in 40 mL VOC vial.
- Add 3 mL 0.2 M sulfuric acid to the soil (3:5 ratio) and let it equilibrate for three hours.
- Measure the pH of the soil slurry at 15 minutes, 1 hour and 2 hours. The pH should read 2, if not add sulfuric acid or sodium hydroxide.

2.2 Chelation solvent extraction (CHELASOL) of mixed contaminants

The chelating agent (CYANEX 301) was added to the soil slurry at approximately 40% (w/w), depending on the level of heavy metals in the contaminated soil. The mixture was placed in an ultrasonic bath and ultrasonicate for 15 minutes. Fifteen mL of cyclohexane (3:1 ratio) was added and ultrasonicated for 15 minutes. The solvent layer was decanted into a filtration system mounted on a round bottom flask. The extraction procedure was repeated two more times using fresh aliquots of cyclohexane. The soil was washed with an additional 5 mL cyclohexane. The total volume of solvent used to recover organics and heavy metals was 50 mL. Excess solvent was used if the soil is heavily contaminated with organics and heavy metals. The extracts were archived for the recovery of solvent and chelant. The levels of heavy metals, PCBs and PAHs were determined in the feed and treated soil using appropriate analytical methodologies.

2.3 Recovery of solvent

A distillation system for the solvent recovery was used for these tests. The extract from the above step was heated to 90 °C in a water bath. Vacuum was applied to the vessel to enhance solvent recovery. The distillate was collected in a graduated cylinder and measure the volume of the solvent recovered.

2.4 Recycling of chelant

Synthetic water was prepared containing Cd, Cu, Pb, Fe and Zn. Add 1.2 g CYANEX 301 to 10 mL synthetic water and extract with cyclohexane. The solvent was evaporated to dryness. Ten mL of 6M sulfuric acid was added and the mixture was stirred for 30 minutes. The heavy metals in the aqueous phase was analyzed using flame atomic absorption spectrophotometry.

3.0 Results and Discussion

3.1 Selection of solvent and chelant

The solvent extraction is only one unit process in a series of unit processes needed to leach contaminants, remove them and recover extraction ingredients from process. For this reason solvent extraction must be compatible with the leaching process which precedes it and the final pre-concentration and recovery procedures, which follow. To make a sound decision on solvent and chelant selection, intensive literature search and quick laboratory experiments were performed. Assistance was also sought from a group of researchers at Queen's University who have developed a computer program to select suitable solvents. Selection of the chelant-solvent pair was based mainly on a combination of experience in science and technology. These chelants were screened further to narrow the list to a group of six chelants and three solvents using shake-out experiments performed on synthetic aqueous solution containing Cd, Cu, Fe, Pb and Zn. Table 2 presents the results of the first tier of screening tests.

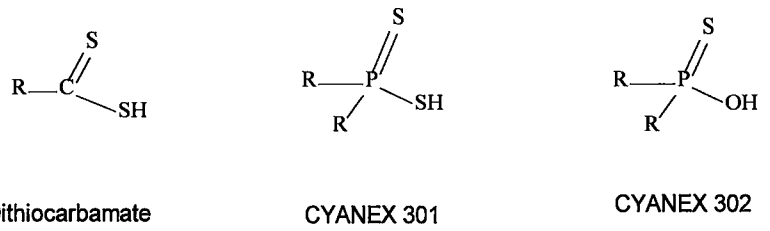
Table 2 Results of Preliminary Tests using Selected Chelants with Dichloromethane.

Chelant	% Removal				
	Cd	Pb	Fe	Cu	Zn
DTC	99	6	100	98	93
CYANEX 417	-	1	7	7	-
CYANEX 302	95	32	32	99	24
LIX 984N	0	1	9	93	40
CYANEX 301	100	99	25	100	100
CYANEX 923	-	1	18	6	64

Initially, dichloromethane was chosen for this set of experiments because it extracted efficiently organic chemicals and chelated heavy metals. Dichloromethane is well known as a good reagent for solvent extraction but it is harmful to the environment and human health, and, therefore, was excluded from subsequent tests. As can be seen, only dithiocarbamate (DTC), CYANEX 301 and CYANEX 302 performed reasonably in removing heavy metals from water. Besides the high removal efficiency, CYANEX 301 has shown a certain degree of selectivity towards Fe, which is a desirable property to reduce consumption of chelant by naturally occurring iron minerals found in soils. Figure 1 depicts the chemical structures of DTC, CYANEX 301 and CYANEX 302.

These three chelants, selected from among other chelants, were investigated further under the same experimental conditions, but this time MIBK and cyclohexane were used in place of dichloromethane. Both solvents performed well in recovering heavy metals from the matrix. MIBK is commonly used to extract DTC-metal complexes from soil and water for analytical purposes. Cyclohexane is known as a general solvent for oils, fats and waxes, and also as a paint remover. Table 3 presents the result of this experiment to select one chelant and one solvent for the CHELASOL process. As can be seen, the removal of chelant metal complexes of DTC, CYANEX 301 and CYANEX 302 worked very well with MIBK but not with CYANEX 302. However, using cyclohexane as the solvent, the removal efficiency of

the three chelants had improved significantly. It was observed that CYANEX 301 has relatively low affinity toward iron, which is, as mentioned earlier, a desirable property. In the case of CYANEX 301, and when the extraction efficiency of both solvents was comparable, cyclohexane was selected. The reason for the choice is that cyclohexane is not very harmful to the environment and human health as demonstrated by many laboratory studies (Yasugi et al., 1994; Aono et al, 1994; Mormile and Suflita, 1996), and it can efficiently extract chelated heavy metals and oily organic chemicals.



Dithiocarbamate CYANEX 301 CYANEX 302

Figure 1 Chemical Structures of Dithiocarbamate (DTC), CYANEX 301 and CYANEX 302

Based on these results, CYANEX 301 and cyclohexane were selected for further testing. Its flammability is low and its boiling point is higher than most solvents and therefore it will not boil off during distillation. The product, however, does possess some toxicity. It will be required therefore that the residual concentration of CYANEX 301 in the treated solid does not exceed limits set out by regulatory agencies.

Table 3 Selection of Solvents and Chelants for CHELASOL Process.

Chelant	**Solvent**	**%Removal**				
		Cd	**Pb**	**Fe**	**Cu**	**Zn**
DTC	MIBK	100	100	98	97	98
CYANEX 301	MIBK	100	100	63	100	99
CYANEX 302	MIBK	-	-	11	4	-
DTC	Cyclohexane	92	92	85	98	75
CYANEX 301	Cyclohexane	99	93	62	84	100
CYANEX 302	Cyclohexane	100	100	70	100	39

3.2 Determination of heavy metal mobile fraction

Before applying CHELASOL process to site remediation, it was important to determine the mobile fractions of the heavy metals in the contaminated site. The Toxicity Characteristic Leaching Procedure (TCLP), EPA Method 1311, was chosen for this purpose. Table 4 presents the results of the TCLP tests, which gives an indication of the mobile fractions of the heavy metals of the solid matrix. It has been found that only Cd and Zn are 100% mobile in the solid waste. Lead, Fe and Cu have shown low mobility, i.e., they are bound to the soil particles and cannot be easily recovered from the contaminated soil.

Table 4 Determination of Heavy Metal Mobile Fractions using TCLP.

Element	% Mobile
Cd	100
Pb	11
Fe	4
Cu	39
Zn	100

3.4. Technology efficiency

The selected solvent-chelant pair was investigated to demonstrate the usefulness of the CHELASOL technology and compare it with those of solvent extraction and soil washing using an authentic solid waste from a site contaminated with heavy metals, PAHs and PCBs among other contaminants. This site, which is a truly "mixed contaminated site", was used to evaluate the proposed technology. Table 5 summarizes CHELASOL removal efficiency of the mixed contaminants from the sediment. As can be seen, CHELASOL did fairly well in removing heavy metals and organics (PCBs and PAHs) from the sediment. As expected from the TCPL study, the recovery of metal bound residues was extremely low. The mobile fraction of Cd was not recovered significantly, only 6% versus 100% available for chelation reactions. One may attribute this low removal to either matrix interference or competition of other metals and inorganic chemicals with Cd to react with the chelant. The mobile portion of Pb and Cu, however, was almost complete, 100% and 74%, respectively. Iron was not appreciably removed by CHELASOL, which is, as mentioned earlier, desirable for chelant recovery. Again, CHELASOL performance in removing PCBs from the soil was satisfactory, 79% CHELASOL versus 55% by solvent extraction, and none removed by applying the soil washing.

Table 5 Removal Efficiency of CHELASOL, Solvent Extraction and Soil Washing.

Contaminant	%Removal*		
	CHELASOL	Solvent Extraction	Soil Washing
Cd	6	-	16
Pb	13	-	-
Fe	-	-	3
Cu	29	9	22
Zn	62	36	56
PCBs	79	55	-
PAHs**	50	47	-

*Average of three replicate experiments performed separately.

** Calculated using PAH values of soil washing samples.

The PAH removals where calculated using the PAH level in the samples subjected to the acid washing procedure. The level of PAHs in the acid washed soils is expected to be similar to the level in the initial soil since it is not expected that the acid washing would remove a significant amount of PAHs. The point of examining the organic results was to compare the CHELASOL results with the solvent

extraction results, which, in this case, showed that the level of PAH removal was similar for solvent extraction and CHELASOL, at about 50% removal.

The recovery of organic contaminants (PAHs and PCBs) was not as high as expected for both CHELASOL and solvent extraction processes. This could be attributed to insufficient volume of solvent used to extract target contaminants. It should be mentioned that the solid waste was heavily contaminated with mineral oil and grease, roughly 10% and heavy metals about 50%, that might have consumed a large portion of the solvent before target contaminants can be extracted. Neverthe less, the results do indicate that CHELASOL can perform as well or better than solvent extraction or soil washing.

3.5 Recovery of cyclohexane and CYANEX 301

An attempt was made to recover the solvent (cyclohexane) and chelant (CYANEX 301) used. In the solvent case, the recovery was between 95% and 100%. On the other hand, the recovery of the chelant (CYANEX 301) using acid treatment was found to be inefficient in stripping off the chelant. Table 6 summarizes the recovery of CYANEX 301 from the metal complex using 6M sulfuric acid. No appreciable recovery of the chelant from the metal - chelant complexes was observed, except that of iron which is about 10%. The CYANEX 301 metal complexes are known to be very strong, and use of 6M sulfuric alone may not be sufficient to de-complex them.

Table 6 Recovery of CYANEX 301 from Chelant Metal Complexes using 6M Sulfuric Acid.

Element	Recovery of CYANEX 301 (%)
Fe	10.47
Cu	0.01
Pb	0.18
Zn	6.08
Cd	0.05

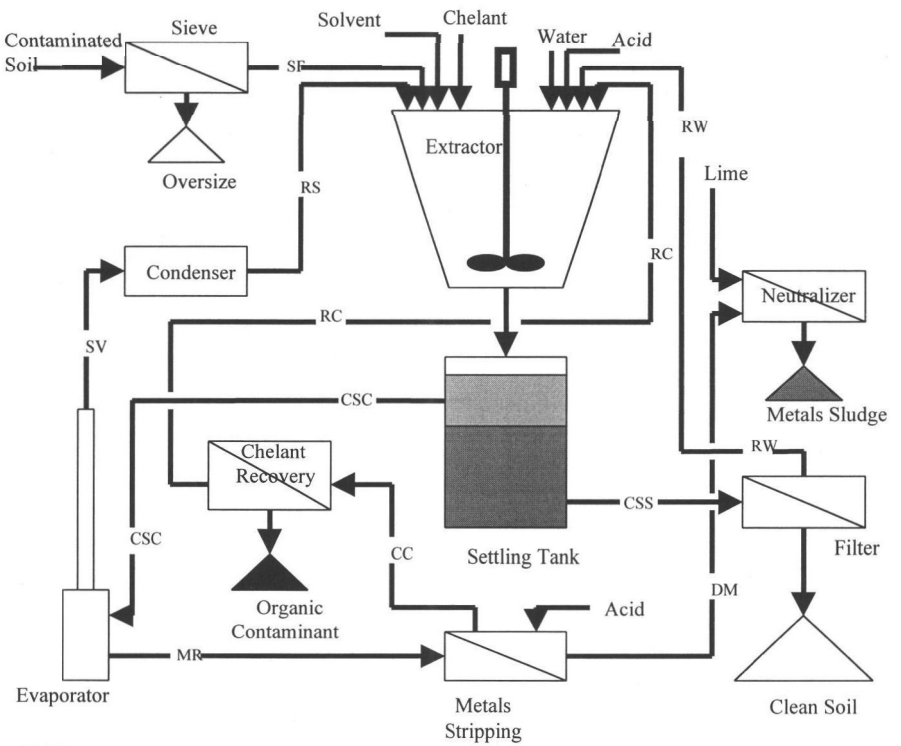
4.0 Field-Scale Process Description

The general outline of CHELASOL includes leaching of heavy metals from the soil, chelation, solvent extraction, and recovery of solvent, chelant and acid. Figure 2 depicts a simplified flow diagram of the process to be considered for site remediation. The following is a brief description of the process steps:

After excavation, the contaminated solid waste is first slurried with water and segregated mechanically into coarse and fine fraction using mechanical separation. The coarse fraction, in most cases, is relatively clean and may not require additional treatment. The soil fine fraction (SF) is directed into a mixing chelation/extraction tank. The following reagents are added to the extraction tank: acid, chelant and then solvent. After chelation and extraction process is complete, the slurry is transferred into a settling tank where phase separation takes place. Depending on soil and solvent physical chemistry properties, the mixture separates into three phases, sediment at bottom, cyclohexane on top and aqueous phase in the middle. The latter is withdrawn and returned to the chelation/extraction tank, thus forming the recycled water stream (RW). The acid that remains in the aqueous phase is returned to the chelation/extraction tank. The clean soil slurry (CSS) is filtered to recover residues of

solvent and chelant. The filtrate is blended with the recycled aqueous stream (RW) and returned to the mixing tank.

The organic phase (CSC) is distilled in an evaporator to recover the solvent. The solvent vapor (SV) is condensed and returned into the extractor (RS). The residue left after evaporation contains organic contaminants, excess chelant and chelant-metal complexes (MR). This residue is treated with acid to strip the metals off the chelant. The choice of a stripping procedure has not yet been finalized. The stripping generates a dissolved metal stream (DM), which will be neutralized before disposal. The recovered chelant (RC) is returned into the extractor.



LEGEND

CC - Contaminated Chelant	CSC - Contaminated Solvent & Chelant	CSS - Clean Soil Slurry
DM - Dissolved Metals	MR - Metals Residue	RC - Recycled Chelant
RS - Recycled Solvent	RW - Recycled Water and Acid	SV - Solvent Vapor
SF - Contaminated Soil Fines		

Figure 2 Flow Diagram of CHELASOL Process

5.0 Conclusion and Further Research Directions

This work has shown that CHELASOL works well for soil heavily contaminated with heavy metals, PAHs and PCBs among other contaminants. When compared to solvent extraction and soil washing, the proposed technology has performed much more better in removing mixed contaminants. Further refinement will be focussed on field site remediation and effective methodology to recover the chelant from the contaminant concentrate and use it for further chelation solvent extraction.

6.0 Acknowledgement

The authors are grateful to Emergencies Engineering Technology Office of Environmental Technology Centre, Environment Canada and Interdepartmental Panel on Energy R&D (PERD) for financial support for this project.

7.0 References

Alguacil, F J. Cobo, A. "Extraction of nickel from ammoniacal/ammonium carbonate solutions using Acorga M5640 in Iberfluid", Hydrometallurgy, Vol. 50, pp. 143-151, 1998.

Almela, A. Elizalde, M P. Danobeitia, I., "Liquid-liquid extraction applied to metals separation from Waelz oxide" Separation Science & Technology, Vol. 33, pp. 2411-2422, 1998.

Aono Rikizo, Kobayashi Hideki, Joblin Keith N, Horikoshi Koki, "Effects of organic solvents on growth of Escherichia coli K-12", *Bioscience Biotechnology & Biochemistry*. Vol. 58, 2009-2014, 1994

Griffiths,-R.A., "Soil-washing technology and practice", J. Hazard. Mater., Vol. 40, pp. 175-189, 1995.

DuTeaux, S. B. *A Compendium of Cost Data for Environmental Remediation Technologies, 2nd Edition.* http://www.lanl.gov/projects/etcap, Department of Energy, 1997.

Federal Remediation Technologies Roundtable (FRTR). *Remediation Technologies Screening Matrix and Reference Guide, Third Edition* NTIS PB98-108590, http://www.frtr.gov/matrix2, 1997.

John, K Saji. Saji, J. Reddy, M L P. Ramamohan, T R. Rao, T P., "Solvent extraction of titanium(IV) from acidic chloride solutions by Cyanex 923", Hydrometallurgy. Vol. 51, pp. 9-18, 1999.

Kyuchoukov, George. Bogacki, Mariusz B. Szymanowski, Jan., "Copper extraction from ammoniacal solutions with LIX 84 and LIX 54", Industrial & Engineering Chemistry Research, Vol. 37, pp. 4084-4089, 1998.

McCarthy,-J.V., "Vitrokele(TM) process successfully removes metals from contaminated soil", Hazard. Waste Consult., Vol. 12, pp.1-13, 1994.

Meckes MC. Tillman J. Drees L. Saylor E., "Removal of PVBs from a contaminated soil using CF-systems(R) solvent extraction process", Journal of the Air & Waste Management Association, Vol. 47, pp.1119-1124, 1997.

Misra,-M.; Mehta,-R.K., "Remediating heavy metals, radionuclides, and organic pollutants from soils", JOM, J. Miner. Met. Mater. Soc., Vol. 47, pp. 45-53, 1995.

Mormile Melanie R. and Suflita Joseph M., "The toxicity of selected gasoline components to glucose methanogenesis by aquifer microorganisms", *Anaerobe.* Vol. 2, 299-303, 1996.

Murphy,-T.M.; Ballard,-R.B.; Losack,-B.J., "Treatment of hydrocarbon and lead contamination by soil washing at a pipe inspection facility, Prudhoe Bay, Alaska", AWMA 86th Annual Meeting and Exhibition, held Denver, CO, USA, June 13-18, 1993.

Pearl,-M.; Wood,-P., "Separation processes for the treatment of contaminated soil", Contaminated Soil 1993, Paper from Proc. 4th Int. KfK/TNO Conf. On Contaminated Soil, held Berlin, Germany, 3-7 May 1993.

Rovira, M. Hurtado, L. Cortina, J L. Arnaldos, J. Sastre, A M., "Recovery of palladium(II) from hydrochloric acid solutions using impregnated resins containing Alamine 336", Reactive & Functional Polymers, Vol.38, pp. 279-287, 1998.

Sarkar, S G. Dhadke, P M., "Solvent extraction separation of antimony(III) and bismuth(III) with bis(2,4,4-trimethylpentyl) monothiophosphinic acid (Cyanex 302)", Separation & Purification Technology. Vol.15, pp. 131-138, 1999.

Sparks, B.D., Meadus, F.W., "Laboratory evaluation of the SESR process: Remediation of fine texture soils contaminated with organic materials", 87th Annual Meeting & Exhibition, Cincinnati, Ohio, June 19-24, 1994.

Srinivasan, T G. Rao, P R Vasudeva. Sood, D D., "Diluent and extractant effects on the enthalpy of extraction of uranium(VI) and americium(III) nitrates by trialkyl phosphates", Solvent Extraction & Ion Exchange, Vol. 16, pp. 1369-1387, 1998.

Yasugi Tomojiro, Kawai Toshio, Mizunuma Kazunori, Kishi Reiko, Harabuchi Izumi, Yuasa Junko, Eguchi Teruko, Sugimoto Ryoichi, Seije Kazunori, Ikeda Masayuki, "Exposure monitoring and health effect studies of workers occupationally exposed to cyclohexane vapor", *International Archives of Occupational & Environmental Health.* Vol. 65, 343-350, 1994.

Evaluation of Lignin Derivatives for Soil and Water Cleanup

K. Volchek, SAIC Canada, Ottawa, Ontario,
M. Raskin, Cellutech LLC, Everett, Massachusetts
M. Weber, McGill University, Montreal, Quebec
email: konstantin.volchek@saic.com

Abstract

Lignin is one of major by-products of pulp and paper industry. It is available in large quantities, is fairly inexpensive and is non-hazardous. In this study, derivatives of lignin (LDs) were evaluated as sequestering agents for heavy metals in soil and water. A series of bench-scale tests were carried out to evaluate the binding of selected heavy metals under various conditions. Experimental techniques included: a) binding with water-soluble fractions of LDs followed by ultrafiltration, and b) column soil leaching. The paper presents test results, a discussion of these results and recommendations for further work.

1.0 Introduction

Contamination of soil and groundwater with heavy metals is one of the most common environmental pollution issues. There have been a large number of technologies developed and used to address this issue (US EPA, 2000). Most of them aim at the removal of metals from either groundwater or soil while some soil treatment techniques employ stabilization of the soil matrix. Many of these technologies involve sequestration, i.e. the binding of heavy metals with inorganic or organic agents. In the case of removal techniques, sequestration may simplify and enhance the process, e.g. through hydroxide or sulfide precipitation. In case of stabilization, sequestration reduces the metals ability to move into the groundwater and contaminate it.

There are a number of commercial sequestering agents available, such as sodium hydroxide or sulfide, water soluble polymers (flocculants and coagulants) and chelants (EDTA). All of them, however, have limitations in terms of either a potential environmental hazard, high cost or other characteristics. Consequently, there is a need to identify, develop and evaluate sequestering agents improved with improved properties.

Lignin, which is one of the major by-products of pulp and paper industry, is known for its ability to bind heavy metal ions (Lin and Lebo, 1995, Varma *et al.*, 1990). Molecules of lignin contain chemical groups such as phenolic, ether, carboxylic, etc. (see Fig. 1), which make this binding possible. Lignin is used to treat boiler and tower cooler water to prevent scale deposition. It is also utilized to bind heavy metals such as iron, copper, zinc, etc. to provide essential micronutrients to plants growing in metal-deficient soils. Lignosulfonates have been evaluated for the removal of some heavy metals (Pb, Cr and Hg) from water and soil leachates (Volchek *et al.*, 1996).

It was reported that the binding ability of lignins may be enhanced by treating them in acidic conditions, followed by oxidative degradation (Raskin, 1999). As a result of this treatment, lignin molecules gain a greater variety of functional groups, which results in stronger complexing properties.

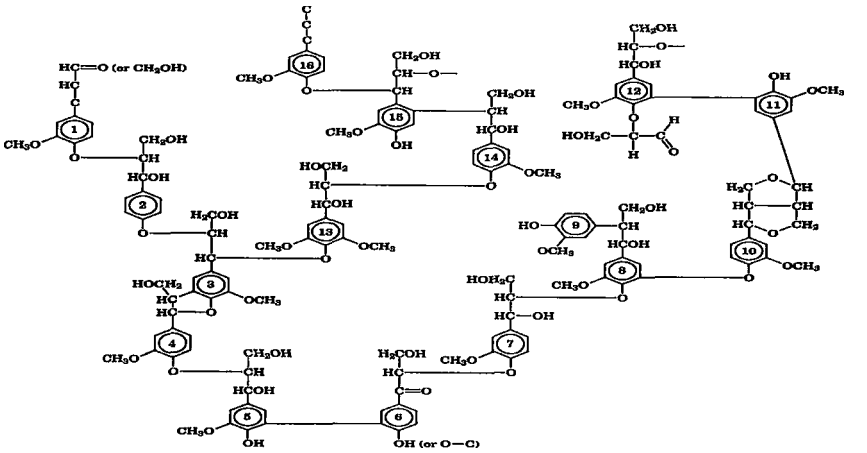


Figure 1. Structural model of spruce lignin.

It was an objective of this work to evaluate those lignin derivatives (LDs) for their ability to sequester heavy metals from water and soil. The focus of the study was on the removal of cobalt and uranium. Both metals make common radionuclides and are found in both soil and groundwater as a result of radiological contamination.

2.0 Experimental Procedures

All tests were carried out on a bench scale using model solutions and spiked soil samples. Non-radioactive (stable) isotopes of cobalt and uranium were used as their chemical properties are identical to those of radioactive isotopes. A majority of experiments was done at the Department of Chemical Engineering of McGill University, as a part of undergraduate laboratory studies. Samples of lignin derivatives were obtained from Cellutech LLC, Everett, Massachusetts. They were produced from an industrial lignin by nitric acid, according to US Patent 5,880,271 (Raskin, 1999).

The tests were performed in two main series:

- Removal of metals from water using binding with lignin derivatives followed by membrane filtration; and
- Removal of metals from soil using leaching with a lignin derivative solution in a column.

2.1 Water Treatment Tests

The LDs were purified via diafiltration to remove low-molecular weight fractions. A LD solution was prepared in deionized water and filtered three times through a semi-permeable membrane with a molecular weight cut-off (MWCO) of 10,000 (G-80 type manufactured by Osmonics Inc.). The concentrate that contained molecular weight fractions larger than 10,000 was used in subsequent tests.

In metal rejection tests different amounts of LDs were added to spiked solutions to produce a LD/metal molar ratio varying from 0 to 5:1. Spiked solutions were prepared by dissolving either cobalt nitrate $Co(NO_3)_2$ or uranyl nitrate

$UO_2(NO_3)_2$ in deionized water. The solution pH was adjusted to a desired level within the pH range of 4 to 10. The solution was then filtered through the 10,000 MWCO membrane. Under the test conditions, all or some of the metal ions became bound with LDs and subsequently rejected by the membrane thus forming the concentrated stream (the concentrate). Any metal found in the permeate (filtrate) was therefore a result of either an incomplete binding or an incomplete LD rejection by the membrane (the latter was largely eliminated by purifying the LDs via diafiltration).

Samples of the concentrate and the permeate were analyzed for the presence of heavy metals thus indicating the effectiveness of binding under specific test conditions. The main parameter determined was the rejection R which was calculated as $R = (C_{conc}-C_{perm})/C_{conc} \times 100\%$.

As well as the metal concentration, the concentration of LDs was monitored in both the concentrate and the permeate to account for possible LD losses due to incomplete rejection.

2.2 Soil Treatment Tests

A slurry of kaolinite clay was mixed with either $Co(NO_3)_2$ or $UO_2(NO_3)_2$ and stirred continuously for 24 hours. The slurry was then permitted to settle to the bottom and the aqueous phase decanted. The solid phase was then mixed with LDs to produce in a LD/metal weight ratio varying from 0 to 100.

The spiked clayey soil was placed a leaching cell and water was filtered through the soil under pressure. This experimental setup was chosen to simulate conditions of an in-situ soil flushing.

The leachate was collected at different time intervals and analyzed for the presence of metals and LDs. A higher metal concentration in the permeate was an indication of a more effective removal from the soil. The removal was defined as a weight fraction of the metal leached from the soil.

2.2 Analyses

Aqueous samples were analyzed for heavy metals using flame atomic absorption spectroscopy. Concentration of lignin derivatives was determined using a total organic carbon analyzer (TOC). Soil samples had to be digested with aqua regia prior to their analyses.

3.0 Experimental Results and Discussion

3.1 Water Treatment Tests

In both uranium and cobalt removal tests, the addition of LDs to the solution resulted in an increased removal of heavy metals. Typical results for cobalt are illustrated in Fig.2. It was observed that higher lignin to metal ratios resulted in higher metal rejections. This regularity was not unexpected and could be explained by a more complete binding of metals when more LDs were available. It should be noted that some metal rejection was observed even in the absence of LDs, due to a partial retention of metal by smaller pores in the membrane. Nevertheless, when LD were added, it increased the rejection significantly.

A higher pH was observed to be beneficial for a higher metal rejection. It was speculated that two factors were involved here: a) a higher binding capability of LDs due to ionization of their molecules and b) metal hydrolysis. Hydrolysis became a

predominant factor at pH 10 when an almost complete rejection of metals was observed even in the absence of LDs.

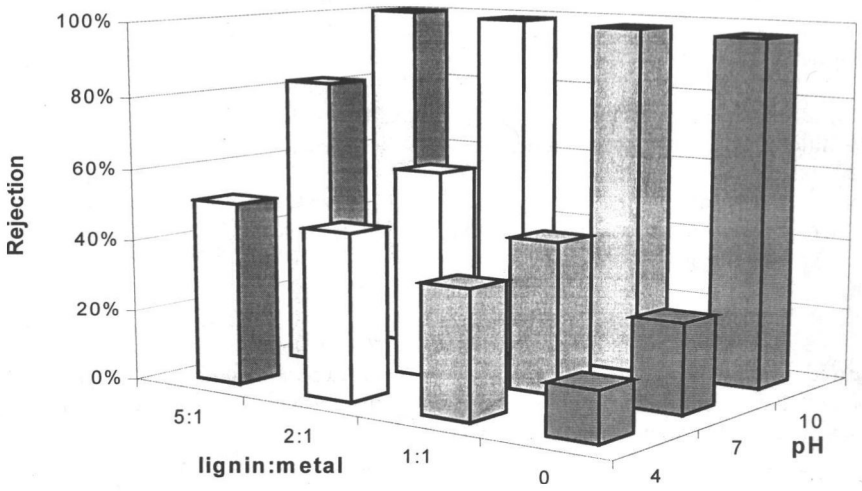


Figure 2. Rejection of Cobalt vs. pH and the Lignin to Metal Molar Ratio.

In order to account for hydrolysis, an "effective" rejection was calculated being a difference between an rejection observed in the presence of LDs and that in its absence. It was found that the "effective" rejection had an optimum pH at which the rejection reached its maximum. It was found to be approximately 6 for cobalt and 9 for uranium.

3.2 Soil Treatment Tests

Typical results of soil leaching tests for cobalt and uranium are presented in Figs. 3 and 4, respectively. It was found for both metals that the more water was filtered through the cell, the larger quantities of metals were extracted. It was also observed that the removal increased when LDs were added to the system.

Leaching tests conducted at pH 6 for cobalt and pH 9 for uranium, corresponding to optimum "effective" rejections of those metals, revealed that in similar test conditions, the removal of cobalt increased from 60% in the absence of LDs to 80% when LDs were added. For uranium this resulted in an increase from 0% to 12%. These results suggest that LDs enhance the removal of metals by likely forming water-soluble compounds with those metals thus enabling them to be removed more efficiently.

Fig. 5 illustrates the effect of pH on the removal of uranium. Contrary to what is normally observed in a typical acid leaching process for soil, when an acidic pH is maintained, a higher pH is better for the metal removal in case of LD-based leaching.

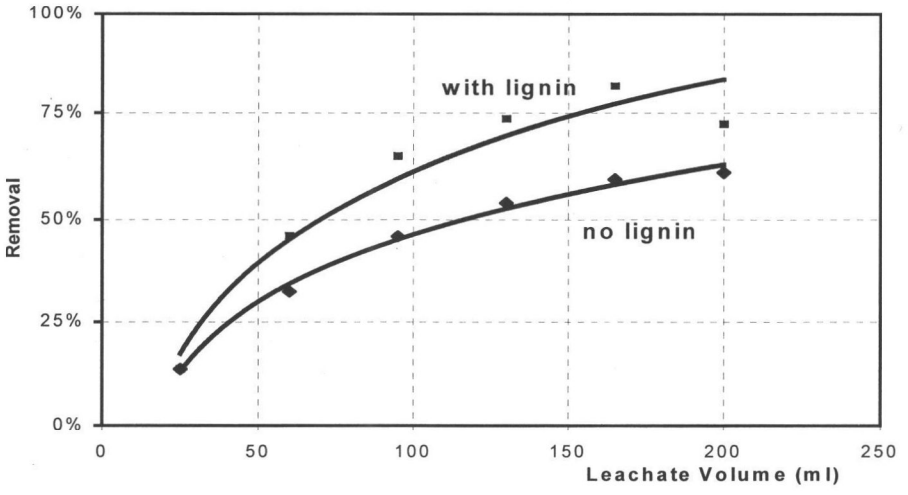


Figure 2. Removal of Cobalt from Clayey Soil.
Lignin/cobalt = 100:1 (w/w). pH 6.

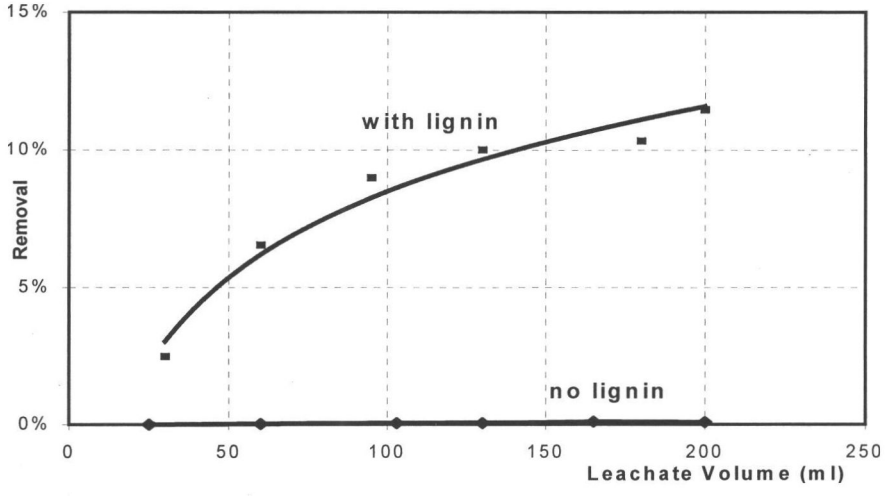


Figure 3. Removal of Uranium from Clayey Soil.
Lignin/uranium = 100:1 (w/w). pH 9.

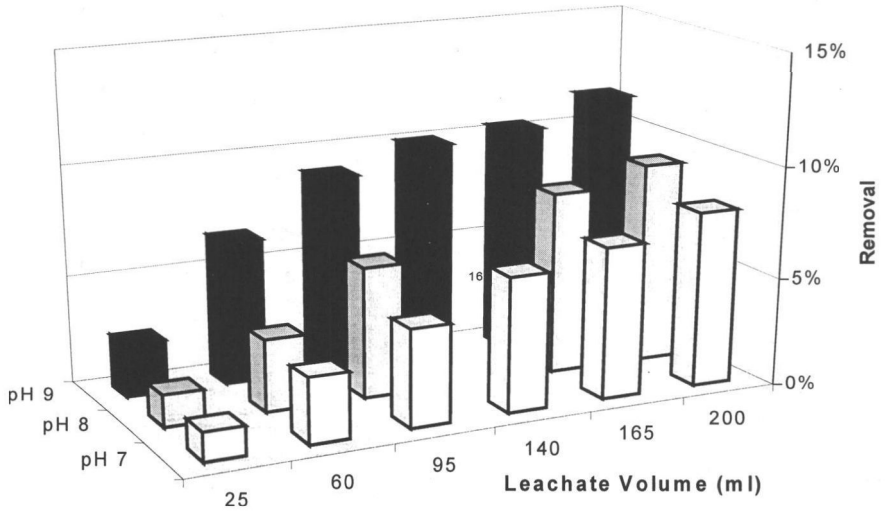


Figure 5. The effect of pH on the Removal of Uranium from Clayey Soil. Lignin/Uranium = 100:1 (w/w). pH 9.

4.0 Conclusions

Lignin derivatives (LDs) were evaluated and found to be applicable to the removal of uranium and cobalt, common radioisotopes, from soil and water. In the case of contaminated water , the results showed that the heavy metals can be removed by adding LDs to the water and filtering it through an appropriate semi-permeable membrane.

The use of LD may be beneficial for in-situ soil treatment. Not only do LDs enhance the removal of heavy metals but they also do this within a "mild" pH range of 6 to 9. This feature is advantageous as working in this pH range would be less damaging for the soil matrix.

Additional bench-scale work appears to be necessary to evaluate the performance of LDs to treat actual contaminated soil and water samples and optimize the conditions of removal.

5.0 Acknowledgements

This work was made possible through the financial support from the Emergencies Engineering Technology Office of Environment Canada.

The authors express their gratitude to students of the Department of Chemical Engineering of McGill University (Project Lab Group No. 5 in 1998/99 and Project Lab Groups No. 6 and 7 in 1999/2000) and their teaching assistants for their valuable contribution to the experimental part of this work.

6.0 References

Lin, S.Y and Lebo, S.E., Jr., "Lignin", in *Kirk-Othmer's Encyclopedia of Chemical Technology*, ed. M.Howe-Grant, John Wiley & Sons, NY, 1995.

Raskin, M., "Polyphenolic Derivative Chelating Agent", US Patent No. 5,880,271. March 9, 1999.

United States Environmental Protection Agency (US EPA), Technology Innovation Office, The Hazardous Waste Clean-up Information Web Site: http://clu-in.org/, 2000.

Varma, K.V.R., Swaminathan, T., and Subrahmanyam, V.P.R., "Heavy Metal Removal with Lignin", Journal of Environmental Science and Health, Vol. A25, No.3, pp. 243-265, 1990.

Volchek, K., et al., "Membrane-Assisted Processes to Remove Heavy Metals from Soil and Water", *Proceedings of the Thirteenth Technical Seminar on Chemical Spills (TSOCS)*, Environment Canada, Ottawa, Ont., pp.313-324, 1996.

Evaluation of a Two-Phase Partitioning Bioreactor for Site Remediation

M. M. Punt[1] and A. J. Daugulis[2]

[1] Environmental Technologies Program
SAIC Canada
Ottawa, Ontario, CANADA
Monique.M.Punt@saic.com

[2] Department of Chemical Engineering
Queen's University
Kingston, Ontario, CANADA

Abstract

SAIC Canada and Environment Canada are undertaking a joint project with Queen's University to assist in the advancement of a biotreatment system developed by researchers at Queen's. This process, called the Two-Phase Partitioning Bioreactor (TPPB), combines solvent extraction and bioremediation for the treatment of organic wastes or soil contaminated with organic compounds. The TPPB can overcome one of the main challenges of conventional biological processes - controlling the contaminant level in the bioreactor to ensure that the concentration is high enough to sustain microbe growth while not being too high such that it is toxic to the microbes.

The feasibility of scaling up this process for the treatment of contaminated soil on the large-scale is being evaluated. The results of the preliminary feasibility study and some bench-scale results are presented below.

1.0 Introduction

The Two-Phase Partitioning Bioreactor (TPPB) process combines solvent extraction and bioremediation for the treatment of soil contaminated with organic compounds. The key to this technology is that the microbes are fed (by means of equilibrium partitioning) only as much contaminant that they can handle, at a rate that is determined entirely by the metabolic activity of the organisms themselves (and is therefore self-regulating). The process begins with an extraction step where a solvent is used to dissolve organic contaminants from soil. The solvent mixture is separated from the soil. The contaminated solvent, being immiscible in water, is then "floated" on top of an aqueous-phase in a bioreactor. Because organic contaminants contained in the solvent are partially miscible in water, a certain amount of the contaminant will transfer from the solvent to the aqueous phase until equilibrium occurs. At the same time the microbes in the aqueous phase breakdown the dissolved contaminants. This, in turn, shifts the solubility equilibrium and, as a result, the contaminants continue to transfer from the solvent to the aqueous phase at the same rate that the microbes are consuming them. In the end, after all the compounds have been broken down, the solvent can be recycled back to the extraction stage.

The advantages of this "self-regulating" system include:

- Eliminates the need for a complicated mechanical feeding system with a controller;

- The microbes are fed only the amount of contaminant that they can degrade at a particular time, therefore, they do not starve as a result of lack of food and they are not killed by an over-abundance of food;
- The system can process wastes and contaminated materials that have very high concentrations; and,
- The bioreactor is not directly affected by soil properties.

2.0 Results Obtained to Date

The application of the TPPB for the removal and biodegradation of organic contaminants in soil has been documented by Collins and Daugulis (1996, 1997 and 1999). This process has been evaluated for the destruction of phenol and a mixture of benzene, toluene and *p*-xylene (BTX) from waste material and soils.

Recent work on the development of the TPPB has concentrated on three main areas: solvent selection, microbe selection and TPPB biodegradation. This work is described in more detail below.

2.1 Solvent Selection

A crucial step in the development of the solvent extraction/TPPB process is the selection of an appropriate solvent for the process. It has been determined that for the solvent selection the following properties must be investigated (Bruce and Daugulis, 1991):

- Aqueous Solubility – The solvent must be immiscible in water to aid in its separation from the aqueous phase and to reduce solvent loss to the aqueous phase.
- Distribution Coefficient – The contaminant of interest must be preferentially dissolved in the solvent as opposed to the aqueous phase, such that only a small amount of contaminant is transferred to the aqueous phase at a time.
- Biocompatibility – The solvent must not be toxic to the microbes used in the bioreactor. It has been determined that the biocompatibility of a solvent increases as the log of the octanol/water coefficient (log P) of that compound increases.
- Biodegradability – The solvent must not be biodegraded by the microbes used in the bioreactor.
- Cost/Availability – For this system to be viable on the large-scale the solvents must be inexpensive and available in bulk quantities.
- Toxicity – The solvent must be non-hazardous. Normally, if the solvent is biocompatible with the microbes it will also be non-toxic.
- Other Physical/Chemical Properties – The solvent must have a low emulsion-forming tendency to aid in its separation from the aqueous phase. The solvents must also be chemically and thermally stable, such that they are not depleted during the operation.

In order to facilitate the selection of solvents, the researchers at Queen's have developed a solvent database called the Extraction Screening Program (ESP) (Bruce and Daugulis, 1991) to allow for the systematic and simultaneous screening of the above parameters. The ESP was used to select solvents for the treatment of BTX and phenol in the TPPB (Collins and Daugulis, 1997 a & b, and 1999).

Environment Canada also provided funding for a preliminary solvent selection exercise using the ESP Database to select solvents that would be applicable to the extraction and destruction of PCBs using the TPPB. The database was used to rank solvent on their ability, based on mass partition coefficient, to extract PCBs.

2.2 Microbe Selection

An important aspect of the TPPB technology is the proper selection of a microbe or microbes for the degradation of the contaminants in question. This task can be difficult because certain microbes exhibit behaviours that may have to be overcome in a biodegradation system, for example:

- a microbe may degrade one compound but may be inhibited by other contaminants in the soil;
- a microbe may degrade a compound at a specific concentration, but then may be inhibited by the same compound at a higher concentration; or,
- the degradation of a compound by a microbe may require that another specific compound be present.

In the case of the phenol degradation work, the microbe chosen was *Pseudomonas putida* ATCC 11172, which is known to degrade phenol (Collins and Daugulis, 1997a). However, it is also known that this microbe is inhibited by phenol concentrations of greater than 500 mg/L. Since, the aqueous solubility limit of phenol is above this level, this microbe may be inhibited in conventional bioreactors. In the case of TPPB, however, the resulting concentration of phenol in the TPPB aqueous phase is driven by the partition coefficient of phenol between the solvent and water. It was determined that the concentration of phenol in the solvent phase could go as high at 20 g/L (or 10 grams in the 500 mL of solvent used with 1 L of aqueous phase) and the concentration in the aqueous phase would only ever reach 420 mg/mL, which is below the microbe inhibition level.

The microbe chosen for the BTX work was *Pseudomonas sp.* ATCC 55595, which is known to simultaneously degrade these compounds (Collins and Daugulis, 1999). However, the microbe will not degrade benzene or *p*-xylene unless toluene is present and *p*-xylene can be toxic to the microbe. As a result, the breakdown of these contaminants follows a complex path.

Environment Canada provided some funding to Queen's University researchers to investigate possible microbes for the degradation of poly-aromatic hydrocarbons (PAHs) as this is a contaminant that is found at a number of contaminated sites and is known to be difficult to treat (Correia and Daugulis, 2000). It was found that limited work has been performed on the degradation of PAHs at contaminated sites, particularly for PAHs having four or more fused aromatic rings. However, the results of this study showed that there are some microorganisms, including *Mycobacteria*, *Sphingomonas* and white rot fungi that have been shown to degrade PAHs with four or more rings. Additional work on the use of TPPB for the degradation of PAHs is planned for the Spring of 2000.

2.3 TPPB Biodegradation

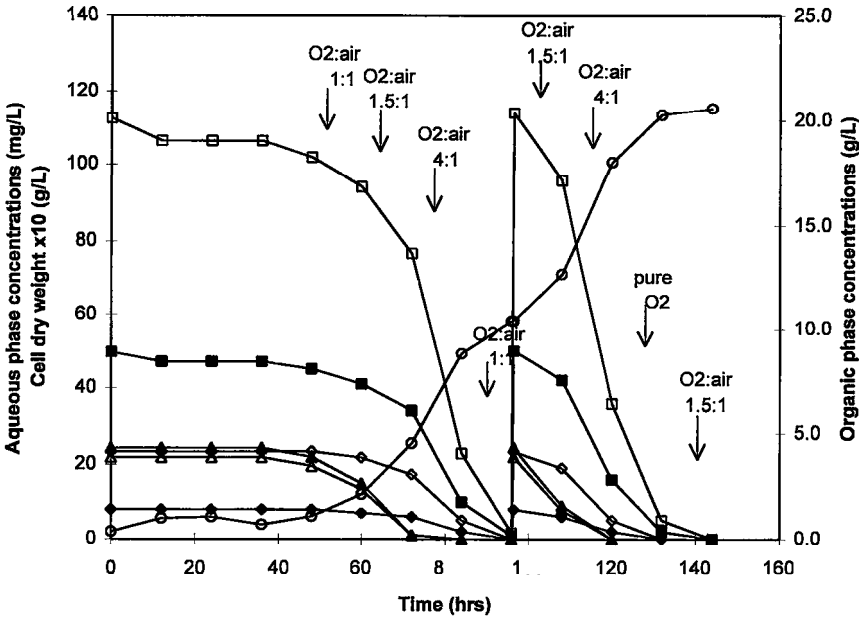
Work on the use of the TPPB for the degradation of contaminants began with a study of phenol degradation (Collins and Daugulis, 1997 a & b). This initial work looked at issues related to the solvent and microbe selection for the TPPB degradation of phenol. Ultimately the solvent selected was 2-undecanone, which has

a low water solubility, relatively high log P, low emulsion forming tendency and insignificant biodegradability by the phenol-degrading microbe, *Pseudomonas putida* ATCC 11172.

The initial set of tests on phenol biodegradation involved spiking the solvent with varying masses of phenol and feeding it to the bioreactor in either batch or fed-batch mode. Fed-batch mode involved removing solvent and replacing it with fresh spiked solvent at regular intervals during the run. During each run the concentration of phenol in the solvent phase and the aqueous phase and the concentration of cells in the aqueous phase were measured over time.

A second set of experiments was performed to evaluate the degradation of BTX (Collins and Daugulis, 1999). As described above the microbe chosen for this work was *Pseudomonas sp.* ATCC 55595. The results of this work showed that the degradation rate of these contaminants could be increased by mixing pure oxygen in the aeration stream.

The results of the phenol and BTX work showed that using a fed-batch mode resulted in the occurrence of only an initial lag time (i.e., the time before the microbes begin degrading the compounds). As such, if the bioreactor is continually fed with new contaminated solvent the lag time only occurs after the initial feed resulting in more contaminant being degraded over a shorter time as would be required for a batch system. Figure 1 shows one set of results from the BTX work where a fed-batch system was used with enriched oxygen. In this set of tests, the selected solvent (an oleyl alcohol) was used to extract BTX from silica sand. The solvent was then contacted with an inoculated aqueous-phase. The concentrations of contaminants in the aqueous and organic phases were monitored over time. Once the concentration of contaminants had reduced to insignificant levels, a second contaminated sand sample, having the same concentration as the first sample, was extracted with the solvent recovered from the system. This solvent was again contacted with the aqueous phase. As can be seen in Figure 1, by introducing this second batch of contaminated solvent at the end of the degradation from the first batch, the second lag time is avoided and the complete degradation of the contaminants occurs more quickly than with the first batch.



■ = aqueous phase toluene concentration, mg/L
▲ = aqueous phase benzene concentration, mg/L
◆ = aqueous phase *p*-xylene concentration, mg/L
○ = cell dry weight x 10, g/L
□ = organic phase toluene concentration, g/L
Δ = organic phase benzene concentration, g/L
◇ = organic phase *p*-xylene concentration, g/L

Figure 1: Example of Degradation of BTX using an Enriched Air Fed-Batch System (Collins and Daugulis, 1999)

3.0 Comparison with other Soil Remediation Technologies

Compared to other soil remediation technologies, the TPPB has several advantages including the fact that it will destroy, as opposed to merely recover, the contaminants and the process can selectively treat contaminants through the proper selection of solvents and microbes.

It is normally difficult to compare the clean-up costs associated with various soil remediation technologies unless the technologies have been evaluated side-by-side at one site. Clean-up costs are very dependent on a number of site specific factors including: the remoteness of the site, the soil properties, the quantity of contaminated soil, the soil moisture content, the type contaminant, the contaminant concentration, the cleanup target concentration for the contaminant and the urgency of the cleanup. There is information on treatment costs in the literature (DuTeaux, 1997, FRTR, 1997), however, it must be fully understood whether the costs quoted include the costs for items such as: equipment transport to the site, excavation of the soil, analytical costs, final disposal of waste streams and decommissioning of the site. As a result, for comparison purposes, it is best to look at the range of costs from various sites.

Being an *ex situ* destruction technology, it is most logical to compare the TPPB system with other *ex situ* destruction technologies. Currently, the most popular technology that falls in this category is thermal desorption with off-gas destruction. The other technologies with which the TPPB technology can be compared are incineration, slurry bioreactors on their own and solvent extraction on its own. Table 1 shows a comparison of the range of costs and limitations of the technologies that can be compared with the TPPB technology. The costs presented in Table 1 are the costs for total treatment of sites contaminated with organic compounds such as petroleum hydrocarbons, volatile organic compounds, poly-aromatic hydrocarbons, chlorinated phenols and PCBs. The size of these sites varied from 3000 tonnes to 100,000 tonnes. In general, the lower value in the cost range would be associated with larger sites.

A full cost analysis of the TPPB has not been performed, however, it is reasonable to assume that the TPPB clean-up costs would be in a range somewhat similar to the costs for slurry-phase bioreactors and solvent extraction. The cost for the TPPB would not be the sum of the costs of these two technologies because both the bioreactor and the solvent extraction cost ranges listed in Table 1 include costs for excavation and materials handling, which should not be added twice. As well, in some cases (likely the higher end of the cost range), the solvent extraction range includes the cost to dispose of the concentrated contaminants, which is not a requirement if the compounds are to be destroyed using the TPPB.

Table 1: Treatment Cost Comparisons (adapted from Du Teaux, 1997; FRTR, 1997)

Technology	**Cost Range ($Cdn/tonne)[1]**	**Limitations of Technology**
Slurry Phase Bioreactor	$85 to $265	- Cannot handle very high contaminant concentrations. - May require off-gas treatment, which will increase costs.
Solvent Extraction	$130 to $640	- Concentrated contaminants require disposal, which will increase costs. - Solvent residue in the treated soil may be toxic. - Organically-bound heavy metals can be carried over into the solvent thus hindering disposal.
Thermal Desorption (with off-gas destruction)	$40 to $775	- Cannot efficiently treat high moisture content soils. - Can be subject to regulatory controls.
Incineration	$260 to $1600 ($2400 to $9600 for PCBs)	- High treatment costs - Low public acceptance. - Strict regulatory controls.

1. Values were converted from theses references using the following factors:
   $U.S.= 1.45 $Cdn
   1 tonne = 1.1 ton
   1 tonne = 1 yd^3 (assuming a soil bulk density = 1.3 kg/L)

Using the above assumptions, the TPPB could be a viable alternative to thermal desorption and incineration. The TPPB could also be cost-effective for use in situations were solvent extraction would normally be chosen, particularly if the costs for disposing of the final concentrated stream were included in the solvent extraction treatment costs. The lower end costs for thermal desorption are normally for sites that have volatile compounds and low moisture contents, so the TPPB may have difficulty competing for these types of sites. The TPPB also could not compete in situations that are applicable to using a slurry-phase bioreactor on its own (e.g., low levels of contamination).

4.0 Preliminary TPPB Design Aspects

No one technology can treat all contaminant types. As such, one of the exercises required in developing a new remediation technology is choosing the type of contaminated site situation for which the technology will be most feasible and understanding the technologies limitations and the situations where it will be unfeasible. Based on the information provided in the above sections, it appears that the most suitable application for the TPPB system is the on-site excavate and treatment of semi- or non-volatile contaminants in soil, particularly for sites having limited contamination areas (e.g., gasoline stations, former spill sites and industrial sites where contamination has not spread considerably).

Looking at the TPPB technology as a two step process, in general the first step of the process – the extraction of the contaminant from the soil - is the limiting step. It is this step that is most affected by both the properties of the soil and the properties of the contaminants. The only way that the soil properties will affect the bioreactor efficiency is if naturally-occurring organic matter is carried over from the soil by the solvent into the bioreactor and this material is preferentially broken down by the microbes. Table 2 shows how the various site characteristics can affect the selection of operating parameters for the solvent extraction and bioreactor stages of the TPPB system. Many of these characteristics along with the following aspects of the process, which are described below, must be further evaluated as part of the scale-up of the technology:

- selection of solvent extraction method;
- selection of solvent;
- selection of microbes; and,
- coupling the extraction phase with the bioreactor.

Table 2: Effect of Site Characteristics on TPPB Steps

Site Characteristic	Effect of Solvent Extraction	Effect on Bioreactor
Soil Properties		
- particle size distribution	*extraction method* - high clay content soils may require several extraction stages or enhancements to achieve sufficient removal.	none
- moisture content	*solvent recovery* – depending on contaminant type and solvent selected, high moisture contents could complicate the solvent recovery step following extraction.	none
- naturally occurring organic matter	*extraction method* - high organic matter soils (e.g., peat soils) may require several extraction stages or enhancements to achieve sufficient removal. *solvent recovery* – high organic matter soils will also absorb solvent and, therefore, reduce the percent of solvent that can be recovered for recycling.	*degradation rate* – if organic matter is carried over to the bioreactor by the solvent, it may interfere with the degradation of the contaminant.
Contaminant Properties		
- chemical composition	*solvent selection* - in general, contaminants will be most easily dissolved by solvents having similar chemical composition (e.g., polar solvents dissolve polar contaminants).	*microbe selection* – microbes must be selected based on the type of contamination in the soil. *biodegradation/chemical reactivity* – chemical type determines whether a compound is biodegradable and its tendency toward non-biological reactions such as hydrolysis, oxidation, and polymerization.
- concentration/ remediation target	*extraction method* – as the concentration of contamination increases and the remediation target decreases, the number of extraction stages required increases.	*operating conditions* – the overall amount of contamination to be fed to the bioreactor will determine the overall degradation time and the quantity of additives required (oxygen and nutrients). *Off-gas treatment* – could be required for the treatment of VOCs or if VOCs are formed during degradation.
- multiple contaminants	*solvent selection* – one solvent may not suffice. Co-solvents may be required.	*microbe selection* – one compound may interfere with microbes that will degrade other compounds. Co-metabolites may be required. *degradation inhibition* – organically-bound heavy metals could be carried over by the solvent and hinder biodegradation.

4.1 Selection of Solvent Extraction Methods

The work to date on the evaluation of the TPPB for soil remediation has involved the use of spiked solvents to evaluate the bioreactor stage on it own or spike silica sand to evaluate the solvent extraction and bioreactor combined process. Using this type of controlled environment allows for a thorough understanding of the behaviour of the system without interference from difficult to control parameters, such as those discussed in Table 2, resulting from using soils from actual sites. Before scaling up the process, it will be important to try to isolate and evaluate the effects of some of these other soil parameters on the system. This will require some further testing using spiked soils having specific physical properties and then testing with soils from actual contaminated sites.

It should be noted that enhanced extraction methods may be required to ensure the near-complete extraction of recalcitrant compounds from soil. As such, further investigation of these processes will be important to determine which could be suitable to be coupled with the TPPB system. This will require some testing of different systems using spiked soils and soils from actual contaminated sites.

If the TPPB were to compete with technologies suitable for VOC treatment, the use of solvent extraction to extract the contaminants directly from the soil would not be economically feasible for these compounds. As such, another lower operating cost soil extraction method, such as soil vapour extraction, should be employed for these compounds, prior to their degradation using the TPPB process.

4.2 Solvent Selection

As discussed in Section 2.1, a crucial step in the development of the solvent extraction TPPB process is the proper selection of the solvent used. The solvents chosen must be able to dissolve the contaminant in question, not be toxic to the microbes used and not be degraded by the microbes used. Depending on the solvent extraction method chosen, further constraints could be placed on the type of solvent used. Appropriate solvents have been selected for compounds such as BTX and phenols; however, additional work will be required to select solvent for other contaminants for which the TPPB appears to be suitable. Some laboratory testing will also be required to test these solvents using the extraction methods chosen.

4.3 Microbe Selection

As discussed in Section 2.2, for every group of contaminants a specific microbe needs to be selected that will degrade that group of contaminants. Microbes have been selected for BTX and phenol degradation and some preliminary work has been performed to select microbes for PAHs and PCBs. Work will have to continue on the selection of microbes appropriate for the contaminants chosen to be investigated using the TPPB process.

4.4 Coupling the Extraction Phase with the Bioreactor

One challenge to be faced in the scale up of the solvent extraction/TPPB system will be the ability to effectively couple these two technologies. Ideally, the most efficient way to set up the process would be to have the two steps (solvent extraction and bioreactor) run in series in a continuous mode where the flowrates handled by each would be the same. In reality this may be difficult because the retention times required for the biodegradation is much longer than that required for

solvent extraction. To run in continuous mode, bioreactors are often placed in series. Therefore, depending on the solvent extraction method chosen, the solvent could be passed through the solvent extraction process to a series of bioreactors and recycled to the solvent extraction process, with soil being added and removed from the solvent extraction process and nutrients and oxygen added to and biodegraded material removed from the bioreactor process.

Further research and development work is still required on the design of a pilot-scale solvent extraction/TPPB process. This will require additional bench-scale work in order to test how various solvent extraction methods can be coupled with the TPPB. As a rough estimate, it can be assumed that a pilot demonstration unit including a solvent extraction system and a 150 L bioreactor would be in the range of $300,000 to $400,000 to implement.

5.0 Conclusions

Considerable work has been performed on the TPPB technology. However, because of the wide range of contaminated soil types that could potentially be evaluated using the TPPB, additional laboratory- and bench-scale work is required before the technology can be developed into a field-scale demonstration unit.

Based on a preliminary evaluation of other *in situ* and *ex situ* technologies for the treatment of soils contaminated with organic compounds, it was concluded that the TPPB system, when solvent extraction is used, would be most feasible for the treatment of semi- or non-volatile contaminants in soil, particularly for sites having limited contamination areas. In evaluating the costs and limitations of other treatment technologies, it was determined that the TPPB could compete with incineration and low temperature thermal desorption and also with solvent extraction, if the costs for disposing of the final concentrated stream were included. For high concentration soils, the TPPB could compete with slurry-phase bioreactors.

Before scaling up the TPPB technology, the following areas must be investigated more thoroughly:

- Selection of solvent extraction method and testing methods using spiked and actual contaminated soils;
- Solvent selection for the contaminants chosen to be investigated using the TPPB process;
- Microbe selection for the contaminants chosen to be investigated using the TPPB process; and,
- Coupling of the extraction step with the bioreactor step.

Additional bench-scale work is required to evaluate the combination of feasible solvent extraction methods with a bioreactor or a series of bioreactors. Based on the results of these tests, a pilot-scale demonstration unit should be constructed.

6.0 Acknowledgment

The authors would like to thank Mr. Brian Mansfield of Environment Canada for providing the funding for this study.

7.0 References

Bruce, L. J. and A. J. Daugulis. Solvent Selection Strategies for Extractive Biocatylists. *Biotechnol. Prog.*, Vol. 1, No. 2, pp. 116 – 124, 1991.

Collins, L. D. and A. J. Daugulis. Characterization and optimization of a two-phase partitioning bioreactor for the biodegradation of phenol. *Appl. Microbiol. Biotechnol.* Vol. 48, pp. 18 – 22, 1997a.

Collins, L. D., and A. J. Daugulis. Biodegradation of phenol at high initial concentrations in two-phase partitioning batch and fed-batch bioreactors. *Biotechnology and Bioengineering*. Vol. 55, No. 1, pp. 155 – 162, 1997b.

Collins, L. D. and A. J. Daugulis. Simultaneous biodegradation of benzene, toluene, and p-xylene in a two-phase partitioning bioreactor: concept demonstration and practical application. *Biotechnol. Prog.*, Vol. 15, No. 1, pp. 74-80, 1999.

Correia, J and A. J. Daugulis. *The Identification of Organisms for the Biodegradation of Polyaromatic Hydrocarbons.* Unpublished Report, 2000.

DuTeaux, S. B. *A Compendium of Cost Data for Environmental Remediation Technologies, 2nd Edition,* http://www.lanl.gov/projects/etcap, U.S. Department of Energy, 1997.

Federal Remediation Technologies Roundtable (FRTR). *Remediation Technologies Screening Matrix and Reference Guide, Third Edition* NTIS PB98-108590, http://www.frtr.gov/matrix2, 1997.

Sodium Cyanide: Properties, Toxicity, Uses and Environmental Impacts

Kerry Ketcheson and Merv Fingas
Emergencies Science Division
Environmental Technology Centre
Environment Canada
Ottawa, Ontario
Ketcheson.Kerry@etc.ec.gc.ca

Abstract

Sodium cyanide (NaCN) is a white crystalline powder and is fairly soluble in water. The major uses of sodium cyanide in the industry are gold cyanidation, flotation, and metal plating. Other minor uses include chemical synthesis, radioactive tracer and sterilization processes.

Sodium cyanide is very toxic to humans. At low concentrations cyanide can be detoxified by the liver but at higher more toxic concentrations it inhibits cellular oxygen and can cause death. In animals and fish sodium cyanide is lethal at very low concentrations.

Spills of sodium cyanide show that there is almost one every year from 1974 to 1995. The biggest importer of sodium cyanide by far is the United States. The most common form of the cyanide spills are cyanide nos, followed by cyanide leachate, then sodium cyanide.

This paper will discuss case studies of various sodium cyanide spills that have occurred on August 1995, May 1998 and January 2000 to demonstrate the detrimental effects on the environment. It will also show properties, toxicity, uses and neutralization reactions.

1.0 Properties

Sodium cyanide (CAS #: 143-33-9) was first made in 1834 by F. and E. Rogers who heated prussian blue (highly coloured mixed oxidation state $Fe^{II/III}$ derivatives) and sodium carbonate together (King, 1994). The mixture was cooled and sodium cyanide was extracted with alcohol. The compound had no intended purpose until J.S. MacArthur and the Forrest brothers patented a process for extracting gold and silver from ores in 1887 (Kirk-Othmer, 1979d)

By 1899, half the European production of cyanide was produced by the Beilby process. By 1900, another process called the Castner process was used to make sodium cyanide up until 1961. The Castner process is shown below:

$$2Na + 2C + 2NH_3 \rightarrow 2NaCN + 3H_2$$

Today, a process based on the neutralization of sodium hydroxide (aqueous) and hydrogen cyanide (gas) is the preferred method, as shown below:

$$HCN + NaOH \rightarrow NaCN + H_2O$$

(Kirk-Othmer, 1993b).

There are a few chemical reactions that occur with sodium cyanide that should be mentioned. In moist air carbon dioxide (CO_2) slowly decomposes sodium cyanide

to hydrogen cyanide according to this reaction:

$$2NaCN + CO_2 + H_2O \rightarrow Na_2CO_3 + 2HCN$$

The salt produced becomes a brownish colour due to the formation of polymerization products of HCN (Ullmann's, 1987).

At elevated temperatures oxygen reacts with sodium cyanide to yield nitrogen, carbonate and carbon dioxide according to the two step reaction:

$$2NaCN + O_2 \rightarrow 2NaOCN$$
$$2NaOCN + 3/2O_2 \rightarrow Na_2CO_3 + CO_2 + N_2$$

(Ullmann's, 1987a).

When sodium cyanide is stored for a long time or heated there is a slow hydrolysis of the 'C≡N' bond as per the equation:

$$NaCN + 2H_2O \rightarrow HCOONa + NH_3$$

(Ullmann's, 1987b).

Table 1 shows some basic physical properties of sodium cyanide. One property to note is that the chemical odour has poor warning properties and is not detectable at concentrations which would provide a margin of safety. Another fact to recall is that sodium cyanide sinks and is quite soluble in water, 480,000 ppm at a temperature of 10°C. There are two different hydrates of sodium cynanide: $NaCN \cdot 2H_2O$ (below 35°C) and $NaCN \cdot ½ H_2O$ (>35°C), the former being more common (Environment Canada, 1984; Ullmann's, 1987).

Table 1 Physical Properties of Sodium Cyanide

Properties	Sodium Cyanide
Appearance	white, granular or crystalline solid (CCOHS, 2000)
Odour	faint, almond-like odor (CCOHS, 2000)
Odour Threshold	0.2-5 ppm (as HCN), poor warning properties, not detectable at concentrations providing a margin of safety (CCOHS, 2000a)
Reaction with water	sinks and mixes with water (CCOHS, 2000b)
Molecular Weight	49.015
Melting Point	561.7°C (98 wt%), 562°C(Kirk-Othmer, 1993c), 560°C(Chemtox, 1999)
Boiling Point	1500 ± 10°C, 1530°C(Kirk-Othmer, 1993c), 1499.9°C(Chemtox, 1999)
Density of solid	1.620 g/cm^3 (6°C, rhombic)

Table 1 Physical Properties of Sodium Cyanide Continued

Density of solid	1.595 g/cm^3 (20°C, cubic), 1.60 (Kirk-Othmer,1993c)
Density of solid	1.19 g/cm^3 (850°C, fused)
Density of liquid at 10%	1.047 g/mL (25°C) (Kirk-Othmer, 1993c)
Density of liquid at 20%	1.098 g/mL (25°C) (Kirk-Othmer, 1993c)
Density of liquid at 30%	1.150 g/mL (25°C) (Kirk-Othmer, 1993c)
Viscosity	4 cP (30°C)(26% aqueous solution)
Biological Oxygen Demand (BOD)	(theoretical) 6%, 7 days (CCOHS, 2000b)
Bioaccumulation and Tainting	No evidence to support any rating (CCOHS, 2000b)
Specific Heat Capacity (Cp)	1.667 kJ/kg-K (0.1°C)
Specific Heat Capacity (Cp)	31.630 kJ/kg-K (15.5°C)
Specific Heat Capacity (Cp)	1.402 kJ/kg-K (25.6°C)
Enthalpy at 25°C (H)	-89.9 kJ/mol
Heat of Fusion	314 kJ/kg
Heat of Formation	-89.9 kJ/mol (Kirk-Othmer, 1993c)
Heat of Vaporization (ΔH_v)	3185 kJ/kg, 3041 kJ/kg (Kirk-Othmer, 1979c), 3190 kJ/kg (CCOHS, 2000e)
Heat of Solution (ΔH_{soln})	-1.548 kJ/mol (Kirk-Othmer, 1993c), 1.51 kJ/mol (CCOHS, 2000e)
Hydrolysis Constant, K_h at 25°C	0.0000251 (Kirk-Othmer, 1993c)
Vapour Pressure (P_v) at 800°C	0.1 kPa, 0.1013 kPa (Kirk-Othmer, 1993c)
Vapour Pressure (P_v) at 1000°C	1.65 kPa
Vapour Pressure (P_v) at 1200°C	11.98 kPa
Vapour Pressure (P_v) at 1350°C	39.10 kPa
Vapour Pressure (P_v) at 1360°C	41.8 kPa (Kirk-Othmer, 1993c)
Index of Refraction	1.452
Solubility (10°C)	480,000 ppm
Solubility (35°C)	820,000 ppm
Solubility of $NaCN{\cdot}2H_2O$ per 100 g of saturated solution	26.01 (-15°C)(Kirk-Othmer, 1993c)

Table 1 Physical Properties of Sodium Cyanide Continued

Solubility of $NaCN{\cdot}2H_2O$ per 100 g of saturated solution	32.8 (10°C)(Kirk-Othmer, 1993c)
Solubility of $NaCN{\cdot}2H_2O$ per 100 g of saturated solution	34.2 (15°C)(Kirk-Othmer, 1993c)
Solubility of $NaCN{\cdot}2H_2O$ per 100 g of saturated solution	45 (34.7°C)(Kirk-Othmer, 1993c)
Solubility in 100 g of Ethanol (100%)	1.235 g (25°C)
Solubility in 100 g of Ethanol (95%)	2.445 g (25°C)
Solubility in 100 g of anhydrous Methanol	6.44 g (15°C)
Solubility in 100 g of anhydrous Methanol	4.58 g (25°C)
Solubility in 100 g of anhydrous Methanol	4.10 g (67.4°C)
Solubility in 100 g of NH_3, liquid	58 g (-31°C)

(Kirk-Othmer, 1979e; Ullmann's, 1987a; Chem-Bank, 1999)

2.0 Toxicity

The average lethal dose of sodium cyanide (LD_{50}) for humans is estimated to be 2.86 mg/kg (Corn, 1993). Cyanide, originating by disassociation of sodium cyanide, complexes with the ferric iron atom (3+) in metalloenzymes, resulting in anoxia through inhibition of cytochrome oxidase, which inhibits cellular oxygen. The enzyme becomes unable to catalyze the reactions in which electrons would be transferred from reduced cytochrome to oxygen. Thus, cellular oxygen utilization is impaired. The inhibition of oxygen causes oxygen 'hunger' to rise in peripheral tissues. Thus, oxyhemoglobin is carried in the venous blood (TPF, 1997). This is what causes the pink or red discolouration of the skin from cyanide poisoning which is the oxyhemoglobin entering the skin to provide the necessary oxygen.

Not all the cyanide that is absorbed by the body undergoes oxygen inhibition. It is known that 80% of the absorbed cyanide is detoxified in the liver by the enzyme mitochondrial rhodanase. The enzyme catalyzes the transfer of a sulphur atom to combine with the cyanide to form the less toxic thiocyanate, which is excreted in the urine. In high exposures to cyanide, the sulphur donors are rapidly depleted and cyanide metabolism is slowed (Pope and Rall, 1995). The half-life for the conversion of cyanide to thiocyanate from a non-lethal dose in humans is between 20-60 minutes (Chem-Bank, 1999).

Other pathways to elimination of cyanide are possible. About 1-2% is lost through the lungs by exhalation. Another 15% of cyanide is released by conversion to 2-aminothiazline-4-carboxylic acid, incorporation into the one-carbon metabolic pool, or the combination with hydroxycobalamin (vitamin B_{12a}) to form cyanocobalamin (Pope and Rall, 1995a).

In normal, healthy human organs, cyanide is present at concentrations ranging up to 0.5 mg/kg (Chem-Bank, 1999), and the relative proportion of thiocyanate to cyanide in body fluids is about 1000:1. Normal plasma thiocyanate levels are 0.01 mg/mL for smokers and non-smokers. Lethal values of thiocyanates range from 0.05-0.2 mg/mL (Pope and Rall 1995b). Smokers are included in the data because heavy

smoking will increase the urinary concentrations of thiocyanate levels and can be misleading for cyanide exposure (Corn, 1993).

Table 2 Blood Cyanide Effects

Whole Blood Cyanide Level Concentrations (mg/mL)	Effect on Body
Less than 0.0002	No symptoms of toxicity
0.0004 (in smokers)	No symptoms of toxicity
0.0005-0.001	Untreated patients may be conscious, flushed, and tachycardic
0.001-0.0025	Stupor and agitation
Greater than 0.0025	Coma and potentially fatal without treatment

(Pope and Rall, 1995c)

Sodium cyanide is known as a very toxic chemical to humans. Table 3 shows some human toxicity data. To put the data into perspective, for oral-human LD_{Lo} 2.857 mg/kg, a human of 70 kg (154 lbs) would only have to ingest 0.2 grams (200 mg) in order to be in the range of a lethal dose. The data in Table 3 demonstrates that even small amounts of sodium cyanide can cause harm to the human body.

Table 3 Human Toxicity Data

Oral-man LD_{Lo} 6.557 mg/kg (gastrointestinal, gastritis)
Oral-human LD_{Lo} 2.857 mg/kg
Unreported-human LD_{Lo} 2.206 mg/kg
Oral-man TD_{Lo} 0.714 mg/kg (hallucinations, distorted perceptions, muscle weakness)

(Chemtox, 1999; CCOHS, 2000c)

Other data from the testing of sodium cyanide from animal species also illustrate the same point, sodium cyanide is very toxic. For example, Table 4 shows that a mere 0.0085 grams of sodium cyanide per kilogram of quail has killed half of the test animals.

Table 4 Animal Toxicity

Oral-rat LD_{50} 6.44 mg/kg
Intraperitoneal-rat LD_{50} 4.3 mg/kg
Oral-quail LD_{50} 8.5 mg/kg
Oral-wild bird species LD_{50} 4 mg/kg

(Chemtox, 1999; CCOHS, 2000c)

When sodium cyanide mixes with water and comes in contact with aquatic life

the results are also detrimental to the health of the species. When sodium cyanide is mixed with water it goes through two possible reactions:

1) $NaCN + H_2O \rightleftarrows NaOH + HCN$ (room temperature)

2) $NaCN + 2H_2O \rightleftarrows NH_3 + HCOONa$ (> 50°C)

(Kirk-Othmer, 1993)

As in the case of accidental spills, equation 1 would be the reaction since the water is not above 50°C. Thus a spill of sodium cyanide in water would form hydrocyanic acid and sodium hydroxide.

In water the pH is affected by how much sodium cyanide is added. Table 5 below shows the concentration of sodium cyanide added correlated to the pH of the water. Notice that the aqueous solutions are strongly alkaline. At pH 9.4, in an aqueous solution of sodium cyanide, half of the total cyanide is present as hydrogen cyanide as in equation 1 above (Ullmann's, 1987b).

Table 5 pH of Sodium Cyanide

Concentration of Sodium Cyanide mol/L	Concentration of Sodium Cyanide ppm	pH
1	49,015	11.64
0.1	4,902	11.15
0.01	490	10.67
0.001	49	10.15
0.0001	4.9	9.6
0.00001	0.5	8.9

(Ullmann's, 1987b)

Sodium cyanide is detrimental to aquatic life because of the dual toxicity effect of an acid and a base impacting the environment. Table 6 shows a range of intolerance, for example bluegill at 96 hours TLm is 0.15 mg/L, whereas oligochaete at 96 hours LC_{50} is 11 mg/L. Thus, it takes 73 times more of sodium cyanide to kill half the oligochaete than it takes to kill half of the bluegill. Table 6 shows the toxicity of sodium cyanide on freshwater aquatic life.

Table 6 Freshwater Toxicity of Sodium Cyanide

Species	Concentration (mg/kg)	Exposure (hours)	Effect
Apple snail	1.6-2.9 (mg/L)	96	LC_{50}
Fathead minnow	0.25	24	TLm
Fathead minnow	0.24	48	TLm
Fathead minnow	0.23	96	TLm
Yellow perch	0.0758-0.337 (mg/L)	96	LC_{50}

Table 6 Freshwater Toxicity of Sodium Cyanide Continued

Bluegill	5	2	Killed
Bluegill	0.1959 (mg/L)	3.36	LT_{50}
Bluegill	0.16	48	LC_{50}
Bluegill	0.16 (mg/L)	72	LC_{50}
Bluegill	0.15	96	TLm
Eurasian water milfoil	22.4 (as CN)		IL_{50}, root weight
Eurasian water milfoil	28.6 (as CN)		IL_{50}, root length
Eurasian water milfoil	20 (as CN)		IL_{50}, stem weight
Eurasian water milfoil	27.3 (as CN)		IL_{50}, stem length
Archiannelid	8.9-11 (mg/L)	24	LC_{50}
Archiannelid	7.1-9.5 (mg/L)	48	LC_{50}
Archiannelid	6.7-8.5 (mg/L)	72	LC_{50}
Archiannelid	5.9-7.6 (mg/L)	96	LC_{50}
River Snail	940 (mg/L)	24	LC_{50}
River Snail	760 (mg/L)	48	LC_{50}
Water flea	<3.4		Immobilized
Water flea	0.09-0.3 (mg/L)	96	LC_{50}
Water flea	0.02-0.05 (mg/L)	120	LOEC REP
Polycelis nigra	30		Threshold concentration
Trout	0.08		Nontoxic
Trout	2	1	100% Mortality
Trout	0.05	124	100% Mortality
Oligochaete	11 (mg/L)	96	LC_{50}
Pond snail	3.3 (mg/L)	24	LC_{50}
Pond snail	3.3 (mg/L)	48	LC_{50}
Pond snail	2.4-2.5 (mg/L)	96	LC_{50}
Fish (*Labeo bata*)	0.4-1.9 (mg/L)	96	LC_{50}
Rohu	0.3-1.9 (mg/L)	96	LC_{50}
Catla	0.5-1.7 (mg/L)	96	LC_{50}
Cyclopoid copepod	0.1-0.3 (mg/L)	96	LC_{50}

Table 6 Freshwater Toxicity of Sodium Cyanide Continued

Calanoid copepod	0.1-0.3 (mg/L)	96	LC_{50}
Scud	0.9 (mg/L)	96	LC_{50}
Rainbow trout	0.05-0.09 (mg/L)	96	LC_{50}
Rainbow trout	0.098 (mg/L)	144	LC_{50}
Minnows	0.4	1	Stopped eating
Minnows	0.33-0.35	2.5	Lethal
Minnows	0.5-0.7	24	25% Mortality
Minnows	0.75	24	50% Mortality
Minnows	0.8	24	100% Mortality
Pouch snail	2.4 (mg/L)	24	LC_{50}
Pouch snail	135 (mg/L)	48	LC_{50}
Stickleback	2		Lethal
Hardy carp	4.3		Paralyzed
Shiner	10	0.06	Killed
Shiner	2	0.2	Killed
Snail	2.9 (mg/L)	96	LC_{50}
Carp, hawk fish	0.37 (mg/L)	96	LC_{50}
Trout fingerlings	0.02		No effect
Gold & green sunfish	0.5	4-6	Lethal
Sea lamprey	5.0	2	Ill, but survived

(Sax, 1989; Aquire database, 1994)

Other facts about cyanide toxicity in relation to fish is that cyanide toxicity increases with any reduction in dissolved oxygen below 100%. There is a slight decrease in toxicity at pH greater than 8.5 due to conversion to CN^-. The presence of zinc and ammonia results in a greater than additive increase in toxicity (Moran, 1998). Fish are about 1000 times more sensitive to cyanide than are humans. Even if the levels are less than lethal there are still toxic effects, including physiological and pathological responses. For example, cyanide can reduce swimming ability, which will leave fish more vulnerable to predators, or interfere with reproductive capacity which can lead to deformed offspring. It should be noted that cyanide toxicity in fish increases 3 fold with a 12°C decrease in temperature. As well, 17 parts per thousand (ppt) of chloride ion or 8.8 ppt (Moran, 1998) is known to decrease the survival time (UNEP/OCHA, 2000d).

There is some saltwater toxicity data as well, although it is not as extensive as freshwater data. The information is presented in Table 7. One can see the detrimental effects of adding sodium cyanide to saltwater aquatic life.

Table 7 Saltwater Toxicity of Sodium Cyanide

Species	Concentration (mg/kg)	Exposure (hours)	Effect
Aquatic sowbug	1.7 (mg/L)	96	LC_{50}
Prawn	0.25	48	LC_{50}
Cockle	>25	48	LC_{50}
Three spine stickleback	0.2254 (mg/L)	3.36	LT_{50}
Three spine stickleback	0.1312 (mg/L)	13.68	LT_{50}
Crab	75	48	LC_{50}

(Sax, 1989a; Aquire database, 1994)

3.0 Categorizations & Guidelines

Table 8 is a compilation of classifications, guidelines and legislative limits. The information from Transport of Dangerous Goods (TDG) states that sodium cyanide is a poison. Other references such as National Fire Protection Association (NFPA), and The Hazardous Materials Identification System (HMIS) identify sodium cyanide as a serious health hazard. The classifications suggest that it is not a flammability hazard and it is not very reactive (stable). Also note that the drinking water standards have been set at 0.2 mg/L for safe drinking water. At a sodium cyanide level of 0.2 mg/L not all of the fish are safe. Note that at this concentration, from Table 6, that half of the bluegill will die after 3.36 hours, rainbow trout after 96 hours, and trout will have 100% mortality after 124 hours.

Table 8 Legislative Limits & Classifications

Topic	Limit
TDG Classification	6.1, 9.2 (9.2 applies if regulated limit is exceeded) Regulated Limit (Schedule XII) S4, UN1689 Regulated Limit (Schedule XIII) 0.5 kg, UN1689(CCOHS, 2000d)
Packing Group	I
Emergency Response Assistance Planning requirements of sections 7.16 - 7.19	for quantities exceeding 1,000 kg or litres net per consignment
Consumer Commodity	Prohibited
Limited Quantity	Prohibited
Passenger road/railway vehicles	Maximum net quantity per package is 5 kg
Standard industry trade classification	52381 (CCOHS, 2000b)

Table 8 Legislative Limits & Classifications Continued

Stability during transport	Stable (CCOHS, 2000b)
RCRA Hazardous Waste	No. P106 (Genium's, 1999)
Fire Diamond (NFPA Hazard Rating)	3 Health Hazard (extreme danger) 0 Flammability (will not burn) 0 Reactivity (stable and not reactive with water) (Genium's, 1999)
The Hazardous Materials Identification System (HMIS)	H 3 (serious health hazard) F 1 (slight flammability hazard) R 1 (slight reactivity hazard) (Genium's, 1999)
Wilson's Risk Scale of Material Hazards (RISK)	R 1 (reactivity: stable at room temperature; may be unstable at elevated temperatures) I 2 (inhalation: TLV 101-500 ppm (vapour) or 1.1-10 mg/m^3 (solid) S 3 (skin contact: severe irritation; tissue corrosion within short time period) K 0 (kindling: will not burn) (Genium's, 1999)
Workplace Hazardous Materials Information System (WHMIS)	D1A (very toxic material) D2B (other toxic effects that are not immediate and serious) E (corrosive)(CCOHS, 2000d)
IDLH	25 mg/m^3 (as CN)
TLV-TWA (Ceiling exposure limit)	4.7 ppm-10 minutes (as CN) skin designation
NIOSH Recommendations	4.7 ppm (hydrogen cyanide & cyanide salts)
Federal drinking water guidelines	0.2 mg/L (cyanide ion)

(CCOHS, 2000d)

4.0 Industrial Uses of Sodium Cyanide

During the 1950's almost all sodium cyanide was used in case hardening and electroplating. In the present time, case hardening is a minor use while electroplating or metal plating, gold & silver extraction, and chemical synthesis are major applications of sodium cyanide (Kirk-Othmer, 1979a).

Figure 1 shows a comparison of how much sodium cyanide is consumed in these processes relative to all of the other major usages from the years 1976 to 1997. It can be seen from the figure that gold cyanidation is the most prominent process. A description of the different processes will follow.

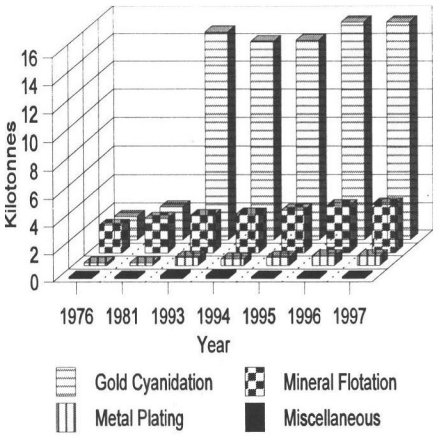


Figure 1 Uses of Sodium Cyanide (Corpus, 1998)

Cyanidation is a chemical process used to recover gold that is very finely distributed in the ore, or gold that is complexed with sulphides. The ore or tailings from amalgamation are added to a cyanide solution (0.2-0.05%), which is aerated to provide oxygen to dissolve the gold into the formation of $Na[Au(CN)_2]$. A typical concentration of cyanide usage is 1-2.5 kg NaCN per metric ton of ore (Kirk-Othmer, 1995), or 0.25-1.0 kg (Ingles and Scott, 1987). This is known as the MacAuthur Process:

$$4NaCN + 2Au + \tfrac{1}{2} O_2 + H_2O \rightleftarrows 2NaAu(CN)_2 + 2NaOH$$

The solution is then treated and clarified and the gold is precipitated by the addition of zinc dust according to the reaction:

$$2Au(CN)_2^{2-} + Zn \rightleftarrows 2Au + Zn(CN)_4$$

(Clayton and Clayton, 1991; Corpus, 1998; Kirk-Othmer, 1980).

Sodium cyanide is used in the extraction of gold and silver from ores because of the very stable linear cyano complexes formed with these metals. The molecular bonding for silver cyano complexes is drawn as, $[:N\equiv C\text{-}Ag\text{-}C\equiv N:]^-$, and similarly for gold complexes, $[:N\equiv C\text{-}Au\text{-}C\equiv N:]^-$ (King, 1994).

Sodium Cyanide is also used in the electroplating industry. Cadmium is usually plated from cyanide solutions from a Still plating process (90-120 g/L NaCN), or Barrel plating (70-90 g/L NaCN). Given that cadmium is very harmful to the environment, the popularity of plating with cadmium is declining (Kirk-Othmer, 1979b).

Reactions that are of commercial importance in electroplating require sodium cyanide. In the reactions shown below silver is dissolved by sodium cyanide solutions as the anode,

$$Ag + 2NaCN \rightarrow NaAg(CN)_2 + Na^+ + e$$

or in the presence or oxygen to form $NaAg(CN)_2$.

$$2Ag + 4NaCN + H_2O + 0.5O_2 \rightarrow 2Na(CN)_2 + 2NaOH$$

(Kirk-Othmer, 1984a).

Brass is plated not only for decorative purposes but also to ensure a good adhesion of rubber to steel wire, which is used in tires. An example of such a bath uses a total concentration of sodium cyanide at 90 g/L, for a 70/30 brass plating, and for white brass plating the total amount of sodium cyanide is 52-60 g/L (Kirk-othmer, 1979c).

In the late 1980's cyanides were largely removed from plating baths due to environmental hazards of using cyanides. Since 1995, cyanide-containing cleaners are rare and only used for special purposes.

Sodium cyanide is also used as a depressant in the mining industry. A depressant is a reagent that selectively prevents the reaction between a collector and a mineral. In other words, a depressant prevents the mineral from flotation. The use of sodium cyanide, in this case, is to selectively depresses sphalerite (zinc sulphide) and pyrite (iron sulphide) but not galena. Thus sodium cyanide enhances flotation of galena (Kirk-othmer, 1995a).

In the process known as cyaniding, carbon and alloy steels are combined at high temperatures in a liquid-bath from which they absorb both carbon and nitrogen simultaneously. The purpose of the nascent nitrogen is to increase the metal's surface hardness. The liquid baths typical composition is 30% sodium chloride, 40% sodium carbonate, and 30% sodium cyanide. The sodium cyanide concentration may range from 97% to 45%. The equations producing nitrogen and carbon are below:

$$2NaCN + O_2 \rightarrow 2NaCNO$$

The sodium cyanate created breaks down to form nascent nitrogen;

$$4NaCNO \rightarrow Na_2CO_3 + 2NaCN + CO + 2N$$

The carbon monoxide (CO) produces carbon dioxide;

$$2CO \rightarrow CO_2 + C$$

The carbon dioxide reacts with sodium cyanide;

$$NaCN + CO_2 \rightarrow NaCNO + CO$$

The carbon monoxide (CO) further reacts to produce more carbon (C) which is shown above.

There are three reactions which lead to the decomposition of the sodium cyanate (NaCNO):

1) $NaCNO + C \rightarrow NaCN + CO$

2) $4NaCNO + 4CO_2 \rightarrow 2Na_2CO_3 + 2CO + 4N + 2C$

3) $4NaCNO + 4CO_2 \rightarrow 2Na_2CO_3 + 6CO + 4N$

(Kirk-Othmer, 1981)

Sodium cyanide is used for case hardening of steels. Trace amounts of iron or nickel oxide are used to cause a rapid oxidation of the cyanide in air first to the cyanate then to carbonate via these reactions:

$$2NaCN + O_2 \rightarrow 2NaCNO$$
$$2NaCNO + 3/2\ O_2 \rightarrow Na_2CO_3 + N_2 + CO_2$$

Case hardening of steel using a sodium cyanide molten bath depends on the above reactions where the active carbon and nitrogen are absorbed into the steel surface. Sodium cyanide is a good reducing agent and the oxides of tin, lead, copper or manganese are readily reduced (Kirk-Othmer, 1993d).

4.1 Chemical Synthesis Using Sodium Cyanide

For chemical synthesis of a phosphorus-carbon bond, sodium cyanide can be used as shown below:

$$PCl_3 + 3NaCN \rightarrow P(CN)_3 + 3NaCl$$

(Kirk-Othmer, 1982)

Ethylene cyanohydrin is obtained from ethylene chlorohydrin and sodium cyanide in this reaction:

$$HOCH_2CH_2Cl + NaCN \rightarrow HOCH_2CH_2CN + NaCl$$

(Kirk-Othmer, 1978).

Sodium cyanide reacts with 1,2-dichloroethane to produce 2-chloropropionitrile in this reaction:

$$ClCH_2CH_2Cl + NaCN \xrightarrow{\text{In Methanol (50°C)}} HOCH_2CH_2CN + NaCl$$

(Kirk-Othmer, 1979a).

Thiacyanocarbons are prepared using sodium cyanide shown below:

$$CS_2 + NaCN \rightarrow NCC(=S)SNa \rightarrow (SNa)_2\text{-}C{=}C\text{-}(CN)_2$$

(Kirk-othmer, 1979a).

A chemical process to synthesize malonates uses sodium cyanide. In this procedure a 25% solution of sodium cyanide in water is heated to 65-70°C. The reaction is shown below:

$$ClCH_2COONa + NaCN \rightarrow NCCH_2COONa + NaCl$$

$$NCCH_2COONa \xrightarrow[H_2SO_4,\ H_2O]{+\ ROH} ROOCCH_2COOR$$

(Kirk-Othmer, 1995b).

Sulphuric acid reacts with sodium cyanide according to the reaction:

$$2NaCN + H_2SO_4 \rightarrow Na_2SO_4 + 2HCN$$

(Ullmann's, 1987a).

4.2 Miscellaneous Uses of Sodium Cyanide

Sodium cyanide is also used as a radioactive tracer, sodium [^{14}C]-cyanide (Kirk-Othmer, 1996).

In the United States another use for sodium cyanide is as an active ingredient on a collar around a sheep's neck. The collar is used as a predator control technique in that if a coyote were to grasp the prey at the neck, the coyote would ingest the contents of the collar, thus poisoning the predator (Kirk-othmer, 1982b).

For the purpose of sterilization, sodium cyanide is used to remove fish, nuisance vegetation, and predators of fry by applying a concentration of 5 ppm to the water. Since sodium cyanide has a rapid rate of deterioration, fry can be restocked soon after the chemical has sterilized the pond (Kirk-othmer, 1978a).

5.0 Imports & Costs

Figure 2 demonstrates the countries that imported sodium cyanide from 1976 to 1997. It can be seen that the United States is a major user of sodium cyanide followed by the United Kingdom.

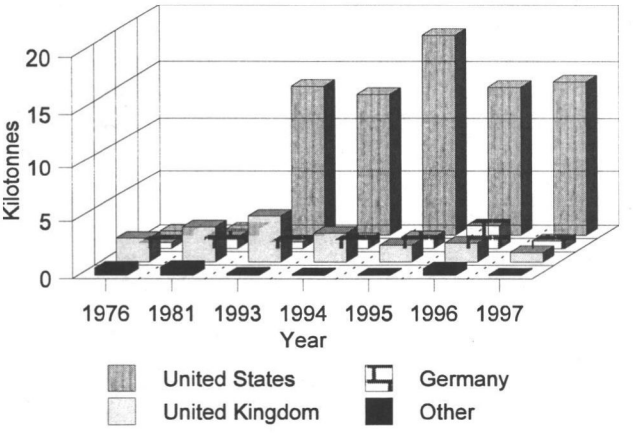


Figure 2 Imports of Sodium Cyanide by Country

(Corpus, 1998)

One can see from Table 9 that the cost ranges within each year depend on supply and demand. Also from 1993 to 1997 cost has risen 77 cents per kilogram from the extreme low to the extreme high end.

Table 9 Price History

	Bulk, Tonnes/Liter delivered mine site: cents/kilogram	
Year	High	Low
1993	153	148
1994	153	153
1995	185	153
1996	225	185
1997	225	225

(Corpus, 1998)

6.0 Spill Data

Cyanide spills in general were tracked using data from National Analysis of Trends in Emergencies System (NATES) from the years 1974 to 1995. Figure 3 shows spills which include cyanide leachates, sodium cyanide, cyanide not otherwise specified (nos) and cyanide/copper tailings. As one can see from Figure 3, cyanide nos is the largest of the spills and may contain any cations with cyanide, or the cyanide ion itself.

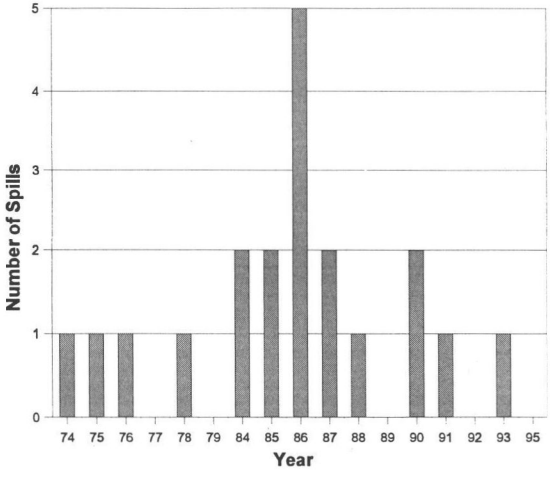


Figure 3 Number of Sodium Cyanide Spills from 1974-1995

(NATES, 2000)

From this same NATES databank was extracted the number of spills of sodium cyanide which occurred from 1974 to 1995. You can see from Figure 4 that the number of spills are normally not more than 2 per year. However, Figure 3 shows that sodium cyanide spills released just under 100,000 litres into the environment from a total of 20 spills recorded in Figure 4.

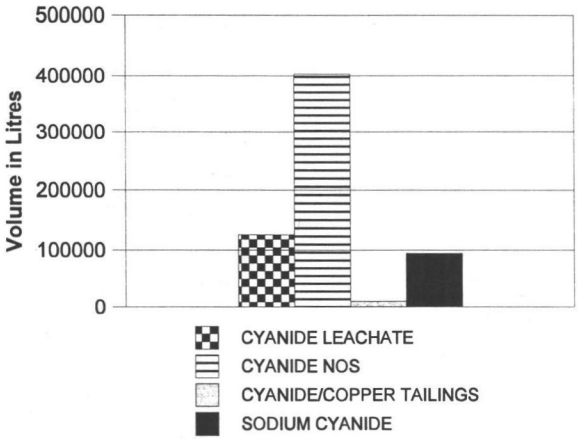


Figure 4 Cyanide Spills from 1974-1995

(NATES, 2000)

7.0 Potential Complexes With Cyanide in the Event of a Spill

Cyanide will form complexes of very stable, insoluble or slightly soluble simple cyanides with heavy metals. Unidentate cyanide always bonds to the metal via its carbon atom but the 'M-C≡N-M' links can be seen in many of the solid cyanides (King, 1994). There may be some settling of heavy-metal cyanide complexes to the sediment. Table 10 shows some of the more stable complexes and their respective dissociation properties.

Table 10 Cyanide Dissociation Equilibria

Dissociation Equilibria	$pK_{dissociation}$	Toxicity Range for Freshwater fish (mg/L)
$[Pb(CN)_4]^{2-} \leftrightarrows Pb^{2+} + 4CN^-$	10.3	
$[Cd(CN)_4]^{2-} \leftrightarrows [Cd(CN)_3]^- + CN^-$	2.5	0.02-0.3
$[Cd(CN)_3]^- \leftrightarrows Cd^{2+} + 3CN^-$	14.7	0.02-0.3
$[Zn(CN)_4]^{2-} \leftrightarrows [Zn(CN)_3]^- + CN^-$	1	0.02-0.3
$[Zn(CN)_3]^- \leftrightarrows Zn^{2+} + 3CN^-$	17.9	0.02-0.3
$[Ag(CN)_2]^- \leftrightarrows Ag^+ + 2CN^-$	20.9	
$[Ni(CN)_4]^{2-} \leftrightarrows Ni^{2+} + 4CN^-$	22	0.4 (pH 6.5), 730 (pH 8)
$[Cu(CN)_4]^{3-} \leftrightarrows [Cu(CN)_3]^{2-} + CN^-$	1.5	0.4-4.0
$[Cu(CN)_3]^{2-} \leftrightarrows [Cu(CN)_2]^- + CN^-$	5.3	0.4-4.0
$[Cu(CN)_2]^- \leftrightarrows Cu^{2+} + 2CN^-$	23.9	0.4-4.0
$[Fe(CN)_6]^{3-} \leftrightarrows Fe^{2+} + 6CN^-$	36	300 (in darkness), <0.2 (in light)

Table 10 Cyanide Dissociation Equilibria Continued

$[Au(CN)_2]^- \leftrightarrows Au^{2+} + 2CN^-$	37	
$[Hg(CN)_4]^{2-} \leftrightarrows Hg^{2+} + 4CN^-$	40.5	
$[Fe(CN)_6]^{4-} \leftrightarrows Fe^{2+} + 6CN^-$	42	
$[Co(CN)_6]^{4-} \leftrightarrows Co^{2+} + 6CN^-$	64	
$[Pt(CN)_4]^{2-} \leftrightarrows Pt^{2+} + 4CN^-$	40	
$[Pd(CN)_4]^{2-} \leftrightarrows Pd^{2+} + 4CN^-$	42	

(Ullmann's, 1987c; Moran, 1998a)

When metal cyanide complexes are formed and released into the environment they begin to decompose at varying rates. The weak cyanide complexes, such as zinc and cadmium will decompose faster than strong complexes such as copper, nickel, iron, cobalt, gold and silver cyanides. Strong cyanide complexes do not break down in the presence of strong acids, such as hydrochloric acid or sulphuric acid, but will decompose when exposed to various wavelengths of light. Cyanide ions will be released when the decomposition process begins (Moran, 1998b).

8.0 Spills of Sodium Cyanide

8.1 Case Study 1: January 30, 2000

A gold mine in Romania called Baia-Mare reported a massive cyanide spill on January 30, 2000 caused by a collapse of the tailings dam due to pressure from snow buildup. Baia Mare is a shared ownership between Romanian company Aurul and Esmeralda Explorations Limited of Perth, Australia. It is estimated that the spill was 26 million gallons (98,410,000 liters) (OSHS, 2000) of waste water, highly contaminated with cyanides and heavy metals (WWF, 2000). The tailings flowed into the Szamos River in Hungary then proceeded to flow down the Tisza River, and then into the Serbian Republic to the larger Danube upstream of Belgrade, Yugoslavia.

The wave of cyanide tailings took several days to travel the rivers to Belgrade. As can be seen on the map shown below, samples taken from Szamos at Csenger on February 1, 2000 were 32.6 ppm cyanide. On February 11 from Tisza at Tiszasziget, the concentrations were 1.49 ppm cyanide. These concentrations can still kill 50% of fish species as can be seen from Table 6. Along the way the authorities closed water intakes and warned the public against any contact with the river water or any dead fish. However, the city of Szolnok, which depends entirely on the Tisza for drinking water was forced to use additional chlorine and ozone as a neutralization method. (OSHS, 2000a).

	Measurement place:	Date:	Max. concentration:
1	Szamos at Csenger	02.01.	32.6 mg/l cyanide
2	Tisza at Lónya	02.03.	13.5 mg/l cyanide
3	Tisza at Tiszalök	02.05.	3.7 mg/l cyanide
4	Tisza at Kiskőre	02.08.	3.8 mg/l cyanide
5	Tisza at Szolnok	02.09.	3.2 mg/l cyanide
6	Tisza at Tápé	02.11.	2.2 mg/l cyanide
7	Tisza at Tiszasziget	02.11.	1.49 mg/l cyanide

Figure 5 Tracking the Sodium Cyanide Spill from Baia Mare

(MTI, 2000)

The company treated the spillage with sodium hypochlorite to neutralize the cyanide. The reaction is shown below:

$$NaCN + NaClO \rightarrow NaCNO + NaCl$$

(McGill and Comba, 1990)

The wave of cyanide had a negative impact on life in Tisza River. It was estimated that 80% of the fish of Tisza River are dead Tiszaderzs, see Figures 6a, 6b and 6c:

Figure 6(a)
(WWF, 2000)

Figure 6(b)
(WWF, 2000a)

Figure 6(c)
(WWF, 2000b)

Figure 6: Pictures showing fishermen from the Tisza region collecting dead fish.

The impact of the spill is summarized in table form below:

Table 11 Impact of Spill

180 tonnes of dead fish (Borsa, 2000), 1000 tons (UNEP/OCHA, 2000a)
Cyanide & cyanide-heavy metal contamination in river beds of Tisza & Szamos
Otters extinct from Tisza & Szamos
Birds & animals die of eating contaminated fish
Ground water resources contaminated
Estimates for ecological rehabilitation for water: 1-2 years
Estimates for ecological rehabilitation for riverbed: 10 years

(Borsa, 2000)

Eight drinking wells were found to be contaminated with cyanide on February 8 (UNEP/OCHA, 2000). On the 15-17 February the water appeared to be safe to drink. On March 6, 17 scientists from 7 countries finished sampling the water of the Danube River (800 km downstream from the mine). It was found that 180 tonnes of dead fish were removed from Hungary's Samos and Tisza Rivers. Pal Pepo, Hungary's Minister for the Environment said that the recovered fish represented only 15% of the total fish killed, while an estimated 15% drifted down the Tisza into Yugoslavia, and 15% were still trapped under ice. The Australian mining company maintained that there was no scientific evidence linking extensive fish kills with the spill of tailing pond water (OSHS, 2000). This comment is in stark contrast to WWF Hungary Conservation Director György Gado who stated, "This spill has, in practical terms, eradicated all life from a stretch of up to 400 km of the Tisza river (WWF, 2000b).

The chairman of the Hungarian parliaments environment committee was very concerned about the heavy metals in the environment since it could pose a far greater health threat in the long term (Citizen Internet, 2000). Given the complexes that cyanide can form with heavy metals there is a great potential for the sediment to be

highly toxic for some time. The contamination in the sediments was found to drop rapidly with increased distance from the source of the spill. The concentration of heavy metals in the Lapus river are high or extremely high (UNEP/OCHA, 2000).

The pond was lined with a plastic membrane and held an estimated 4.43 million tons of flotation solid wastes, which was 93 hectares in area and about 20 metres high. Unfortunately, there was an imbalance between water burden, unexpected quantities of water by the addition of snow and rain, and safe storage volume, the capacity of the pond was insufficient to safely store the slimes. It was estimated that 50-100 tons of cyanide was released into the river (UNEP/OCHA, 2000).

Although the company was operating within Government permits, there was no contingency planning. The emergency preparedness and response procedures were rudimentary when one considers the quantities used so close to the human population and the river systems (UNEP/OCHA, 2000b).

Recommendations were to complete a risk assessment on the entire system, reduce the process water ponds to sizes which can be handled in emergencies, and prepare emergency water supplies (UNEP/OCHA, 2000c).

8.2 Case Study 2: August 19, 1995

On August 19, 1995 at the Omai Gold Mines Limited (OGML) mine in central Guyana, a Canadian (Cambior Inc.) and U.S owned company, there was an uncontrolled release of cyanide waste water. The failure of the dam was caused by massive loss of core integrity from internal errosion of the dam fill, a process called piping (Vick *et al.*, 1995). On August 24 the spill was contained and diverted within an open pit mine. It was estimated that 2.6-2.7 million cubic meters of water flowed into the Essequibo river, which is Guyana's largest river.

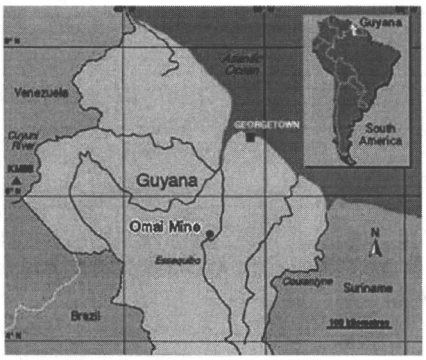


Figure 9 Map of Guyana Showing the Location of Omai Mine
(Guyana map, 1995)

The spill had a red colour to it because of the red clay saprolite core material of the dam. The release flowed into the Omai river (3-5 meter wide river), then into the Essequibo river. The Essequibo river is the major river of the country and it is used for drinking, bathing and fishing (NEEC Alert, 1995). It was estimated that the dilution factor would be 150:1 in the Essequibo river, and would increase

downstream as the river expands. The initial concentration of total cyanide was 25 mg/L from the water discharging from the tailings pond. In the Essequibo river the cyanide level was, an average from one location, 0.12 mg/L. After the spill, 200 dead fish were sighted in the Omai river (Feasby, 1995). There were no human casualties.

There was concern that if a 7 kg infant drank 5 ppm of cyanide in water, the child would be consuming a lethal dose. An adult weighing 60 kg would reach lethal doses if the water had a concentration of cyanide of 34 mg/L (Feasby, 1995a). The Pan American Health Organization (PAHO) reported cyanide levels in the Omai river to be 5.42 ppm and rising as of 21 August. Officials informed the people not to drink the water and began distributing drinking water to affected communities (NEEC, 1995a). Helicopters were mobilized to inform people of the potential dangers (NEEC Alert, 1995). Environment Canada believes that the long term impact of the spill will be negligible since cyanide rapidly degrades. Also, the high volume of the Essequibo River diluted the cyanide levels so that there were no visible environmental impacts down stream from the entry point of the spill where the Essequibo and Omai Rivers intersect (Trip and Blakeman, 1995).

8.3 Case Study 3: May 20, 1998

On May 20, 1998 in the central Asian nation of Kyrgyzstan, a truck travelling to the Kumtor gold mine in a convoy veered out of control and crashed through the railing of a narrow bridge. The truck carried 20 tonnes of sodium cyanide in the Barskoon river near the town of Barskoon. This river empties into Lake Issyk-kull (CBC, 1998). A picture of the broken bridge as a result of the truck breaking through the barrier and a picture of the river from the bridge are both shown below.

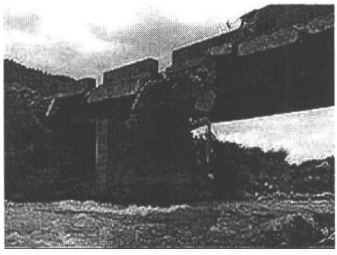


Figure 10
The bridge where the truck broke through
(CBC, 1998a)

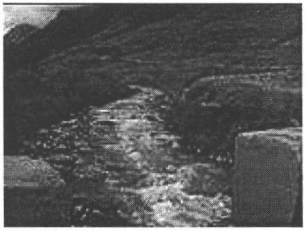


Figure 11
The perspective from the bridge
(CBC, 1998b)

The police were not told immediately of the spill and so five hours passed until the public was notified. The company employees were preoccupied by attempts from the convoy to save the driver from the truck, and then to get the container out of the water. It was found that 1,762 kg of cyanide was missing. Kyrgystan's Ministry of Environmental Protection found cyanide levels in the Barskuan River to be 1,600 times the maximum acceptable level during the spill, but a day later the concentrations fell to acceptable levels.

Hours after the accident water samples 20 meters from the spill site showed free cyanide concentrations of 79.5 mg/L. This sample does not include cyanates,

thiocyanates, cyanogen, cyanogen chloride, ammonia, chloramine, or metal cyanide complexes that are forms of cyanide related compounds (Moran, 1998c).

The pH of the river before the spill was likely to be less than 9, therefore most of the dissolved cyanide would have formed hydrocyanic acid (HCN) a toxic gas that would have dissipated into the air. After a few hours, sodium hypochlorite was added which would have resulted in the formation of cyanate and cyanogen chloride. Cyanogen chloride can cause throat and eye irritations and, being heavier than air, could have traveled significant distances from the spill (Moran, 1998c).

Villagers started showing up at the hospitals two days after the spill which evidently confused the responders. A representative of Cameco (owner of the mine) stated it was, "highly unlikely, if not impossible" that the villagers were showing up because of the cyanide spill. The argument being, "cyanide poisoning would manifest itself almost immediately" (OSHS, 1998). At the children's hospital in Kyrgyzstan a professor of pediatric medicine remarked,"I saw the sick people. One was in serious condition, we barely saved her. Others had enlarged livers. So I am telling you that I did see the symptoms. I don't know what others are telling you" (CBC, 1998). Another report suggested that the spill lead to a fish kill but there were no confirmed reports of sickened villagers and livestock (OSHS, 1998).

Here are some comments in Table 12 to demonstrate the confusion. Each row in Table 12 is from the stated reference.

Table 12 The Proposed Number of People Affected by Cyanide Spill

Number of Dead	Number Effected
2	"2,533 poisoned, most from local village of Barskaun" (Ling, 1998)
"No one died as a result of the spill of sodium cyanide"	"Although there was potential for up to 16 people to become exposed as a result of cyanide ... no medical evidence has been supplied to the commission to support these cases as being affected by cyanide" (Internet, 1998)
"A second person has died from cyanide poisoning "	"444 people remain in hospital since the May 20 accident, including six who are in grave condition" (Perreaux, 1998)
"a woman has died after a river has been contaminated with cyanides"	"Kyrgyz officials...say a total of 506 local residents had been hospitalized by June 3" (Financial Post, 1998)
"doctor blames cyanide for a woman's death"	"Hundreds flooded to hospitals complaining of being sick" (CTV, 1998)
"she died of sodium cyanide poisoning that aggravated a previous illness"	"some 600 people have sought medical treatment for poisoning. About 100 of those have been hospitalized" (Globe and Mail, 1998)
"no cyanide related deaths"	"maximum of 16 potential cases of direct cyanide exposure" (CNW, 1998)

9.0 Neutralization of Cyanide Spills

A typical cyanide neutralization is shown below:

For alkaline chlorination:

1) $NaCN + 2NaOH + Cl_2 \rightarrow NaCNO + 2NaCl + H_2O$

2) $2NaCNO + 4NaOH + 3Cl_2 \rightarrow 6NaCl + N_2 + 2H_2O + 2CO_2$

This procedure uses sodium hydroxide, pH has to be maintained at a pH above 9, preferably pH 9 to pH 11, to avoid formation of nitrogen trichloride (Kirk-Othmer, 1993).

Hypochlorite neutralization is shown here:

$$NaCN + NaClO \rightarrow NaCNO + NaCl$$

(McGill and Comba, 1990)

The cyanide solutions are oxidized to the less toxic cyanate (Corn, 1993a). Cyanates are toxic to trout at concentrations ranging from 13-82 mg/L cyanate (Moran, 1998a).

Cyanide spills can also be neutralized with peroxide via the Degussa method in which the pH is maintained above 9 (between 9.0-10.5) to avoid formation of NCl_3, nitrogen trichloride. The Degussa method is shown below:

1) Oxidation:

$CN^- + H_2O_2 \rightarrow CNO^- + H_2O$

$2Cu(CN)_3^{2-} + 7H_2O_2 + 2OH^- \rightarrow 6CNO^- + 2Cu(OH)_2 + 6H_2O$

2) Precipitation:

$Fe(CN)_6^{4-} + 4Na^+ + 2CuSO_4 \rightarrow Cu_2Fe(CN)_6\downarrow + 2Na_2SO_4$

3) Hydrolysis of cyanate:

$CNO^- + 2H_2O \rightarrow CO_3^{2-} + NH_4^+$

4) Side reactions:

$S^{2-} + H_2O_2 \rightarrow S^\circ\downarrow + 2OH^-$

$SCN^- + H_2O_2 \rightarrow S^\circ\downarrow + CNO^- + H_2O$

(McGill and Comba, 1990a)

Peroxide was used at River Wey at Surrey, UK on 14 May, 1999. A metal plating factory spilled 200 liters of cyanide into the river which caused the fish to gasp on the surface. Once the peroxide is added it breaks down into water and oxygen. It also raises the pH of the polluted water causing the cyanide to break down more rapidly. The fish were saved by the additional oxygen added. The Environment Agency's Thames Region now includes peroxide crystals, or sodium carbonate peroxyhydrate in their response kits for cyanide spills(OSHS, 1999).

An example of how the peroxide increases the oxygen content occurred on 3 June, 1999. A small pond of fish about 0.1 hectare had a low oxygen content of 13%, within 2 hours after adding some 200 kg of liquid sodium peroxide the percentage oxygen rose to 35% (OSHS, 1999).

10.0 Conclusion

There is no doubt from this paper that sodium cyanide is highly toxic to humans and the environment. Its usage in the mining industry has called into question the responsibility of the owners and operators to create a safe environment. As can be seen in the case studies, cyanide spillages into water ways cause catastrophes. A recent comment on March 22, 2000 regarding a helicopter spillage of sodium cyanide shows the changing tide for tolerating cyanide spills. Says Mr. Evens of the Mineral Policy Institute in Sydney, Australia, "There is mounting evidence that using cyanide to extract gold is inherently dangerous. The high risk of cyanide accidents outweigh the dubious benefits of mining gold. We are being forced to question whether cyanide usage in gold mining should be limited or even banned" (Evans, 2000). These are questions that could change the future of the usage of sodium cyanide.

11.0 Acknowledgments

I would like to acknowledge Carol Lau from the office of NEEC, Environment Canada for her help in providing information from the NATES database.

12.0 References

Aquire Database, Vol. 1-6, June 1994.

Borsa, *Impacts of the Romanian Mine Accidents*, http://www.zpok.hu/~jfeiler/baiamare/impacts.htm, 11 March, 2000.

CBC, The National Online, *Poisoned Partnership*, http://www.tv.cbc.ca/national/pgminfo/ppartner/index.html, 24 June, 1998.

CBC, The National Online, *Poisoned Partnership*, http://www.tv.cbc.ca/national/pgminfo/ppartner/index.html, pp. 1, 24 June, 1998a.

CBC, The National Online, *Poisoned Partnership*, http://www.tv.cbc.ca/national/pgminfo/ppartner/index.html, pp. 2, 24 June, 1998b.

CCOHS, Canadian Centre for Occupational Health & Safety, "Sodium Cyanide", Chempendium Compact Disc, *NIOSH pocket guide*, 2000-1, expires June 2000.

CCOHS, Canadian Centre for Occupational Health & Safety, "Sodium Cyanide", Chempendium Compact Disc, *MSDS -A & B*, 2000-1, expires June 2000a.

CCOHS, Canadian Centre for Occupational Health & Safety, "Sodium Cyanide", Chempendium Compact Disc, *CHRIS*, 2000-1, expires June 2000b.

CCOHS, Canadian Centre for Occupational Health & Safety, "Sodium Cyanide", Chempendium Compact Disc, *RTECS*, 2000-1, expires June 2000c.

CCOHS, Canadian Centre for Occupational Health & Safety, "Sodium Cyanide", *The Chemical Advisor*, Compact Disc, 2000-1, expires June 2000d.

CCOHS, Canadian Centre for Occupational Health & Safety, "Sodium Cyanide", Chempendium Compact Disc, *HSDB*, 2000-1, expires June 2000e.

Chem-Bank, "Sodium Cyanide", SilverPlatter Information, Compact Disc, ERL Compliant, Health & Safety Publishing, November 1999.

Chemtox Database, "Sodium Cyanide", *Chemtox Database Compact Disc*, December 1999.

Citizen Internet, Ottawa Citizen Online, *River Killed "for many years to come" After Cyanide Spill, Official Says*, The Canadian Press, http://www.southam.com/ottawacitizen/newsnow/cpfs/world/000215/w21546.html, 15 February, 2000.

Clayton, G. D., Clayton, F. E., *Patty's Industrial Hygiene & Toxicology*, John Wiley & Sons, Inc., Vol. 1, Part A, pp. 2021, 1991.

CNW, Canada NewWire, *The International Scientific Commission Present Its Final Report on the Cyanide Spill*, http://www.newswire.ca/releases/September1998/25/c6477.html, 25 September, 1998.

Corn, Morton, *Handbook of Hazardous Materials*, Academic Press, Inc., San Diego, California, pp. 169, 1993.

Corn, Morton, *Handbook of Hazardous Materials*, Academic Press, Inc., San Diego, California, pp. 167, 1993a.

Corpus, CPI Product Profiles, *Sodium Cyanide*, pp. 1-3, April, 1998.

CTV, CTV New and Current Affairs, *A Canadian Company is at the Centre of an Environmental Mishap Overseas*, Thursday 4 June, 1998.

Environment Canada, "Sodium Cyanide", *Manual for Spills of Hazardous Materials*, Minister of Supply and Services Canada, Ottawa, Ontario, 516 p., 1984.

Evans, G., Media Release, *PNG Cyanide Accident: Water Testing Results*, http://www.zpok.hu/~jfeiler/baiamare/News/mpi2203.htm, Wednesday, March 22, 2000.

Feasby, G., *The OMAI Tailings Water Spill, An Uncontrolled Release of Cyanide-Contaminated Water*, Natural Resources Canada, Health Canada, pp. 1-2 & 6, September 1, 1995.

Feasby, G., *The OMAI Tailings Water Spill, An Uncontrolled Release of Cyanide-Contaminated Water*, Natural Resources Canada, Health Canada, pp. 8, September 1, 1995a.

Financial Post, The Financial Post, *Death reported after Cameco spill in Kyrgyzstan*, Reuters, Friday 5 June, 1998.

Genium's Handbook of Safety, Health, and Environmental Data for Common Substances, Material Safety Data Sheets update 52, Compact Disc, "Sodium Cyanide", Genium Publishing Corp., 1999.

Globe and Mail, *Cameco Denies Cyanide Spill Killed Woman Doctors in Kyrgyzstan Say Previous Illness Was Aggravated by Poison in Nearby River*, Friday 5 June, 1998.

Guyana map, wyxiwyg://17/http://www.geocities.com/RainForest/2651/, 1995.

Ingles, J., J. S. Scott, *State-of-The-Art of Processes for the Treatment of Gold Mill Effluents*, Mining, Mineral and Metallurgical Processes Division, Industrial Programs Branch, Environmental Protection Programs Directorate, pp. xv, March 1987.

Internet, *Information on the May 20, 1998 Truck Accident and Sodium Cyanide Spill*, http://www.cameco.com/investor/news_releases/1998-Sep-29.html, Saskatoon, Saskatchewan, Canada, September 29, 1998.

King, B. R., *Encyclopedia of Inorganic Chemistry*, John Wiley & Sons, Inc., Vol. 2, pp. 558, 1994.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 3rd Edition, Vol. 1, pp. 345, 1978.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 3, pp. 201, 1978a.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 7, pp. 365, 1979.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 5, pp. 725-726, 1979a.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 8, pp. 841, 1979b.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 8, pp. 856-7, 1979c.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 7, pp. 320, 1979d.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 7, pp. 320, 1979e.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 11, pp. 973, 1980.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 15, pp. 316, 1981.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 17, pp. 497, 1982.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 19, pp. 634, 1982a.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 18, pp. 318, 1982b.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 21, pp. 197, 1984.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 3rd Edition, Vol. 21, pp. 4, 1984a.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 4th Edition, Vol. 7, pp. 768, 1993.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 4th Edition, Vol. 7, pp. 765, 1993a.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 4th Edition, Vol. 7, pp. 769, 1993b.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 4th Edition, Vol. 7, pp. 766, 1993c.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 4th Edition, Vol. 7, pp. 767, 1993d.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 4th Edition, Vol. 16, pp. 741, 1995.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 4th Edition, Vol. 15, pp. 75, 1995a.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 4th Edition, Vol. 15, pp. 932, 1995b.

Kirk-Othmer, *Kirk-Othmer Encyclopedia of Chemical Technology*, John Wiley & Sons, Inc., 605 Third Ave., New York, NY, 4th Edition, Vol. 20, pp. 861, 1996.

Ling, C., *Famed Kyrgyz Lake Fights Aftermath of Chemical Spill*, http://www.nando.com/newsroom/ntn/health/070798/health4_5314_noframes.html, Reuters News Service, 1998.

McGill, S. L., P. G. Comba, *A Review of Existing Cyanide Destruction Practices*, US Bureau of Mines, Reno Research Center, Nevada Mining Association, Nevada Department of Wildlife, Wildlife/Mining Workshop, Reno, Nevada, pp. 11, 29 March, 1990.

McGill, S. L., P. G. Comba, *A Review of Existing Cyanide Destruction Practices*, US Bureau of Mines, Reno Research Center, Nevada Mining Association, Nevada Department of Wildlife, Wildlife/Mining Workshop, Reno, Nevada, pp. 15-16, 29 March, 1990a.

Moran, R., *Cyanide Uncertainties, Observations on the Chemisty, Toxicity, and Analysis of Cyanide in Mining-Related Waters*, Mineral Policy Center, MPC Issue Paper No. 1, http://www.zpok.hu/~jfeiler/baiamare/docs/cyanideuncertain.htm, pp. 9, 1998.

Moran, R., *Cyanide Uncertainties, Observations on the Chemisty, Toxicity, and Analysis of Cyanide in Mining-Related Waters*, Mineral Policy Center, MPC Issue Paper No. 1, http://www.zpok.hu/~jfeiler/baiamare/docs/cyanideuncertain.htm, pp. 10, 1998a.

Moran, R., *Cyanide Uncertainties, Observations on the Chemisty, Toxicity, and Analysis of Cyanide in Mining-Related Waters*, Mineral Policy Center, MPC Issue Paper No. 1, http://www.zpok.hu/~jfeiler/baiamare/docs/cyanideuncertain.htm, pp. 7, 1998b.

Moran, R., *Cyanide Uncertainties, Observations on the Chemisty, Toxicity, and Analysis of Cyanide in Mining-Related Waters*, Mineral Policy Center, MPC Issue Paper No. 1, http://www.zpok.hu/~jfeiler/baiamare/docs/cyanideuncertain.htm, pp. 12, 1998c.

MTI, *Spread of the cyanide spill from Baia Mare*, Ministry for Environmental Protection Hungary, Environmental Inspectorates, MTI Co. Media Data Bank, http://www.zpok.hu/~jfeiler/images/mapen.jpg, 20 February, 2000.

NATES, National Analysis of Trends of Emergencies System, Environment Canada, TDG, Transport Canada, Ottawa, 2000.

NEEC Alert, The National Environmental Emergency Center of Environment Canada, Urgent fax from United Nations, Environment desk of Dept. of Humanitarian Affairs, 22 August, 1995.

NEEC Alert, The National Environmental Emergency Center of Environment Canada, Urgent fax from United Nations, Environment desk of Dept. of Humanitarian Affairs, Information Report No. 1 - Guyana Cyanide Mine Waste Spill, NEEC # 1503,22 August, 1995.

OSHS, Oil Spill Hazardous Substances, *Panic Reported After Cyanide Spill in Kyrgystan*, Global News on the Marine Chemical Response Industry by Cutter Information Corp., Vol. I, No. 4, 4 June, 1998.

OSHS, Oil Spill Hazardous Substances, *UK Using Peroxide to Stem Fish Kills from Sewage, Cyanide*, Global News on the Marine Chemical Response Industry by Cutter Information Corp., Vol. II, No. 12, 17 June, 1999.

OSHS, Oil Spill Hazardous Substances, *UN Team Calculates Cyanide Damage*, Global News on the Marine Chemical Response Industry by Cutter Information Corp., Vol. III, No. 5, 9 March, 2000.

OSHS, Oil Spill Hazardous Substances, *Cyanide Spill Purges Hungarian River En Route to Danube*, Global News on the Marine Chemical Response Industry by Cutter Information Corp., Vol. III, No. 3, 10 February, 2000a.

Perreaux, L., The Saskatoon StarPhoenix, *Kumtor Boss Quits after Second Death Blamed on Spill*, Tuesday June 9, 1998.

Pope, A. M., Rall, D. P., *Environmental Medicine, Integrating a Missing Element into Medical Education*, National Academy Press, Washington, D.C., pp. 318, 1995.

Pope, A. M., Rall, D. P., *Environmental Medicine, Integrating a Missing Element into Medical Education*, National Academy Press, Washington, D.C., pp. 317-8, 1995a.

Pope, A. M., Rall, D. P., *Environmental Medicine, Integrating a Missing Element into Medical Education*, National Academy Press, Washington, D.C., pp. 323, 1995b.

Pope, A. M., Rall, D. P., *Environmental Medicine, Integrating a Missing Element into Medical Education*, National Academy Press, Washington, D.C., pp. 322-3, 1995c.

Sax, *Dangerous Properties of Industrial Materials*, 7th Edition, Vol. 9, No. 5, New York, Van Nostrand Reinhold, pp. 76, 1989.

Sax, *Dangerous Properties of Industrial Materials*, 7th Edition, Vol. 9, No. 5, New York, Van Nostrand Reinhold, pp. 77, 1989a.

TPF, *Toxicological Profile for Cyanide*, U.S. Department of Health & Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, Division of Toxicology/Toxicology Information Branch, Atlanta, Georgia, pp. 70, 1997.

Trip, L., and B. Blakeman, Advise to Minister on Subject: *Cambior Inc. Cyanide Spill in Guyana*, Letter from Environmental Protection Service, pp. 1-2, 14 February, 1995.

Ullmann's, *Ullmann's Encyclopedia of Industrial Chemistry*, Federal Republic of Germany, 5th Edition, Vol. A8, pp. 165, 1987.

Ullmann's, *Ullmann's Encyclopedia of Industrial Chemistry*, Federal Republic of Germany, 5th Edition, Vol. A8, pp. 166, 1987a.

Ullmann's, *Ullmann's Encyclopedia of Industrial Chemistry*, Federal Republic of Germany, 5th Edition, Vol. A8, pp. 167, 1987b.

Ullmann's, *Ullmann's Encyclopedia of Industrial Chemistry*, Federal Republic of Germany, 5th Edition, Vol. A8, pp. 171, 1987c.

UNEP/OCHA, United Nations Environment Programme/Office for the Co-ordination of Humanitarian Affairs, *Spill of Liquid and Suspended Waste at the Aurul S.A. Retreatment Plant in Baia Mare*, Assessment Mission, Romania, Hungary, Federal Republic of Yugoslavia, pp. 7, 23 February - 6 March, 2000.

UNEP/OCHA, United Nations Environment Programme/Office for the Co-ordination of Humanitarian Affairs, *Spill of Liquid and Suspended Waste at the Aurul S.A. Retreatment Plant in Baia Mare,* Assessment Mission, Romania, Hungary, Federal Republic of Yugoslavia, pp. 45, 23 February - 6 March, 2000a.

UNEP/OCHA, United Nations Environment Programme/Office for the Co-ordination of Humanitarian Affairs, *Spill of Liquid and Suspended Waste at the Aurul S.A. Retreatment Plant in Baia Mare*, Assessment Mission, Romania, Hungary, Federal Republic of Yugoslavia, pp. 44, 23 February - 6 March, 2000b.

UNEP/OCHA, United Nations Environment Programme/Office for the Co-ordination of Humanitarian Affairs, *Spill of Liquid and Suspended Waste at the Aurul S.A. Retreatment Plant in Baia Mare*, Assessment Mission, Romania, Hungary, Federal Republic of Yugoslavia, pp. 45-8, 23 February - 6 March, 2000c.

UNEP/OCHA, United Nations Environment Programme/Office for the Co-ordination of Humanitarian Affairs, *Spill of Liquid and Suspended Waste at the Aurul S.A. Retreatment Plant in Baia Mare*, Assessment Mission, Romania, Hungary, Federal Republic of Yugoslavia, pp. 54-5, 23 February - 6 March, 2000d.

Vick, S., R. Squires, R. Dundee, R. Pedroni, N. Watson, *Preliminary Report on Technical Causation OMAI Tailings Dam Failure*, Submitted to Guyana Geology and Mines Commission, http://www.antenna.nl/wise-database/uranium/mdgr.html, 16 November, 1995.

WWF, World Wide Global Network: Press Release, *The biggest ever freshwater disaster in Central and Eastern Europe*, http://www.panda.org/news/press/news.cfm?id=1850, 9 February, 2000.

WWF, World Wide Global Network: Press Release, *Dam must be secured to prevent further damage, warns WWF*, http://www.panda.org/news/press/news.cfm?id=1852, 18 February, 2000a.

WWF, World Wide Global Network: Press Release, *WWF demands immediate government action on toxic spill*, http://www.panda.org/news/press/news.cfm?id=1848, 14 February, 2000b.

The Impact of Styrene on the Environment

Richard Lawuyi and Merv Fingas
Emergencies Science Division
Environmental Technology Centre
Environment Canada
Ottawa, Ontario
Lawuyi.Richard@etc.ec.gc.ca

Abstract

Large-scale production of styrene based on the dehydrogenation of ethylbenzene started in the 1930s. As with many chemicals, commercial demand grew during the second World War as a result of acute shortage of natural rubber and the need to find new rubber substitutes. Polystyrene and co-polymers are now one of the cheapest thermoplastics on cost-per-volume basis. The World capacity has been estimated at over 17 x 10^6 tonnes per year.

Some previous spill experience will be discussed as well as several misconceptions about polystyrene materials such as being non-recyclable, non-degradable, toxic on burning, carcinogenic, ozone depleting, landfill-choking, and wild-life killers.

1.0 Introduction

Styrene is a naturally occurring liquid found in many plants such as cinnamon, coffee beans, peanuts, and balsam storax from which it was first isolated in the nineteenth century. For many years no use could be found for this substance. The discovery of the dehydrogenation of ethylbenzene to produce styrene by Farben in Germany and Dow in the United States in the 1930s led to the commercialization of styrene as an industrial chemical. As a result of natural rubber shortage during World War 2, many large-scale plants were built for the manufacture styrene and polystyrene, both in Germany and United States to provide a synthetic substitute (Boundy and Boyer, 1952). Even after the World War 2 ended, demand for styrene continued to grow and several more uses were found for the polymer. Rapid growth was also seen in Japan and Western Europe and the Pacific Rim after World War 2.

There are many reasons why styrene is the most successful industrial chemical, a) it is very cheap to make as the precursors can be produced at low cost, b) it is a safe, stable, and easy to handle liquid, c) polystyrene is easy to mold, handle and transport, d) the manufacturing technologies produce high yields of the polymer, e) the raw materials benzene, and ethylene can be produced in large quantities and very cheaply, f) manufacturing technologies are very simple and cheap to build on a large scale.

2.0 Modern Industrial Uses

Over 65 percent of styrene monomer produced is converted to polystyrene and copolymers. It is used essentially as a feedstock in a number of polymer materials such as, thermoplastics, elastomers, dispersions, and thermoset plastics. The main end-uses are: reinforced plastics, polyester resins, polystyrene emulsions, styrene-modified acrylics, expandable polystyrene beads, styrene-acrylic polishes, styrene latex, ABS

resins, styrene-butadiene latex (Lattime, 1997; Camford, 1998). Polystyrene can be made into toys, housings for air conditioners, television cabinets, cassetts, combs, furniture parts, insulation board, loose-fill packaging, disposable food containers.

On the other hand, styrene-butadiene is used for passenger car tires, industrial hoses and footwear. Styrene -butadiene latexes is used in tufted carpet, paper coatings, and in latex paints. There are also the styrene-acrylonitrile (SAN), used for making drinking tumblers and battery cases, and the terpolymers of acrylonitrile, butadiene, and styrene (ABS) used for piping, automotive components, refrigerator door liners and shower stalls.

Styrene can also be polymerized with unsaturated polyester resins to produce fiberglass reinforced boats, storage tanks, shower units, and simulated marble products.

3.0 Spill Profile

Despite its large volume, according to the latest spill numbers styrene monomer is not a frequently spilled substance (NATES, 2000). The graph below shows the annual spill frequency of styrene monomer since 1992.

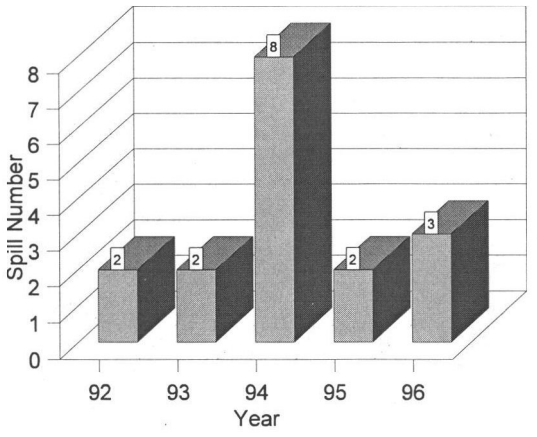


Figure 1 Annual Spill Frequency of Styrene Monomer Since 1992.

In a research study on the "Priority List Ranking of Hazardous Chemicals" done about ten years ago, styrene was placed fourth. Our main goal then was to determine the minimum number of hazardous chemicals that were most frequently spilled (Fingas et al., 1991). The list was developed by a simple ranking of: a) reported spill frequency b) supply volumes c) historical spill volumes and d) toxicities.

Table 1. Priority List Ranking of Sulphuric Acid

CHEMICAL	RANKING	SPILL NUMBER	SPILL VOL.	SUPPLY VOL.
Ammonia	1	107	470	3700
Chlorine	2	36	120	1700
Tetraethyllead	3	4	72	26
Styrene	**4**	**24**	**5000**	**630**
PCBs	5	334	89	-
Sulphuric acid	6	155	13000	3700
Sodium cyanide	7	3	83	12
Hydrochloric acid	8	123	3300	170
Potassium chloride	9	31	12000	-
Pentachlorophenol	10	19	110	1.5
Phenol	11	10	14	68
Zinc sulphate	12	3	68	1500
Phosphorus	13	16	46	68
Toluene	14	13	110	430

Exposure to styrene during a spill often causes irritation. In many cases, high concentrations can cause central nervous system depression with symptoms that include
drowsiness, headache, confusion, lack of coordination and unconsciousness. As far as is known, no deaths have been reported from exposure to styrene.

IMMEDIATE CONCERNS DURING SPILLS

HAZARD: Flammable reactive liquid. Avoid all sources of ignition. Penetrating odour. May polymerize at room or elevated temperatures releasing large quantities of heat..

HUMANS: At high concentrations (100 ppm), causes immediate eye and nose irritation, headache, fatigue and a feeling of drunkenness. At higher concentrations, can cause decreases in coordination, nausea, headache, fatigue. Prolonged exposure can cause respiratory tract obstruction and liver damage.

ENVIRONMENT: Styrene will accumulate in fish producing tainting.

PROTECTION: Wear solvent-resistant clothing and gloves. Wear full-face respiratory protection

3.1 Emergency Response to Spills

HUMANS

Inhalation: Move victim to fresh air immediately. Give artificial respiration, if breathing has stopped. Keep person warm at rest. Seek medical attention.

Skin: Remove soaked clothing. Wash skin with plenty of water for 5 minutes. Seek medical attention

Eyes: Remove any contact lenses. Wash eyes with large quantities of water. Seek medical help.

Ingestion: Get medical help. Do not induce vomiting

ENVIRONMENT:

Spills on Land: Remove all sources of ignition. Prevent persons not wearing protective clothing from entering spill site. Ventilate area. Absorb liquid in vermiculate, dry sand, earth and store in sealed containers. If large, dyke, or build walls. Then incinerate or recycle refuse.

Spills on Water: Lay boom around spill to prevent from spreading. Pump spill into a septic tank and recycle.

4.0 Industrial Aspects and Production in the United States, Canada and Worldwide.

Nova is now the biggest styrene producer in North America as a result of acquiring Huntsman's styrenics businesses. Lyondell is another big producer that has well positioned itself in the styrene market. Styrene is also produced in large quantities in developing countries due to the cheap and simple technology required for processing. Styrene monomer is produced by two main methods namely, dehydrogenation and co-reaction of propylene oxide with ethylbenzene.

The price range for styrene monomer is 75-160 cents/kg reflecting the price of benzene which is the main starting material. The price of styrene is also governed by variations in supply and demand.

The total capacity of styrene in Canada in 1997 is 805 kilotonnes/year while in the United States it is 5,605 kilotonnes/year (Camford, 1998). Canadian import of styrene from the United States totalled 27.41 kilotonnes, while the United States imported 313.38 kilotonnes from other countries in 1997. Lately, real growth in styrene market has occurred in Western Europe, Japan and the Pacific Rim. The total world production of styrene in 1995 is roughly 16.5 x 10^6 tonnes. Future projections are that the market will keep growing. Below are the names of North American maanufacturers:

Canadian Manufacturers.

Company	**Plant Location**
Dow Chemical Canada	Sarnia, Ontario
Nova Chemicals	Sarnia, Ontario
Shell Canada Chemical	Scotford, Alberta
United States Manufacturers	
Amoco Chemical	Texas City, TX
Chevron Chemical	St. James, LA
Cos-Mar	Carville, LA
Dow Chemical	Freeport, TX
Huntsman Chemical	Bayport, TX
Huntsman Chemical	Odessa, TX
Lyondell	Channelview, TX
Sterling Chemicals	Texas City, TX
Westlake Polymers	Lake Charles, LA

World Capacity by Regions

There are over 80 companies all over the World that manufacture styrene monomer. The total World capacity for styrene in 1993 was estimated at 17x10^6 t/a. The distribution is as follows:

Region	Percentage
North America	35
Western Europe	27
Japan	16
Korea	7
Far East	5
Eastern Europe	5
South America	4
Middle East	1

5.0 Environmental Chemistry

While styrene will undergo all the usual reactions of unsaturated compounds including addition reactions, oxidation, substitution, only the environmental relevant ones are very few and are described below:

In a reversible process, styrene is produced from ethyl benzene which is also manufactured from ethylene and benzene. One of the routes to production of styrene is the dehydrogenation of ethylbenzene which accounts for 85 percent of the total commercial production, the remaining 15 percent comes from the production of propylene oxide and styrene. Some of the byproducts of the ethylbenzene dehydrogenation process are benzene, ethylene, toluene, hydrogen and carbon. This is an endothermic reaction.

$$C_6H_5CH_2CH_3 \rightleftharpoons C_6H_5CH{=}CH_2 + H_2 \qquad (1)$$

The main reaction of styrene is the exothermic polymerization and copolymerization to form polystyrene and other copolymer products in the presence of a catalyst:

$$nC_6H_5CH{=}CH_2 \xrightarrow[\text{catalyst}]{} (C_6H_5CH_2\text{-}CH_2\text{-})n \qquad (2)$$

Styrene is known to polymerize at room temperature with heat release in the liquid phase and even more rapidly at higher temperatures.

When exposed to the air, styrene will produce high molecular weight peroxides through free radical polymerization. Styrene can also be oxidized to various other compounds such as benzaldehyde, benzoic acid, styrene oxide, formaldehyde, and formic acid. It is strongly recommended that styrene be not stored with strong oxidizing agents as oxidation reactions can occur.

6.0 Environmental Fate and Behaviour

Most of the impurities in styrene production do find their way into the environment. The amounts and types of impurities depend on the kind of process and other variables such as temperature, purity of reagents and the purification of products. These impurities include aldehydes, polymers, peroxides, inhibitors, xylene, vinyl toluene, n-propylbenzene, ethylbenzene etc.

Styrene is a reactive monomer and will undergo exothermic polymerization readily. It is also flammable. Lack of proper control of the temperature can result in runaway polymerization and explosive vapour cloud. The weight average molecular

weight for commercial polystyrene can range from 200,000-400,000. The weight average molecular weight for spontaneous polymerization is inversely proportional to the rate of polymerization. Use of the right initiators and other additives during polymerization of styrene can produce polymers of the desired molecular weight.

Styrene and butadiene polymers such as elastomers, emulsion and solution are one of the largest volume synthetic rubber. They encompassed tires, tread rubber, other tire-related goods, mechanical products, flooring, shoe products, plastic goods, chewing- gum base goods and adhesives. Many of these products often end up in landfills and dump sites.

Polystyrene is a photodegradable polymer and has no effects on the ozone layer as it does not contain chlorine atoms. It does absorb sunlight above the 290 nm. Efforts are being made to enhance the degradability by adding or copolymerizing with photosensitizers such as ketones and carbonyl containing compounds. This is especially good for the environment as more and more polystyrene goods end up in dumpsites and landfills. Polystyrene materials are not readily biodegradable probably due to their low water-solubility. Increased water solubility has been partially achieved by the addition of hydrophilic and water hydrolyzable groups such as amides and esters. Inclusion of other groups such as cyclic ethers that can readily undergo ring opening have also been made.

7.0 Toxicity and Standards

Concerns have been raised about migration of styrene residues from polystyrene materials that in food is often stored. Styrene monomer is mildly toxic and safe if handled properly (Lattime, 1997). Styrene is not a confirmed carcinogen but it is considered a suspect or probable carcinogen. Below are the acute effects to over exposure to styrene:

Table 2. Acute Effects of Exposure to Styrene

Area Exposed	Effects
Eye	Slight to moderate irritation
Skin	Slight irritation; repeated exposure may produce severe irritation including blistering.
Inhalation	May cause headache, nausea, dizziness, muscle weakness; produces central nervous system depression,; irritates nose, throat and lungs.
Ingestion	May cause nausea, headache, dizziness, muscle weakness; produces central nervous system depression, and diarrhea; may be aspirated into lungs if swallowed, resulting in pulmonary edema and chemical pneumonitis.
Adults and children	leaching from polystyrene products to foods and from toys is in traces amounts only.

The recommended exposure limits are OSHA permissible exposure limits (PEL) 50 ppm, and ACGIH TLV 50 ppm, STEL/Ceiling is 100 ppm.

8.0 Previous Spill Experience

Even though a high-volume cheap chemical, styrene is not a commonly spilled substance within the last decade as shown in the spill profile section. One spill that has been well documented occurred in British Columbia, Canada (Wile, 1994).

On April 8, 1994, the Panamanian registered tanker M/V FUKUSHIN spilled an estimated 10 tonnes of styrene monomer during a loading operation at Pacific Coast Terminals. This resulted in the release of about 2 tonnes of the chemical into the waters of Burrard Inlet. The remaining 8 tonnes was contained on the deck of the vessel. The floating chemical product was completely contained inside a boom surrounding the vessel. The containment was already in place around the vessel, in accordance with standard operating procedures required by the Vancouver Port Corporation and the Canadian Coast Guard. In accordance with the directions from Environment Canada technical personnel, a safety zone was established, and it was agreed that the clean-up operations would not be initiated until the next day in order to permit the chemical vapours to dissipate

The chemical residue inside the boom was herded using an absorbent pad drag line and the material was pumped into a septic tank truck. The recovered waste was transferred to a secure storage site located at Pacific Coast Terminals under the direction of the BC Ministry of Environment.

Environment Canada took air samples of the spill area and recommended an evacuation of all personnel from a 300 metre radius around the ship. As strong vapour was present the Emergency Response Officer attempted to contact Ministry of Health to address potential health concerns raised by nearby residents. The Medical Health Unit could not be reached since it was after normal working hours. The Emergency Response Officer's attempts to reach Emergency Health Authorities through local hospitals, Fire department and RCMP failed. Due to the flammability and toxicity of the product and the inability to effect any safe clean-up of the spill, it was decided to leave the styrene in a containment overnight to evaporate and polymerize. Foam was applied to the spill surface area to reduce vapour emissions.

Environment Canada biologists carried out an initial environment impact assessment to determine if there were any obvious effects to fish or wildlife in the immediate area and also to determine if any significant quantities of the chemical had escaped the boomed area. The results of the survey indicated no obvious environmental impacts and no chemical residues outside the boomed area.

The clean-up of the spilled chemical has been completed by Burrard Clean Operations Limited, as a result of a joint response by Canadian Coast Guard, Environment Canada, and the BC Ministry of the Environment. The initial environmental impact assessment conducted by my officials indicated that there were no visible effects to fish or wildlife in the vicinity of the spill site. A plan is being developed with Regional Marine Resource specialists to carry out a more comprehensive assessment of the residual chemical contamination in the marine environment including water, sediments and biota. The spill is also currently under a legal investigation by both Canadian Coast Guard and Environment Canada.

8.1 Lessons to be Learned

- The response agencies involved responded in a coordinated and effective manner but were not equipped to clean up a spill of styrene monomer. Accurate information on a method to clean up a spill of this substance was not available.

- The Pacific Coast Terminals' Contingency Plan was inadequate for response to a spill of styrene monomer. While the plan addressed the substance, the response directions were inaccurate and incomplete. The plan assumed that response would be provided by TEAP. The plan is currently under review by federal agencies.

- Pacific Coast Terminals, Shell Canada, and the agencies responding did not have the capability to provide clean-up or recovery of styrene monomer.

- The role of Transportation Emergency Assistance Plan team in spill response will be reviewed in relation to the expectations of industry and its reliance for providing response on the team in contingency plans.

- Notification of Ministry of Health Officers, after hours, is currently being reviewed by the Ministry of Environment, Lands and Parks.

- Emergency response plans are rarely exercised or tested by companies. A formal process to require environmental audits for prevention/risk evaluations, contingency plans for response, and to require verification of a company's response capability is needed.

9.0 Conclusion

Styrene is a high-volume chemical that is not spilled often. It is mildly toxic to humans and it is a suspect carcinogen. There is not enough data to determine the accurate dose-response properties and mutagenicity of this substance.

10.0 References

Boundy, R.H., and R.F. Boyer, "Styrene, Its Polymers, Copolymers, and Derivatives", Reinhold Publishing Corp., New York, 1952.

Camford Information Services Inc., "Styrene", *CPI Product Profiles*, Scarborough, Ontario, 1998.

Fingas, M., N. Laroche, G. Sergy, B. Mansfield, G. Cloutier, P. Mazerolle, "A New Chemical Spill Priority List". *Proceedings of the 8th Technical Seminar on Chemical Spills,* Environment Canada, Ottawa, Ontario. 1991.

IARC, *IARC Monographs on the Evaluation of Carcinogenic Risk of Chemicals to Man.* (World Health Organization, Internation Agency for Research on Cancer, Lyon, France).

Lattime, R. R., "Styrene-butadiene Rubber", in *Encyclopedia of Chemical Technology,* ed. M. Howe-Grant, Vol 22 , fourth edition, John Wiley & Sons, New York, New York, pp. 956-1013, 1997.

NATES Database, National Analysis of Trends in Emergencies System, Environment Canada, Ottawa, 2000.

Wile, K., "Spill from Tanker Fukushi at Pacific Coast Terminals, Port Moody, British Columbia", Emergencies Section, Pacific and Yukon Region, Environment Canada, Vancouver, British Columbia.

The Shipwreck of the "Fenes" Bacteriological and Chemical Aspects of Wheat Fermentation in a Marine Environment

M. Marchand (1), E. Jacq (2), P. Le Guerroue(1),
S. Corre (2) and B. Moullec (2)

(1) *Cedre*, Brest, France, E-mail : mmarchan@ifremer.fr
(2) MICROMER, Brest, France

Abstract

On September 25th, 1996, the wheat carrier " Fenes ", carrying 2650 tons of wheat, ran aground south of the Lavezzi Islands in the Bouches de Bonifacio (Corsica). A week later, a heavy storm damaged the holds of the ship and caused the spillage of the entire cargo of wheat to depths of 10 to 20 meters, over an area of approximately one hectare. The immediate effects of the wheat on the posidonia herberium were mortalities by physical effects.

A further problem, at first minimized, was the fermentation of the wheat and its undesirable effects. The effect of the organic matter present in the wheat mass, very rapidly favoured the development of a sulphate reducing anaerobic microflora which gave a high production of hydrogen sulphide resulting from the reduction of sulphate of the sea water. Hydrogen sulphide is a chemical reactive gas and extremely toxic to plants, animals and humans. This study enables us to follow the bacteriological aspects of this pollution and the chemical consequences, which could have an impact around the accident zone.

1.0 Introduction

On September 25th 1996, the Panamanian cargo ship " Fenes ", transporting 2650 tons of wheat to Albania, ran aground on the rocks in the Bouches de Bonifacio, to the south of Corsica (France). The place of the accident, Lavezzi Island, is a sensitive ecological area, registered as a Lavezzi nature reserve (Fig.1). The site is characterised by the existence of posidonia herberium (Posidonia Oceanica), a species protected in France and more generally in the signatory countries of the Barcelona Convention for the Mediterranean.

Immediately after the accident, the French authorities ordered the ship's captain to prevent the pollution coming from the ship and its cargo (Marchand, 1997). On October 20th, after the gradual breaking up of the ship, the entire cargo was lying on the seabed, over a surface estimated at more than one hectare around the ship. The thickness of the layer of wheat was between 50 cm to 2 m. Autumn storms increased the impact of the wheat over a larger area (5 to 6 hectares) and three zones of concentrated wheat were visible around the ship. On December 4th, the pumping of the wheat was started using a pump (1200 m^3/h). The wheat was drained and stocked on a barge, then reimmersed in the sea at depths of over 300m.

Divers working on the site very rapidly noticed a deterioration on the surface of their diving belts and people working on the barge were subjected to nausea,

sickness and irritations caused by the strong effects of hydrogen sulphide (H_2S) linked to the wheat fermentation. The levels of hydrogen sulphide measured in the surrounding air were high enough (up to 20 ppm) for the authorities to decide to temporarily suspend the wheat recuperation. Operations were restarted at the end of December and finally stopped on January 13th, 1997. The residual thickness of the wheat was less than 40 cm and it is accepted that the percentage of the wheat evacuated was over two thirds of the « Fenes' » cargo.

The immediate ecological impact of such a spillage is shown in the covering of seaweed communities (Cystoseria balearica) and phanerogames (Posidonia oceanica) localised over one to two hectares (Meinesz et al., 1998). The second point concerns aspects linked to the bacterial degradation of wheat in a marine environment. We give the results of a study carried out from September 1996 to June 1998 to follow the bacteriological aspects of this wheat spillage in the marine environment and the chemical consequences that could have direct ecotoxicological effects on the flora and fauna in the area where the "Fenes" was grounded.

2.0 Material and Methods

During the first mission in December 1996, several samples were taken on the recuperation barge and at two points (A and B) in the marine zone where the wheat was accumulated: samples of wheat, interstitial waters taken from -10 to -20 cm in the wheat mass, water taken from the interface with the wheat mass and water strained from the recovered wheat on the barge. The samples collected during three following missions (May, August, October 1997) were taken from two stations A and B, localized in the same wheat accumulation zone: samples of wheat, sediment and waters (interstitial waters, sea/wheat interface waters, waters at + 0.2 and + 1.0 m above the wheat mass) (Fig. 2). The last collection of samples was taken in June 1998; no residual wheat was found and the results of this last mission can be considered as a new reference situation of the zone where the "Fenes" spilled its cargo. To summarize, 5 series of samples were collected successively 3, 8, 11, 13 and 21 months after the "Fenes" shipwreck.

Chemical analyses carried out on the water samples, were based on the following parameters: pH, dissolved oxygen (O_2) and hydrogen sulphide (H_2S). Dissolved oxygen was measured according to the Winkler method (Aminot, 1983). The measuring of the hydrogen sulphide was done using the colorimetric method, after a complex of sulphur with dimethyl-phenylenediamine (Fonselius, 1983). Measures of pH were carried out with a pHmeter fitted with a glass electrode and a Calomel reference electrode (Ag/AgCl).

For bacteriological analyses, samples were taken in sterile airtight plastic flasks for aerobic bacteria; these flasks were degassed under N_2/CO_2 (80:20) for the enumeration of anaerobic bacteria. Marine Agar and Plate Count Agar media respectively were used for the enumeration of heterotrophic bacteria capable of developing in different saline conditions. The enumeration of the sulphate reducing bacteria (SRB) was carried out over two culture media LAYE (Hardy, 1981) prepared with artificial or natural aged seawater. Ten ml of the medium containing Na-acetate and Na-lactate (respectively 2 and 4 g per litre) were prepared in anaerobic tubes

(Hungate's method) under N_2/CO_2 atmosphere. One ml of a sample (or dilution) was injected through the rubber seal with a sterile syringe. After 3 weeks of incubation at 30°C, all tubes with a black FeS precipitate were counted and the results were determined using a MPN table. The enumeration of the sulphur-oxidizing bacteria (SOB) was carried out over two culture media, either the TB (Tuttle & Jannasch, 1972) or S° (Wirsen et al., 1986) with flowers of sulphur environments. One ml of a sample was added to 9 ml of media. The cultures were incubated at room temperature (20°C ± 2°C) for 3 weeks under constant shaking. A positive response was indicated by the fall in pH (at least 0.5 unit) and/or a presence of sulphur (Durand, 1992), associated with microscopic observations.

3.0 Results

3.1 Bacteriological Aspects

In December 1996, three months after the shipwreck of the "Fenes", the input of organic matter is also shown in the development of the heterotrophic bacterial communities in the interstitial waters collected in the wheat mass, with densities as high as $1.2\ 10^8$ aerobic bacteria per ml of water and $2.5\ 10^8$ facultative anaerobic bacteria per ml of water. At the interface of the wheat mass, densities of heterotrophic bacteria are lower (10^5 to 10^6 bacteria per ml of water). The densities of the heterotrophic bacterial communities in the wheat appear to be relatively similar in the four samples studied, between 10^7 and 10^8 cells per gram of wheat for the facultative anaerobic and aerobic microflora.

During 13 months, high levels of sulphate-reducing bacteria (SRB) were also observed in the wheat. It is calculated as being between 10^7 and 10^8 cells per gram of wheat and no significant difference has been found between samples taken from the surface of the wheat mass and samples taken below the surface (-20cm). On average, the SRB represented about 27% of the anaerobic bacteria. Moreover, no significant difference has been found between samples collected in December 96 and those collected later in May, August and October 97 (table 1). The sulphate-reducing bacteria (SRB) were particularly present in interstitial waters from December 96 to October 97 ($7.9\ 10^4$ to $2.5\ 10^7$ bacteria per ml). At the interface between the wheat and the sea water, the sulphate-reducing bacteria were also present with lower densities of between $1.9\ 10^2$ and $2.5\ 10^4$ bacteria per ml. Measures carried out in the water column showed that SRB densities very rapidly dropped when samples were taken above the wheat mass, becoming insignificant at 1 m above the wheat (table 2). From December 96 to October 97, there was a relative stability of the distribution of SRB densities in the marine environment surrounding the wheat deposit during the 13 months which are followed the spillage of the wheat. In June 98, 21 months after the shipwreck of the « Fenes », the residual wheat was completely dispersed over the marine environment and the SRB densities in the studied area were insignificant (2.5 to 6 bacteria per ml).

In the sediment, a fall in densities was observed as samples were taken further away from the wheat mass. A dramatic gradient is recorded from the enumerations observed in the sediment under the wheat mass ($0.8 - 1.7\ 10^7$ SRB/gram), sediment

collected at the limit of the wheat deposit (1.7 - 2.8 10^5 SRB/gram) and those taken at 4 - 5 m from the accumulation zone (6.6 10^2 SRB/gram).

The characterization of the sulphate reducing bacteria (SRB) isolated from wheat, sediment and interstitial water samples, taken from different culture environments has not shown any conclusive result of a preferential development of species such as Desulfobacter and Desulfotomaculum (Acetate Yeast Extract environment) or Desulfovibrio (Lactate Yeast Extract environment).

If, during the 13 months after the shipwreck; a strong activity of sulphate-reducing bacteria (SRB) was continuously reported in the wheat, sediment and water, simultaneously, a strong activity of sulphur-oxidizing bacteria (SOB) was also reported in the wheat (up to 1.1 10^6 cells per gram of wheat in October 97), the water just above the wheat mass (up to 2.5 10^4 cells per ml of water) and around the wheat deposit. A regular increase of the SOB densities was observed both in the wheat and interstitial water from May to October 97. The development of these two bacterial populations (SRB, SOB) in the area where the wheat was grounded and the evolution of environmental parameters versus time can explain some chemical aspects reported in this study.

3.2 Chemical Aspects

The initial presence of a sulphate reducing microflora in the wheat mass accounts for strong concentrations of hydrogen sulphide found as much in the surrounding air of the wheat sample taking area (significant measures of 10 to 20 ppm) as in the air taken in the wheat mass stocked on the barge (> 200 ppm). These high H_2S concentrations in ambient air forced the French authorities to temporarily stop the response work in December 96 for safety reasons. Work restarted one week later after protective masks had been issued. The first measurements made in the drained water also confirmed an extremely high concentration of H_2S, 1.0 to 3.9 mM. [personal communication of the French Navy].

Results of measurements of H_2S in the interstitial waters taken in May 97 were higher (18 - 57 mM) and the absence of oxygen underlines the totally anoxic nature of the wheat masses deposited on the sea bed. A strong acidity was also noted in interstitial waters (pH 4.8 - 6.2). From the interface on the wheat mass to a height of over 1 m in the water column, the presence of hydrogen sulphide decreases successively at the two points measured, from 112 to 10µM and from 65 to 40 µM. Conversely, the oxygen gradient increases from 9.1 to 15.2 mg/l and from 11.6 to 15.8 mg/l respectively and the pH values as well (table 3).

From August 97, 11 months later the shipwreck, we observed a dramatic decrease of the H_2S content in interstitial water, a 1 000 fold decrease from 18-57 mM to <10 - 36 µM in spite of always a permanently activity of sulphate-reducing bacteria (3.4 to 5.0 10^7 cells per gram of wheat). This decrease of the H_2S content, from May 97 to October 97, is easily related to the increase of pH values (4.8-6.2 to 6.6-7.8), dissolved oxygen (0.0 to 3.1-5.2 mg/l) and sulphur-oxidizing bacteria (4.0 10^2 in May to 6.4 10^5 in August and 1.1 10^6 cells per gram of wheat) (table 4).

4.0 Discussion

The massive spillage of a food product (wheat) led to a pollution problem, linked not only to the physical covering of the marine flora, but also to wheat fermentation and an associated high production of hydrogen sulphide.

The spillage of the wheat from the « Fenes » provoked a high input of organic matter in the marine environment. The area concerned very rapidly changed into an anoxic environment with only a slightly oxygenated layer on the surface of the wheat deposit. This created favourable conditions for wheat fermentation by heterotrophic aerobic and facultative anaerobic microflora. Fermentative bacteria are able to degrade macromolecules and to produce numerous metabolite products, such as hydrogen, low molecular weight fatty acids (acetate, lactate, propionate) and alcohols (Caumette, 1992). In this new marine anoxic environment where there is an unlimited presence of ion sulphate (SO_4^{2-}) in the seawater (28mM), sulphate-reducing bacteria have also found exceptionally favourable conditions for their development. They can use compounds of low molecular weight as electron donors (acetate, ethanol, fumarate, lactate, fatty acid) which are fermentation products resulting from the anaerobic bacterial degradation of carbohydrates, proteins and other macromolecules.

It is accepted that sulphate-reducing bacteria and methanogenic bacteria can compete for the same substratum as the two metabolisms can ensure the final stage of degradation in an anaerobic environment. Generally, it is the presence, or absence of sulphate, which determines the advantaged communities, as sulphate-reducing bacteria in a marine environment seem to have a higher "performing" metabolism than methanogenic bacteria (Caumette, personal communication). Thus, the activity of the sulphate-reducing bacteria of the marine environment participates in the process of using of organic matter in an environment, which has become anoxic. Such a situation cannot be extrapolated from other aquatic environments, such as fresh water environments.

The production of hydrogen sulphide is directly related to the development and the activity of sulphate reducing bacteria (SRB). The presence of this toxic substance has had effects on the personnel responsible for the depollution of the site and eventually on the marine flora and fauna.

Hydrogen sulphide is an insidious poison and highly toxic if inhaled or touched. Depending on the levels of concentration in the atmosphere, inhalation causes nasal, throat and eye, headaches, nausea and vomiting, which can lead to unconsciousness and even death. The Treshold Limit Value (TLV), which is used as a guide to the maximum average exposure to a chemical (8 hours and 5 days per week), is given at 10 ppm for H_2S. The Short-Term Inhalation Limit (STEL), which is the maximum concentration to which workers can be continuously exposed for a period up to 15 minutes without suffering irritation or chronic and irreversible effects, is given at 15 ppm (Environment Canada 1984). High measurements of 10 to 20 ppm of H_2S were reported in the surrounding air of the barge where the wheat was pumped and stored.

The contribution of sulphate-reducing microflora to the degradation of organic matter on the site has had some negative effects as the hydrogen sulphide production has proved to be high). Such conditions are known in anoxic basins (The Black Sea,

Norwegian Fjords). Production measures of H_2S in such sedimentary environments are from 1.3 to 115 mg m^{-2} day^{-1} in the Black Sea and from 167 to 198 mg m^{-2} day^{-1} in a Swedish fjord (Dyrssen, 1986). Concentrations of hydrogen sulphide studied in the reducing environments vary from 40 to 7500 µM (Dyrssen, 1986), results quite comparable to those found on the site of the "Fenes" (18-57 mM in interstitial water, 10 to 112 µM in the adjacent water column). These values are very much higher than the hydrogen sulphide concentrations measured in seawater, estimated at an average of 2nM in the Mediterranean (Luther and Tsamakis, 1989).

When hydrogen sulphide is in contact with an oxic environment, it can, on the one hand participate in the metabolism of sulphur bacteria, on the other hand be rapidly oxidized by oxygen in the seawater. The half-life of hydrogen sulphide is 26 h to 25° C (Millero et al. 1987). It is, therefore, not ruled out that significant concentrations of hydrogen sulphide being dispersed in the seawater in concentrations of some µM (or even more) could have had direct ecotoxicological effects on the flora and fauna communities of the zone. Lethal concentrations of hydrogen sulphide on fish are to be found ranging from 3 to 25 µM, values actually measured on the site. In terms of chronic toxicity the lowest concentrations causing any noticeable effect are between 0.2 and 0.8 µM and the highest concentrations for which there is no toxic effect are between 0.1 and 0.3 µM (Environment Canada, 1984). These indicative data show that ecotoxicological impact of hydrogen sulphide stemming from the fermentation of residual wheat on the ecosystems close to the « Fenes » cannot be excluded. During this period, up to May 97, divers observed that fish did not approach the area of the sea bottom, which was recovered by wheat deposit. After May 97, although the sulphate-reducing bacteria (SRB) did not decrease, there was a dramatic decrease of the hydrogen sulphide content in interstitial water (about 1000 times lower). This coincided with a significant increase of sulphur-oxidizing bacteria (SOB) densities in the wheat mass. This BSO development was favoured by a progressive oxygenation of interstitial water (total anoxic condition in May 97, 3 to 5 ml/l of dissolved oxygen in August and October 97). During the wheat fermentation, we could therefore observe two bacterial communities, one producing, the other neutralizing the hydrogen sulphide. This cycle strongly limited the diffusion of H_2S in the water column and after this period, the divers noticed fish coming close to the residual wheat.

5.0 Conclusion

The wheat fermentation in the marine environment rapidly favoured the development of sulphate-reducing anaerobic bacteria, which is remained high for one year after the shipwreck of the "Fenes". A high production of hydrogen sulphide was observed, resulting from the reduction of sulphate of the seawater. The levels of hydrogen sulphide measured in the surrounding air were so important that they could have represented a safety hazard for people working on the barge where the wheat was being recuperated.

For, at least, the first six months after the shipwreck, the diffusion of hydrogen sulphide into the water column might have induced an ecotoxicological impact on the marine species. As the residual wheat mass was progressively

oxygenated, a sulphur-oxidizing bacteria developed, without decreasing the former activity of sulphate-reducing bacteria. As a direct result, a very significant neutralisation of hydrogen sulphide was observed inside the wheat mass. This process was reported 11 months after the spillage. From an operational point of view, these results show that the response of the vigorous mixing of the wheat mass can accelerate the oxygenation of the in-situ deposit and the development of a aerobic sulphur-(oxidizing) bacteria. This allows the neutralisation of hydrogen sulphide and thus limits the diffusion of this particular toxic compound in the environment.

6.0 Acknowledgements

This study was carried out by Cedre using its own budget from the Ministry of the Environment. It has had the active support of numerous colleagues who we wish to thank most sincerely. We would, in particular, like to thank J.M. Culioli and P. Peschet of the Cerbical and Lavezzi Islands, who took samples on the diving site of the Nature Reserve. Several teams from the IFREMER Centre, Brest, helped in the preparation and carrying out of the bacteriological and chemical aspects of the study. We would also like to thank Professor Caumette from Bordeaux University for the interest he has shown in this work and for the advice and comments given for the supervision of the study.

7.0 References

Aminot. A. Dosage de l'oxygène dissous. In: Manuel des Analyses Chimiques en Milieu Marin. A. Aminot & M. Chaussepied eds, Publ. CNEXO, Paris , 75-92, 1983.

Caumette P. Bacterial communities in coastal lagoons. An overview. Vie Milieu, vol. 42, n°2, 111-123, 1992

Durand P. Taxonomie des bactéries oxydant les composés soufrés réduits en milieu hydrothermal profond : cas du sud ouest Pacifique. Thèse d'Université. Université de Bretagne Occidentale, Brest, 1992.

Dyrssen D. Stagnant sulphidic basin waters. The Science of the Total Environment, vol. 58, 161-173, 1986

Environment Canada. Manual for Spills of Hazardous Materials. Environmental Protection Service. Environment Canada, Ottawa, (Ontario), 1981.

Fonselius S.M. Determination of hydrogen sulfide. In : Methods of Seawater Analysis. Grasshoff et al (ed), Verlag. Chemie , 72-80, 1983

Hardy J.A. The enumeration, isolation and characterization of sulphate reducing bacteria. Br. Corros. J., vol.18, 190-193, 1981

Luther G.W. & E. Tsamakis. Concentration and form of dissolved sulfide in the oxic water column of the ocean. Marine Chemistry, vol. 27, 165-177, 1989.

Marchand M. Accident du Fenes. Synthèse des informations (Septembre 1996 - Mai 1997). Rapport Cedre. Brest, 1997

Meinesz A., J. de Vaugelas, J.M. Cotta Lorda, D. Chiaverini, J.P.Panzani, J.M. Culioli & P. Pesechet Impact de l'échouage du M/V Fenes sur l'environnement de la Réserve naturelle des Iles Lavezzi. 3ème rapport. Laboratoire Environnement Marin Littoral. Université de Nice-Sophia Antipolis, 50 pp, 1997.

Millero F.Y., S. Hubinger, M. Fernandez & S. Garnett (1987). Oxidation of H_2S in seawater as a function of temperature, pH and ionic strength.. Environ. Sci and Technol., vol. 21, 439-443, 1987.

Tuttle J.M. & H.W. Jonnasch. Occurrence and type of Thiobacillus like bacteria in the sea. Limnol & Oceanogr. Vol. 17, 532-543,1972.

Widdel F. & F. Bak Gram-negative mesophilic sulfate reducing bacteria. In : The Prokariotes, vol. 4, ed. A. Balows et al., Springer Verlag, Berlin, 3352-3378; 1992.

Wirsen C.O.,. J. M. Tuttle & H.W. Jannasch. Activities of sulfur-oxidizing bacteria at the 21°N East Pacific Rise vent site. Mar. Biol., vol. 92 : 449-456, 1986.

Table 1. Bacterial densities in the wheat mass *(results expressed in cells per gram)*

Microflora studied	Culture media	Period	Bacterial Densities
Sulphate Reducing Bacteria (SRB) (*)	LAYE (artificial seawater / natural seawater)	December 96 May 97 August 97 October 97 June 98	3.5 E+07 1.2 E+07 / 4.1 E+07 4.7 E+06 / 3.4 E+07 1.0 E+07 / 5.0 E+07 (wheat dispersed)
Sulphur-oxidizing Bacteria (SOB) (**)	TB / S°	December 96 May 97 August 97 October 97 June 98	- 4.0 E+02 6.4 E+05 / 8.4 E+05 1.1 E+06 / 3.6 E+05 (wheat dispersed)

(*) samples taken at -20cm

(**) Samples taken from the surface of the wheat mass.

Table 2. Bacterial densities in seawater (May, August and October 97, June 98)
(results expressed in cells per ml in term of geometric mean)

Microflora studied	**Culture media**	**Samples**	**Geometric mean of Bacterial Densities (points A and B)**			
			May 97	August 97	October 97	June 98
Sulphate Reducing Bacteria (SRB)	LAYE (artificial seawater)	Interstitial water	2.5 E+06	2.5 E+03	2.5 E+07	
		Seawater/wheat interface	1.9 E+02	6.0 E+03	5.5 E+02	2.5 E+00
		Water column + 0.2 m	6.3 E+01	3.9 E+01	2.5 E+01	<1.0 E+00
		+ 1 m		1.1 E+01	2.5 E+01	<1.0 E+00
		+ 5 m		5.0 E+00	1.2 E+01	
		+ 10 m	1.5 E+00	<1.0 E+00	7.9 E+00	
Sulphur-oxidizing Bacteria (SOB)	TB / S°	Seawater/wheat interface	3.0 E+02	6.0 E+03	5.5 E+02	2.5 E+00
		Water column + 0.2 m		6.0 E+02	2.5 E+04	2.5 E+00
		+ 1 m		2.5 E+02	1.3 E+03	<1.0 E+00
		+ 5 m		1.3 E+01	1.3 E+03	
		+ 10 m		<1.0 E+00	1.0 E+03	

Table 4. Chemical analyses in water samples (May 1997) Results of measurements from two stations

	pH		Dissolved O_2 (mg/l)		H_2S (µM)	
Stations	**A**	**B**	**A**	**B**	**A**	**B**
Interstitial water (- .2m)	4.8	6.2	0	0	$18\ 10^3$	$57\ 10^3$
Wheat/water interface (0.0 m)	7.8	7.9	9.1	11.6	112.5	65.1
Water column (+ 0.2m)	8.0	8.1	13.1	15.2	55.8	35.1
Water column (+ 1.0m)	8.0	8.1	15.2	15.8	10.3	39.8

Table 5 Evolution of H_2S concentrations and other parameters in interstitial water

	May 97	**August 97**	**October 97**	**June 98**
H_2S (µM)	$18 - 57\ 10^3$	< 10 - 36	< 10	< 10
pH	4.8 - 6.2	7.5 - 8.1	6.6 - 7.8	8.1
O_2 (mg/l)	0.0	3.1 - 5.2	4.0	6.5
SRB in wheat (cells/g)	$4.1\ 10^7$	$3.4\ 10^7$	$5.0\ 10^7$	wheat dispersed
SOB in wheat (cells/s)	$4.0\ 10^2$	$6.4\ 10^5$	$1.1\ 10^6$	wheat dispersed

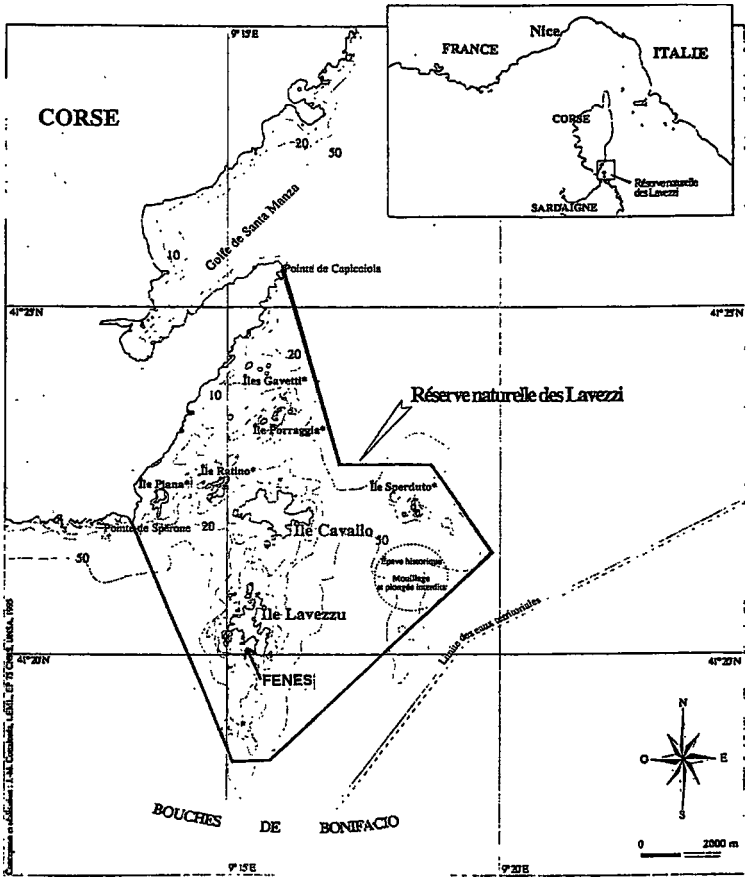


Figure 1 Location of the shipwreck of the *Fenes*

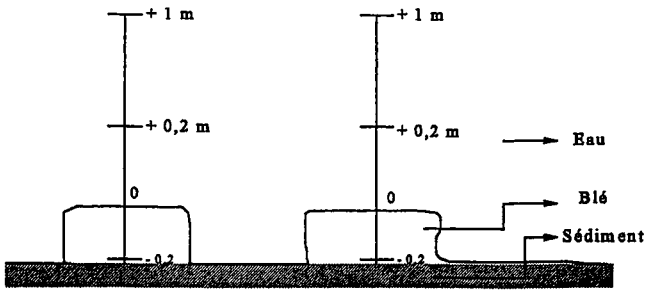


Figure 2 The Strategy of Sampling to Study Wheat Fermentation

Stability of Volatile Organic Compounds in Water Accommodated Fraction Samples

Ken Li and Merv Fingas
Emergencies Science Division, Environment Canada, Environmental Technology Centre, River Road, Ottawa, Ontario.
li.ken@etc.ec.gc.ca

Abstract

At Emergencies Science Division (ESD), water accommodated fraction (WAF) samples are analysed routinely on a Headspace (HS)-GC/MSD system for a target list of 22 volatile organic compounds (VOC) consisting alkanes and aromatics. Each sample is equilibrated for the same amount of time using the constant heating time (CHT) magazine on the HS sampler. Up to 21 samples can be stored in the CHT magazine so the last samples can wait more than 20-hr and be subjected to above room temperature since the CHT is above the heated oil bath. This study examines the short-term stability of WAF samples in various conditions during a 1-day period. VOC loss was measured for samples sitting in the CHT and compared to that at room temperature for a 10 and 1-ppm water solution. Long term stability was also evaluated to measure loss of VOC of stored samples, with and without any HS in a cool and under room temperature. For the 10-ppm solution, short and long term stability was well less than 10 %, probably insignificant in view of the variability of the HS measurement. For the 1-ppm solution, the worse VOC loss occurred in the long term (10 days period) in a half-filled vial. To test the validity of the finding, an actual sample, a well-aged ASMB WAF was used in the short/long term experiments. Loss was found to be more severe due to the low concentration of VOC. Nevertheless, our protocol of HS analysis stipulates a storage period of 3 days are validated from this study.

1. 0 Introduction

In an oil spill, soluble components of the oil can have an adverse impact to aquatic life. Measurement of volatile organic compounds (VOC) is therefore an important parameter to access their toxicity effect to the environment. A WAF sample is defined to include water-entrained dispersions of oil, in addition to the soluble species, although if the former is allowed to separate from the aqueous phase one is left with the water soluble fraction. On standing, after equilibrium has been established, a WAF sample is taken to be containing only the soluble VOC in the starting solution. In ESD, an appreciable amount of work has been spent to standardise the conditions for generating WAF. To test and validate the proposed protocol, WAF samples were generated from different kinds of oil or petroleum products under controlled loading, stirring rate and equilibrium times. The benefits are such that toxicity tests in different labs are directly comparable. It was found under gentle stirring conditions several days were required to generate stable VOC concentrations in WAF (Blenkinsopp *et al.*, 1997).

As part of the VOC analytical protocol, samples are usually analysed within 2-3 days. Since concentration is generally in the low ppm level, for simplicity and the advantage of automation, we have been using HS analysis to characterise VOC in

WAF samples. A Hewlett Packard HS sampler (HP 19395A) with a CHT magazine for 21 samples was connected to a HP 5890 Series II GC/ 5971 MSD via a heated transfer line.. Prior to analysis, the samples are transferred to 20-mL HS vial and capped. They are then placed in a constant heating time (CHT) magazine on top of the HS-GC/MSD system. Each vial is dropped in a cavity in the heating bath of the HS sampler and waits for the previous sample to complete the GC program run. Generally a nominal 30-min period is used for HS to equilibrate. Details of the analytical setup can be found in earlier work (Li *et al.*, 1996a; Blenkinsopp *et al.*, 1996b).

This study was carried out to investigate the stability of WAF samples under normal lab operating conditions. Artificial and natural water samples were left on the sampler to simulate automated HS analytical conditions. Samples were also left at room temperature and at above ambient temperature to assess volatility loss in the HS vials. Longer term stability was studied by completely filling 20-mL screw top vials and analysed at regular intervals to simulate actual samples waiting for HS analysis. As a control, identical samples were stored half- full to amplify effect of volatility loss by inclusion of HS in the sample container.

2. 0 Experimental

2.1 Samples Preparation

An internal standard of d8-toluene is added to all samples and standards alike. Samples are loaded onto the constant heating time (CHT) magazine. Each sample is equilibrated at 85 °C for a nominal time of 40-min in the sample carousel heated by a silicone oil bath.

2. 2 Standards

A 20-components volatile organic mixture was created by weighing known amounts of solid/liquid neat compounds and dissolved in an alkane mixture (D3710 Quantitative Calibration Mixture, Catalogue No: 4-8879). Addition of 1 µl of this mixture to 10-mL of water gives a final concentration of 8 ppm (nominal) including BTEX and alkanes from C-5 to C-15. The stock solution was diluted 10 and 100 times to prepare WAF of lower concentrations.

Instrumentation Parameters
Hewlett-Packard (HP) 19395A Headspace Analyser

Equilibration time:	40 min (nominal)
Bath temperature:	85° C
Sample loop:	1-mL
Valve/loop temperature:	90 ° C
Valve timing:	pressurise 10 sec
	vent/fill loop 5 sec
	inject 10 sec
Carrier gas	
(at sample transfer line):	Helium 50 mL/min
Aux pressure:	1.5 bar

HP 5890 (Series 2) GC	
Conditions	
Inlet temperature:	225 ° C
Inlet mode:	split operation, split ratio 1:5
Split vent flow:	40 mL/min
Oven temperature:	40 ° C hold 5 min, rate 10 ° C/min to final temperature 250 ° C
Column:	30 meter SPB-1, 0.53 mm id, 1.5-µm film
Column flow:	7 mL/min nominal
Linear velocity:	40 cm/sec at 100 ° C
HP 5971 MSD	
Interface:	Open-split, restrictor flow 0.7 mL/min nominal
Operating mode:	Selective Ion Monitoring
Interface temperature:	280 ° C
Detector temperature:	160 ° C nominal
Tune:	Autotune
Electron multiplier:	2000 V nominal
Data Station:	HP ChemStation (DOS-series)

Detection Limit and Precision

Aliquots of the neat calibration standard mixture (A and B combined) are spiked to a series of water samples to cover the range of concentration expected of the samples. A standard with nominal concentration of 8 ppm is used daily to check the response of the system. Defection limit is found to be 0.05 ppm in BTEX, 0.1 ppm for other compounds. Higher concentration can be analysed after suitable dilution.

Precision for a 0.5 ppm VOC in water was found to be better than 4 % RSD (relative standard deviation) for 5 replicate runs (Figure 1).

3. 0 Results and Discussions

3.1 Short-term Stability

The HS sampler has provisions for 24 samples, however, when the CHT module is used only 21 samples can be analysed because allowance is made to ensure each sample is equilibrated for the same amount of time equal to the GC cycle time, which includes the actual program time plus time for the oven to cool off to the initial starting 40 ° C. For a batch of 21 samples, a potential problem exists with the stability or volatility loss for the last samples in the batch, which would remain in the CHT for more than 20 hours. Since the CHT is above the heated oil bath in the sampler, samples on the CHT will be subjected to convection heating, generally about 5 ° C above room temperature. To study this effect, a series of 9 standard aqueous solutions (10 ppm) were interspersed with water blanks and analysed. The samples were analysed at intervals of 2 hr with the last sample at 18 hr. As a control, the same solutions in HS vials were left at room temperature and in a cooler at 4 ° C for about 12 hr. Tabulations of area counts for 21 peaks are summarised in Table 1 and graphically illustrated in Figure 2. It can be seen for a majority of VOC RSD values is

about 6 %, not significantly different from back to back replicate runs. The target list consists of alkanes up to C-15, aromatics covering BTEX to C-4 benzene and PAH (naphthalene). Although having very different distribution coefficients (equilibrium concentration ratio of HS and in initial aqueous phase), there is no appreciable difference during a 18-hr period. It should also be pointed out the RSD includes the instrumental variation due to drift or changes in response.

The scope of the short term standing on VOC loss was then broadened to include low concentration solution as well as actual WAF samples. The WAF sample was generated from Alberta Sweet Mixed Blend (ASMB) which had been stored in a 20-L carboy for over 1 year. It was not representative of ASMB WAF but presented a stable water with dissolved VOC. They were run against freshly made standards as controls, which consisted of solutions in HS vials at 10, 1 and 0.1 ppm and allowed to stand in room temperature as well as in the CHT overnight (ca. 12 hr). Results indicate no difference in VOC response of 10 and 1 ppm at either conditions of room temperature and in the CHT (Figure 3). However, the lowest standard of 0.1 ppm in the CHT showed higher results, which is likely due to analytical uncertainty near the stated detection limit of the HS instrument.

For ASMB WAF, concentration of BTEX was below 1 ppm, reflecting the well-aged state of this WAF (a freshly prepared WAF from ASMB has up to about 50 ppm BTEX) . Though not representative of a true ASMB WAF it is a test for volatility loss for very low level VOC samples. When compared to control WAF samples (the same WAF stored at 4 °C), loss of VOC was apparent: up to 47 % of p/m-Xylenes were lost when standing in the CHT. Standing at room temperature seems to have the same pattern of loss. Good repeatability of the control samples indicates the stability of the instrument at least over a one day period.

3. 2 Long-term Stability

The above study concentrates on the stability of WAF in a ready- to- analyse sub-sample, that is, in a HS vial which is half filled (10 mL water in 20-mL vial). For the long term VOC loss study, the samples are stored in appropriate size vials completely filled to the top and stored under cool, dark condition to simulate actual received samples as specified in the method protocol. Studies were carried out to simulate ideal and non-ideal storage conditions the samples were subjected to prior to analysis.

Using 22-mL vials with holed screw cap with Teflon/silicon septum (Supelco catalogue number 27021), a series of 10 and 1 ppm solutions were made up and stored without any HS. By way of comparison, a series of half-filled vials to investigate the effect of excessive HS. Each day a set of filled and half-filled sample was analysed, together with a freshly made standard which served as a base for comparison. This study was carried out over a 10-day without any interruption. Results are shown in Figure 4. For clarity only the sum of VOC was tabulated and plotted. Notice the absolute response was used for comparison. Instrumental stability up to a 10- day period was demonstrated by the control samples, with variation better than 5 % RSD from the beginning to the end of the study. Results indicate stored solution of both 1 ppm and 10 ppm seem to do be stable, with concentration towards the end dropped by less than 10 %, considered insignificant within experimental

error. By comparison, half full solutions of 1 ppm lost about 40 % whereas 10 ppm by 26 %. It must be pointed out these are extremely cases in which the ratio of HS/aqueous is 1:1. Nevertheless, this underlies the requirement WAF samples to be collected and stored without HS. In fact, an even longer term study which is still ongoing suggests properly stored HS samples retains the VOC well past 20 days when measured against reference standard solutions. In these very long term studies, the ratio of response of native to a deuterated toluene internal standard was used in order to account for instrumental variation over such a long period.

It was interesting to note instrument variation was found to be minimal over a 7-day period. This is demonstrated by plotting the absolute response of BTEX for 10 and 1 ppm standard; repeatability expressed as % RSD ranged from 4.9-7.8 % for the 10 ppm and 4.0-12 % for 1 ppm (Figure 5)

3.3 Long-term Storage for Actual WAF Samples

Two series of ASMB WAF solutions were stored in Supelco vials: one set filled without any HS and the other half full. They were analysed over a 4-day period. Results are shown in Figure 6. As expected from standard solutions of very low concentrations, there were more loss in comparison to higher concentrations. Toluene and p/m-Xylenes show more variability (RSD 23 and 15 %) due to the low concentration in the water. By comparison, half-filled vials saw VOC concentration dropped steadily started with the first day. The exaggerated rate of loss in contrast to the 1-ppm standard (Figure 4) can be attributed to the very low VOC concentration coupled to a greater analytical error. As specified in the protocol, the method of internal standard quantitation may offset this effect but the internal standard has to be added at a comparable concentration. It may also be advantageous by keeping the samples cool in the CHT. This can be in the form of a cooling jacket on the outside of the CHT.

4. 0 Conclusion

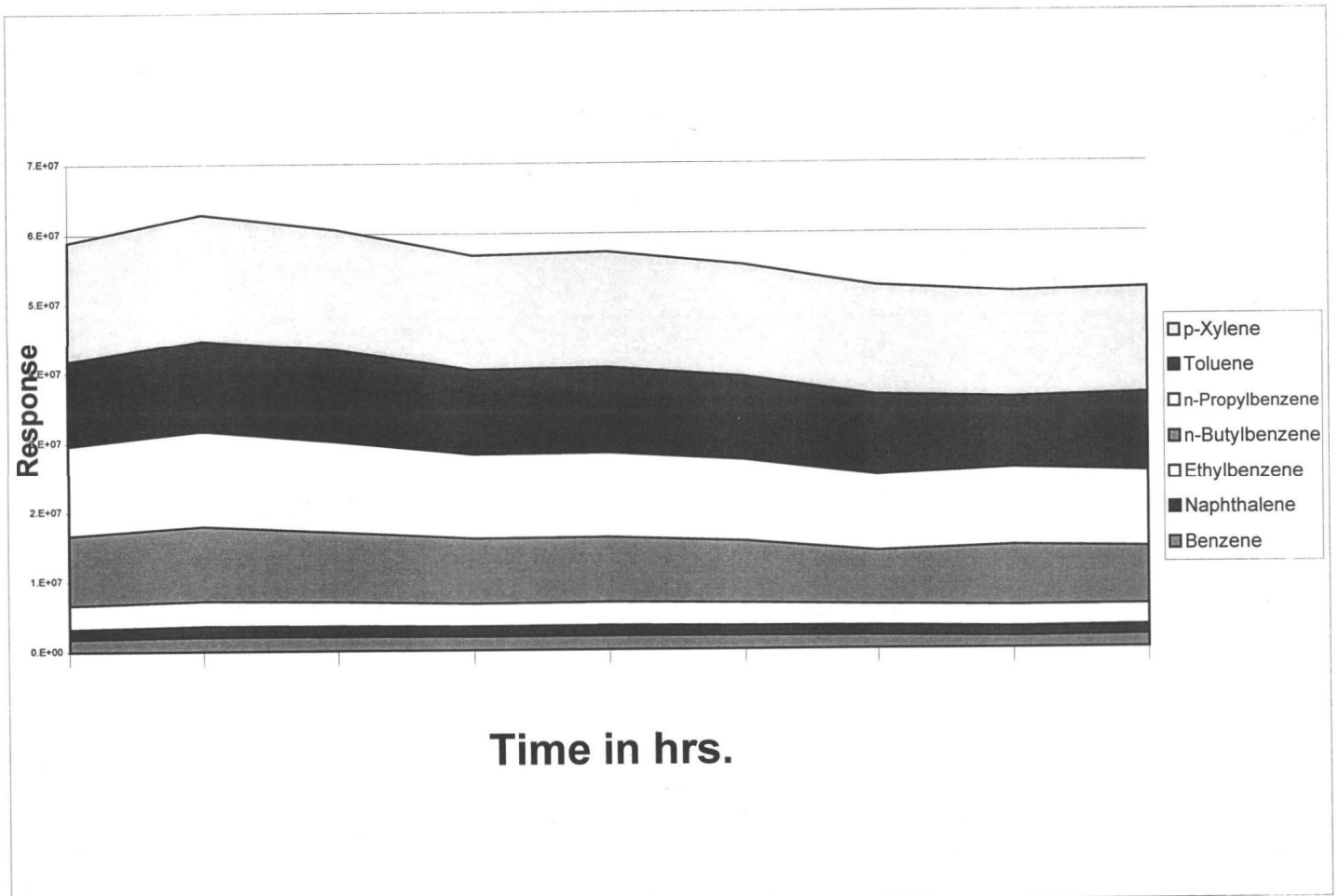
The VOC loss in short-and long- term storage of WAF samples were studied. Problems introduced by the HS instrument, namely storing the samples in the CHT in a 21-sample batch were found to be minimal. Properly stored WAF samples in cool, dark condition and in a full vial was stable for at least one month while WAF samples in less than full condition caused a significant decrease of 40 % in sub-ppm solutions. On the other hand, very low concentration solutions (represented by a depleted ASMB WAF , not typical of WAF samples) experienced some loss by sitting in CHT prior to analysis. VOC loss over a 4 day period was found to be up to 23 % for the least abundant component. Instrumental variation from 1 day up to a 10- day period was insignificant (5-10 % RSD), making comparison of data relatively easy. The protocol specifies WAF samples to be analyzed within 3 days and seems to be well within the stability of normal WAF samples.

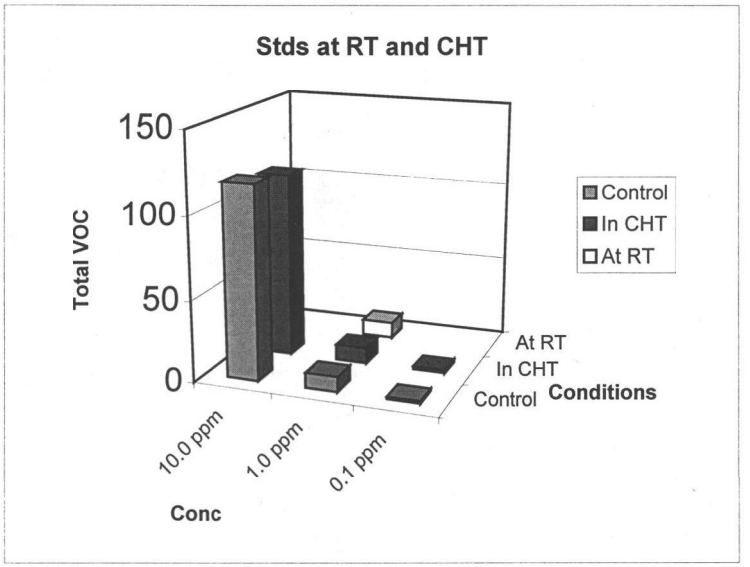
5. 0 References

Li, K., M. F. Fingas, P. Boileau, S. Blenkinsopp, J. R. J. Pare, J. Belanger and M. Llompart."Comparison of Purge and Trap and Headspace Determination of Dissolved Organics in the Water Soluble Fraction from Crude Oils, plus a quick look at MAP-HS", *Proceedings of the Nineteenth Arctic and Marine Oil Spill Program (AMOP) Technical Seminar*, Environment Canada, Ottawa. Vol. 1: 89-111,1996.

Blenkinsopp, S., G. Sergy, K. Doe, G. Wohlgeschaffen, K. Li and M. Fingas. "Toxicity of the Weathered Crude Oil Used at the Newfoundland Offshore Burn Experiment (NOBE) and the Resultant Burn Residue", *Spill Science and Technology Bulletin.* Vol. 3(4): 277-280,1996.

Blenkinsopp, S., G. Sergy, K. Doe, G. Wohlgeschaffen, K. Li and M. Fingas. "A Method for Exposing Fish to Water-accommodated Fractions of Oil", *Proceedings of the 1997 International Oil Spill Conference*. pp 941-42, 1997.


7.E+07
6.E+07
5.E+07
2.E+07
1.E+07
0.E+00
Response
p-Xylene
Toluene
n-Propylbenzene
n-Butylbenzene
Ethylbenzene
Naphthalene
Benzene
Time in hrs.



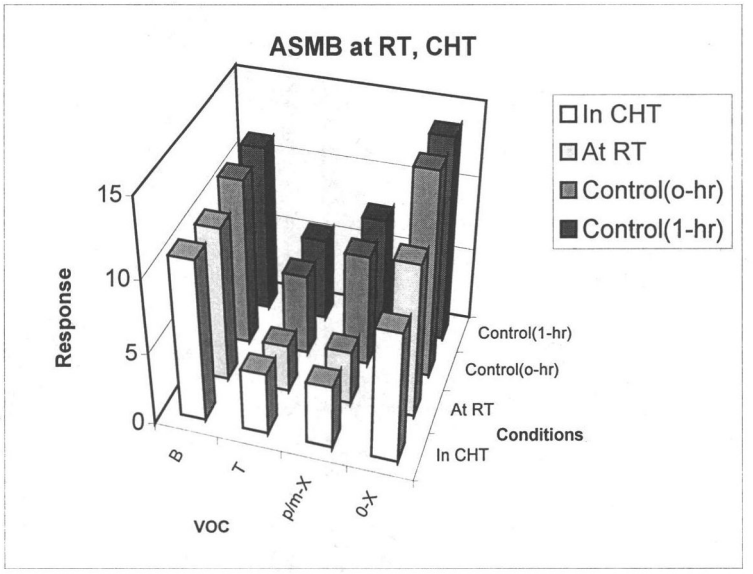
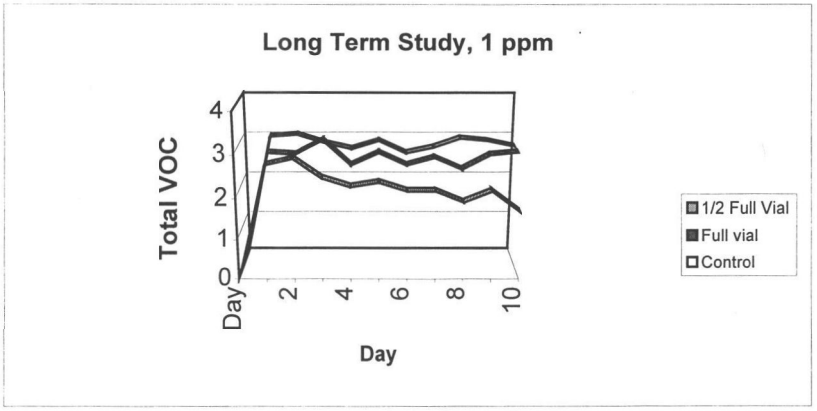


Figure 3: VOC Loss at Room Temperature and in the CHT



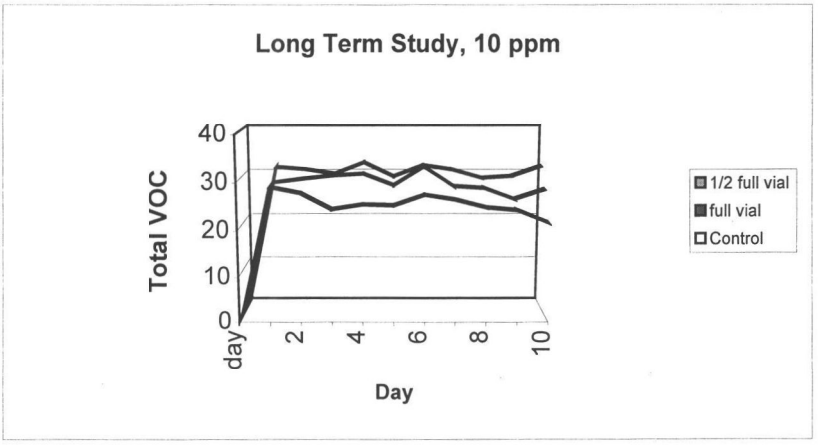
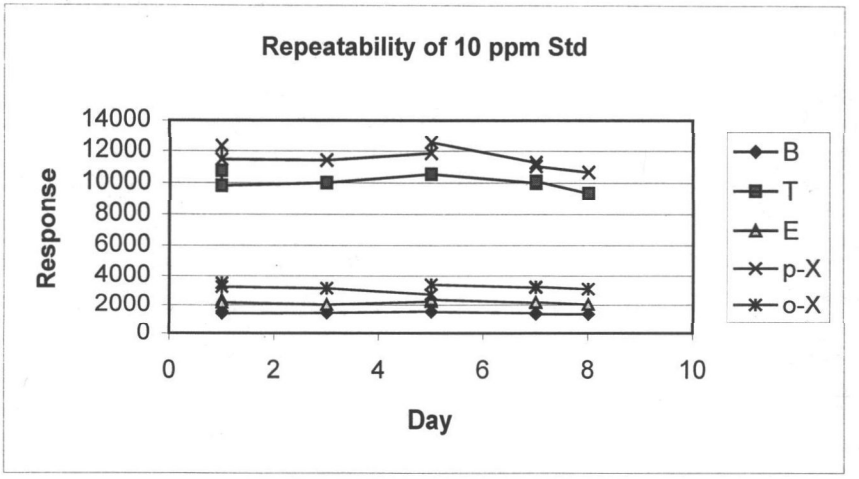


Figure 4: Long term Standard Solution Stability



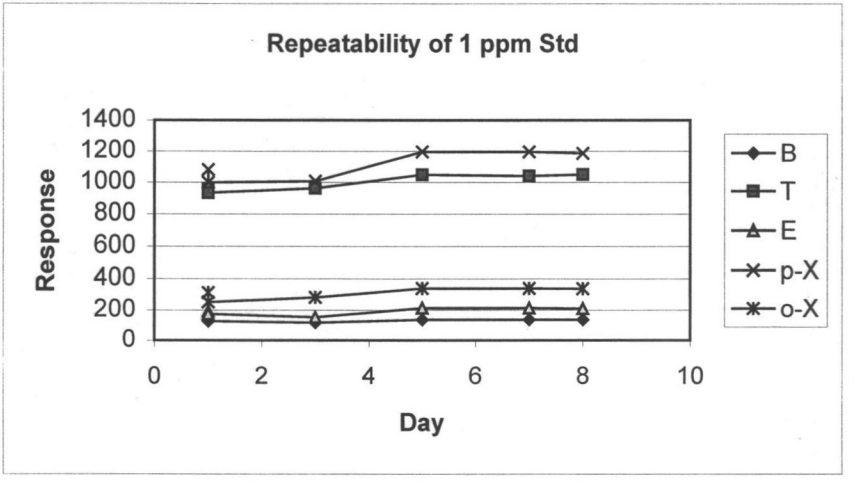
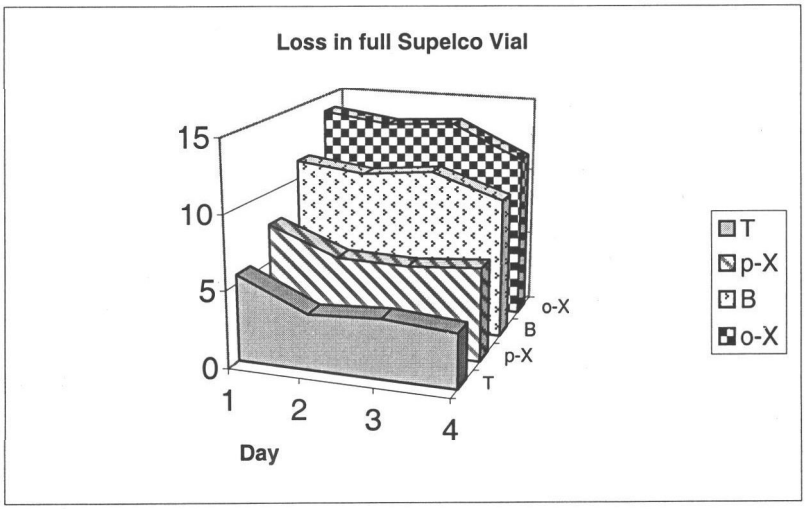


Figure 5: Repeatability of WAF Std over 7 Days



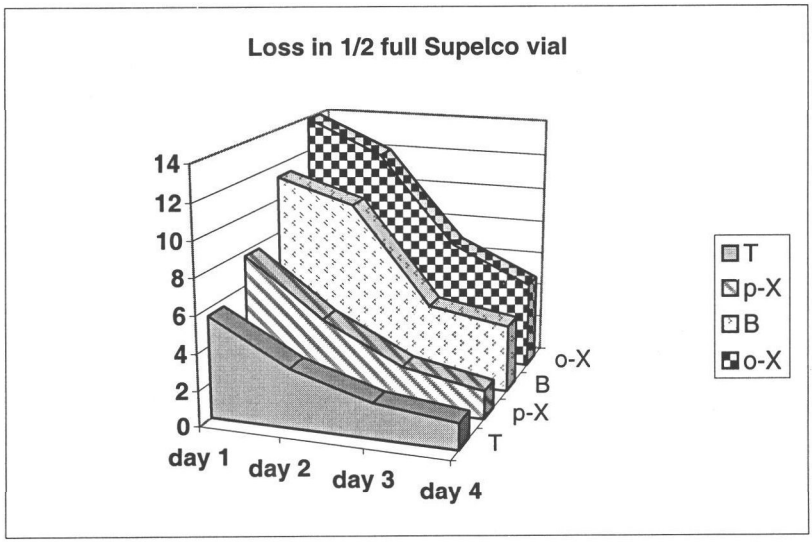


Figure 6: Long-term VOC Loss in ASMB WAF

Table 1: Stability During a 18-sample Batch HS Analysis the HS Sampler

		Time in Hrs										
		0	2	4	6	8	10	12	14	16	Mean	**RSD, %**
1	2-Methylbutane	4194479	5465591	5543061	5267294	5246034	5041682	4801125	5040555	4522175	5013555.1	**8.8**
2	Pentane	4471367	5919886	5985009	5685891	5758743	5565814	5313075	5443845	5023375	5463000.6	**8.8**
3	2-Methylpentane	6092036	7678143	7775169	7452532	7410522	7157015	6922968	7026383	6602238	7124111.8	**7.5**
4	Hexane	5129557	6500199	6518475	6235507	6252025	6069694	5781893	5741466	5619066	5983098	**7.6**
5	2,4-Dimethylpentane	6822900	8577820	8634662	8289676	8277672	8042413	7702982	7669271	7422224	7937735.6	**7.4**
6	Benzene	1786498	2052514	2027734	1950903	1981000	1926242	1832656	1646773	1800131	1889383.4	**7.0**
7	Cyclohexane	12568114	15743593	15823522	15145903	15162225	14515924	13977982	14175264	13716580	14536567	**7.2**
8	Heptane	393549	453115	432146	407880	430375	431348	361252	317731	371399	399866.11	**10.8**
9	Toluene	12101899	12981078	13169556	12125688	12274467	11963863	11442241	10114391	11209456	11931404	**7.8**
10	Octane	8587598	10424039	10566341	10128560	10161752	9716069	9267442	9584888	9224413	9740122.4	**6.6**
11	Ethylbenzene	3414886	3625832	3470166	3256117	3331339	3246931	3057249	3102661	3009831	3279445.8	**6.2**
12	p-Xylene	17172839	18137918	17301513	16473646	16660532	16143885	15833042	15317201	15259069	16477738	**5.8**
13	o-Xylene	4942950	5375489	5223850	4881388	4983801	4783089	4165329	4552303	4484405	4821400.4	**7.8**
14	n-Propylbenzene	13008374	13793784	13127265	12202833	12251401	11778695	11092221	11275192	11033670	12173715	**8.0**
15	Decane	8919821	10176459	10023002	9719320	9513543	9170859	8637924	9013147	8555257	9303259.1	**6.3**
16	n-Butylbenzene	10015325	10717881	9996543	9350982	9325027	8923074	7695932	8614836	8243147	9209194.1	**10.3**
17	Naphthalene	1419677	1534596	1511223	1463587	1484231	1410487	1391193	1353049	1350370	1435379.2	**4.6**
18	Dodecane	9912571	11309252	10147783	10493739	10262494	10178651	10043250	9874402	9164071	10154024	**5.6**
19	Tridecane	6619396	7484582	6569889	6858097	6750842	6545503	6615264	6689734	6004989	6682032.9	**5.7**
20	Tetradecane	6177266	7001651	5960274	6467331	6364004	6079100	6202001	6226480	5672901	6239000.9	**5.9**
21	Pentadecane	5484872	6230646	5402175	5682053	5574219	5497717	5575457	5646596	4964088	5561980.3	**5.9**
	Sum	149235974	171184068	165209358	159538927	159456248	154188055	147712478	148426168	143252855	155356015	**5.9**

Electronic Nose Instruments: Sniffing Out the Facts

M. Goldthorp
Goldthorp Consulting
Kemptville, ON, CA
goldthorp.michael@etc.ec.gc.ca

Abstract

As opposed to defining a scientific method, the term "electronic nose", or commonly e-nose, is used to describe instruments which detect a wide array of airborne compounds. The concept of a "universal" detector is most certainly attractive, but, considering the number of varied commercial and experimental approaches to this concept, a single superior method has not yet emerged. The methods used to achieve this vary quite widely, as do the applications driving the development of such an instrument. In support of this approach to on-site detection of chemical spills, much of the development to date involves portable technologies. Also, with the recent increase in attention to biological agents, this type of instrument may be destined to become a front-line tool in military and hazmat applications. This paper summarizes development of this technology, specifically with respect to chemical spill response.

1.0 Introduction

The human sense of smell uses an array of approximately 10,000 sensors in the epithelium (Ressler *et al.*, 1993). The concept of an instrument which mimics the way the human sense of smell works is nothing new. While humans define how things smell with a subjective pattern recognition, the idea of constructing an electronic version to objectively determine odours was forwarded by Persaud and Dodd in 1982. Instruments designed for this purpose have been in development for at least 10 years (Gardner *et al.*, 1990). Recently, however, this technology has become viable for a portable, multi-purpose instrument. Much of the recent advancement has been due to improved sensor and microprocessor design. Due to the relative newness of e-nose technologies and the wide variety of scientific approaches and potential applications, there are fewer defining factors and thus there is greater difficulty in comparing one to the other. Of specific interest is the ability to detect and/or reject unknowns. It has become obvious that a compound library, similar to that which can be purchased with a traditional GC/MS, is more difficult to package for this group of instruments which relies on "sensor training" for unique compound identification.

An electronic nose instrument employs a pattern recognition system to determine the identity of a specific compound (Gardner and Bartlett, 1998). The technology typically uses an array of partially-specific sensors. The degree to which these sensors, used in harmony, respond to a given compound produces an aggregate response which can be compared to a known pattern. Much as the human brain would have to learn the identity of a new scent to be able to recall it in a later instance, a computing device which stores and compares patterns is used in conjunction with the sensor array.

In an effort to help define and promote this emerging industry, a Europe-based organization, called NOSE (Network on Artificial Olfactory Sensing) was formed in 1999. Part of the efforts of this group is to provide a forum whereby industry members, along with those participating in research and development, can participate in the development of terms, identification of performance characteristics, and development of test procedures. When these objectives are met, there will ideally be greater ease in assessing suitability to various applications and in comparison between different instrument types. Short courses and workshops to disseminate theoretical and practical applications of electronic nose technology are planned throughout 2000.

As this technology has developed, some instruments are now available in a portable format. This allows these instruments, among many potential applications, to be employed at a chemical spill to produce rapid qualitative and, in some cases quantitative, data characterizing contamination in air and in headspace from water and soil samples. Since the diversity of compounds encountered in the chemical spill application is so great, those instruments which have the most flexibility will have an advantage in this application.

2.0 Instrumentation

2.1 Instrument Types

While some e-nose instruments use an array of sensors, others use separation techniques and a single sensor. While a greater array of sensors holds the promise of greater differentiation, the pattern recognition portion of the instrument must be more adept in order to maintain an advantage. Not only do the instrument styles vary, but so do the sensors themselves. No one technology has yet emerged as the future of e-nose instruments, but strengths and weaknesses of the various technologies are becoming better known. In order to broaden the application of their instrument, many manufacturers use a combination of sensors.

2.2 Sensors

One familiar technology is the quadrupole mass selective detector (MS). The variance with traditional GC/MS is that the headspace vapour is drawn directly into the MS detector with no separation. Understandably, the determination of unknowns is not performed, but rather a comparison against a limited library is performed, suited more towards quality control processing in a high sample thoughput operation.

Those sensors which operate at room temperature can be considered "cold" sensors. Sensors in this category include conducting polymers (CP) and quartz resonator sensors. Two popular types of quartz resonator sensors are the Quartz Crystal Microbalance (QCM) and the Surface Acoustic Wave (SAW) sensors. Due to minimal heating (stabilized temperatures are important for reproducible results), these sensors tend to have very low power requirements. They have shown to be easy to miniaturize, further enhancing their suitability to portable applications.

Some sensor arrays require high operating temperatures and could be grouped as "hot" sensors. These include the semi-conducting metal oxide sensors (MOS). These sensors may or may not be doped with other compounds to enhance sensitivities to certain compounds. Although these sensors have a greater power requirement, they have an advantage over cold-type sensors in their recovery time and water sensitivity.

Sensor types and information is summarized in Table 1. In almost all cases, the technologies are under development and applications are still being defined.

Table 1. Sensors used in e-nose instruments.

Sensor Type	Advantages	Restrictions	Target Gases
Conducting Organic Polymers and Oligomers(CP)	highly selective easy to miniaturize low power needs	high cost slower response short life water sensitivity	Polar Molecules, Organic Vapours
Metal Oxide (MOS)	good response/recovery good sensitivity low sensitivity to H_2O low cost	low selectivity high power needs	Alcohols, Ketones, Combustible Gases, Fixed Gases
Quartz Crystal (QCM)	fast recovery low power needs high sensitivity	some water sensitivity	large molecules
Acoustic Wave (SAW)	low power needs high sensitivity fast response	some water sensitivity	wide array
Mass Selective Detector (MS)	broad range of detection highly sensitive	high cost poor selectivity requires vacuum pump	all volatiles
Ion Mobility Spectrometer (IMS)	broad range of detection highly sensitive	high cost	wide array
Field-Effect Transistor (MOSFET)	fast response/recovery low sensitivity to H_2O low power needs	poor selectivity	Alcohols, Ketones, Comb. Gases
Electrochemical (EC)	highly selective	limited vapours	CO, H_2S, SO_2, NH_3, etc.
Discotic Liquid Crystal (DLC)	still in development	still in development	non-polar compounds
Optical Glass Fibre (Milanovitch, 1994)	high sensitivity wide dynamic range low power needs no EM interference	still in development	TCE, H_2S, O_2, BTEX

2.3 Commercial Availability

The instruments shown in Appendix A are known manufacturers of e-nose instruments. Along with those, there are numerous research groups in North America, Europe, and Japan with in-house systems, some of which have already spawned commercial enterprises. Also, some larger companies maintain research agreements with some of the smaller companies, even those with competing technologies. For example, Hewlett-Packard and Cyrano Sciences have collaborated to further develop the Cyrano product line.

It is apparent that certain technologies better lend themselves to portable applications. While the adaptability of an MS detector is attractive, the vacuum pump and power requirements reduce the practicality for on-site use.

3.0 Applications

With this technology still in development, new applications are continually emerging. The driving industry for the electronic nose is the food/beverage industry. The ability of the e-nose to determine contamination, spoilage, by-products, and/or off-gases, and to do so without subjective bias is very valuable to this industry. Other key applications include medical testing, military (chemical and biological agents), product quality control and perfumes. Of particular interest is the ability to identify volatile chemicals in environmental emergencies or site investigations.

One of the strengths of the e-nose technology is the potential for detecting a wide variety of compounds. Positive results have been shown for differentiating diesel fuels (Feldhoff *et al.,* 1999), volatile organic compounds (VOC) (Horrillo *et al.*, 1998), TPH-g (Williams *et al.*, 1996), dioxins/furans screening (Staples *et al.*, 1998), and chlorinated hydrocarbons (Williams *et al.*, 1997). The zNOSE instrument combines a GC column for separation with a SAW detector for a rapid (10 seconds) analysis of an array of volatile and semi-volatile compounds at ppb levels in air and sub-ppb levels in water samples (Staples, 2000).

Also of interest is the ability to detect nerve agents and other biological and chemical warfare agents of concern to anti-terrorist activities. The ability to perform these analyses rapidly is of utmost importance in this application, where undoubtably a GC/MS would be capable of identifying these compounds but would be too cumbersome and slow in response to be effective. Environics, for example, has a military version (M90) of their industrial instrument (MGD-1) for this specific application.

Two instruments have been used to monitor air quality in spacecraft. The e-nose used in the STS-95 (space shuttle Discovery) was developed in-house by NASA (Ryan *et al.*, 1998), while the HKR QMB6 was used on the MIR space station.

As a means of bringing samples to a bench-top e-nose, solid-phase microextraction (SPME) fibres have been used to collect volatile samples and then to desorb directly onto a sensor for rapid qualitative analysis (Azodanlou *et al.*, 1999).

4.0 Difficulties

One of the main difficulties with the e-nose instruments in general is with calibration of sensors, often referred to as "training the sensors". In order for identification to be possible, the instrument must have been introduced to the compound previously. Unlike chromatography, the compounds cannot be introduced

in a mixture, but as a single "visible" vapour, mixed only with an inert carrier. Because of the variability from sensor to sensor, a calibration must be done for each vapour for each sensor, eliminating the convenience of a ready-made library. Certainly, those instruments which use some chromatography (zNOSE) avoid some of these problems. Some e-nose sensors have been shown to drift over time, requiring a re-training process.

To varying degrees, many of the sensors used in e-nose instruments are sensitive to water vapour. This a problem especially with the CP sensors, which rely on material swelling for resistance variations to detect changes. As the technology develops, this will likely be solved by filters and/or compensators integrated into the instrument. Other hindrances to sensitivity for some sensors include alcohol, carbon dioxide, and acetic acid.

Of the sensors commonly used in e-nose instruments, the CP sensor has the shortest lifespan at 6-9 months. The quartz resonator sensors are expected to last somewhat longer at 9-12 months and the MOS sensor have a longevity of 18-36 months. While MS detectors are more durable than most, other considerations such as the need for a vacuum pump must be taken into account, especially when a field instrument is desired.

Certainly one of the difficulties with this industry is the fact that the technology development is still in progress and that perhaps the evolution to the "next generation" is just around the corner. While this development goes on, there is no doubt that the end result will yield a better technology, at the cost of potential purchasers who resist investing in a technology that still shows growing pains.

5.0 Conclusions

As a developing technology, the final chapter on the e-nose is yet to be written. Recently, the technology has been shown to have a great deal of promise in the area of chemical spill response, among others. Of the benefits of the e-nose, the speed is the most obvious. The ability to make rapid, on-site analyses, even if used only for screening, is a benefit to many applications. Considering the sensitivity which has been demonstrated by these sensors (ppb, sub-ppb), there is remarkably minimal sample preparation. Regardless of the sensor(s) used, this technology has shown that reliable and reproducible results can be produced in a rapid manner.

The problems associated with the e-nose technologies will likely be solved to at least some extent. Development of sensor technology will enable longer sensor life and reduced sensor drift and sensitivities to water and poisoning. Improved pattern recognition mechanisms will enable greater confidence levels and, in turn, better calibration systems. Also, as the market increases, cost will conceivably go down.

Considering the rapid pace of development of this technology and the proven performance to date, it is likely that e-nose instrumentation will have a place in the hazardous materials response field. The combination of fast response, wide adaptability, and on-site portability should contribute to securing a place in the chemical spill responder's inventory in the years to come.

6.0 Acknowledgements

The author would like to thank the Emergencies Science Division (EC) for access to resources used in research.

7.0 References

Azodanlou, R., C. Darbellay, J.L. Luisier, J.C. Villettaz, R. Amado, "A new concept for the measurement of total volatile compounds of food", *Zeitschrift fur Lebensmitteluntersuchung und -forchung A*, Vol. 208, No. 4, pp. 254-258, 1999.

Feldhoff, R., C.A. Saby, P. Bernadet, "Discrimination of diesel fuels with chemical sensors and mass spectrometry based electronic noses", *The Analyst*, Vol. 124, pp. 1167-1173, 1999.

Gardner, J.W., E.L. Hines, M. Wilkinson, "Application of artificial neural networks to an electronic olfactory system", *Measurement Science and Technology*, Volume 5, pp. 446-451, 1990.

Gardner, J., P. Bartlett, *Electronic Noses: Principles and Applications*, Oxford University Press, 1998.

Milanovich, F., S. Brown, B. Colston, and P. Daley "A fiber-optic system for remote long-term monitoring of soil and groundwater contamination", *Proceedings of the 10th Optical Fibre Sensors Conference*, SPIE 2360:98, 1994.

Horrillo, M.C., J. Getino, L. Ares, J.I. Robla, I. Sayago, F.J. Gutierrez, "Measurements of VOCs with a semiconductor electronic nose", *Journal of the Electrochemical Society*, Vol. 145, No. 7, pp. 2486-2488, 1998.

Ressler, K.J., S.L. Sullivan, K.B. Buck, *Cell*, Volume 73, p. 597, 1993.

Ryan, M.A., M.L. Homer, J.T. James, STS-95 press kit, 1998.

Staples, E.J., "Field Analysis using a Novel Electronic Nose as an Environmental Tool", *Proceedings of OnSite Conference*, Lake Las Vegas, CA, 2000.

Staples, E.J., D. McGuirre, G.W. Watson, S. Viswanathan, T. Matsuda, "Screening for Dioxin/Furan Using a Fast GC and SAW Detector", *Proceedings of Dioxin 98*, Stockholm, Sweden, 1998.

Williams, D., E.J. Staples, G. Watson, D. McGuire, G. Pappas, "Use of a Surface Acoustic Wave Detector Incorporated into a Field Portable Rapid Gas Chromatograph to Detect Chlorinated Hydrocarbons from DNAPL Contaminated Ground Water", *Proceedings of the Fifth Symposium on Field Screening Methods for Hazardous Wastes and Toxic Chemicals*, AWMA, Las Vegas, Nevada, 1997.

Williams, D., D. McGuire, E. Staples, "Total Petroleum Hydrocarbon Analysis (TPH-g) Using a SAW/GC: Real-Time Analytical Data for Environmental Clean-Up Operations", *Proceedings of the U.S. EPA Region IX Technology Symposium*, EPA, Palo Alto, CA, 1996.

Instrument brochures and technical bulletins of those instruments identified.

Appendix A: Commercially Available e-Nose Instruments

Manufacturer	Product	Sensor Array	Portability
Agilent (formerly Hewlett-Packard)	4440B	MS	No
Airsense	Airsense	MOS x 10	Yes
Alpha MOS	Fox	MOS,CP, and/or QCM x 6-24	No
Bloodhound Sensors	BH114	CP and DLC x 14	No
Cyrano Sciences	Cyranose 320	CP x 32	Yes
Element	FreshSense	MOS	No
Environics Industry Oy	MGD-1, M90	IMS	Yes
Environmental Sensor Technology (Estcal)	zNOSE	SAW x (6-15)	Yes
HKR Sensorsystems	QMB6	QCM, MS	No
Lennartz Electronic	MOSES II	QCM x 8, MOS x 8, EC, calorimetric	No
Marconi Applied Technologies (formerly Neotronics(EEV))	e-NOSE 5000	CP, MOS, QCM x 12	No
Microsensor Systems	VaporLab	SAW	Yes
Motech (see also Lennartz Electronic)	VOCcheck	QCM x (4-8)	Yes
Nordic Sensor Technologies	NST	MOS, MOSFET	No
Osmetech (formerly AromaScan)	Multisampler-SP	CP x 48	No
SMart Nose	SMart Nose	MS	No

Air Emissions Monitored at a Polyvinyl Chloride Plastic Fire

P. Lambert and M. Fingas
Emergencies Science Division, Environment Canada
Ottawa, Ontario, Canada, K1A 0H3
Lambert.Patrick@etc.ec.gc.ca

Abstract

On June 23rd 1999 an incident involving the burning of polyvinyl chloride (PVC) at a production facility in Quebec provided the opportunity for Environment Canada to collect data on the emissions from a PVC fire. Samples were collected of the fire's volatile emissions and the soot deposited downwind. It was noted from the analysis of the samples that PVC fire resulted in an small increase in a wide range of chemical compounds. In the smoke plume itself, results showed there was a general increase in the concentration of small volatile organic compounds such as chloromethane, propene, butane, 1,3-butadiene and naphthalene. This was not evident in the samples collected outside the smoke plume in the local community. The concentrations measured in the smoke plume were well below health criteria. Results from the analysis of surface wipe samples showed that the concentration of dioxin/furans in the soot, which had deposited downwind of the fire, to be slightly higher than samples collected in the nearby community. The concentrations were still well below Québec provincial criteria.

1.0 Objectives

The objectives of this paper is to provide information on the air emissions measured at a "spill-of-opportunity" involving a industrial sized fire of polyvinyl chloride plastic.

2.0 Introduction

Polyvinyl chloride $(C_2H_3Cl)_n$ is a synthetic plastic commonly used in many applications throughout our daily lives. A detailed summary related to the production, use and chemistry of PVC can be found in the paper titled *Environmental Impact of Polyvinyl Chloride and Vinyl Chloride (PCV/VC)* by Lawuyi and Fingas (1998). With such widespread use in our society there is a high probability that an incident such as a fire at a PVC production and storage facility may occur. Experience has shown that, at incidents involving PVC fires there is a lot of interest on the part of the general public as to the chemical composition of the smoke plume and the effect on the local health and environment.

The common combustion products of all organic material are carbon dioxide (CO_2), water (H_2O), carbon monoxide (CO) and soot (elemental C). Burning PVC results in some unique combustion products. In the paper by Lawuyi and Fingas (1998) the author divides the thermal degradation products into two categories. Those products that are generated at low temperatures from the melting PVC and those oxidized and decomposition products resulting from a high temperature fire. At low temperatures of 225 °C to 475 °C the PVC is not burning but will lose up to 60% of its weight through a degradation-type process. Near 450 °C numerous chemical

processes take place resulting in a change in the structure of the compounds to form polycylic aromatic hydrocarbons (PAHs) with the release hydrogen chloride (HCl) gas. At temperatures above 475 °C combustion is initiated. The type and quantity of compounds produced is influenced by the fire's temperature. Literature (Wheatley *et al.*, 1993) sites the formation of aromatic and PAH compounds, nitrogen-containing PAHs, polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), polychlorinated biphenyls (PCBs), aliphatic hydrocarbons and HCl.

A spills-of opportunity can be used to compare laboratory and field data on the composition of the smoke plume originating from this PVC fire. On the evening of June 23rd, 1999 an incident occurred involving the release of burn emissions from a plastics fire at the Superior Plastics Inc. facility near Beauharnois, Québec. From the initial reports, information indicated that 400 tons of plastic were on fire and the smoke plume may have impacted the residents of the local community of Beauharnois. Additional information can be found in the Pollution Incident Reports available from Environment Canada's (EC), National Environmental Emergencies Centre (NEEC, 1999). Two scientific staff from the Emergencies Science Division (ESD) were dispatched from the Environmental Technology Centre (ETC) in Ottawa. The ESD staff used the Division's specially equipped emergency response vehicle (Bissonnette *et al.*, 1994) and departed the ETC at approximately 2130 hours to provide onsite assistance to staff arriving from the EC Quebec Regional office in Montreal, Quebec. The ESD staff met the EC Quebec Regional staff at the "west" entrance to the Superior Plastics Inc. facility on Rue St. Laurent at approximately 2330 hours on June 23rd . Shortly thereafter, the site assessment commenced. The assessment activities for the day were completed at approximately 0200 hours on June 24/99 and ESD staff returned to ETC in Ottawa at approximately 0400 hours. The following day the samples collected were submitted to various ETC laboratories for analysis.

3.0 Procedures

The following paragraphs describe the steps taken to prepare the samples and the methods used to for analysis. No field screening analysis was undertaken by ESD staff during this incident as time was limited and it was felt that under the conditions at this site the portable instrumentation available in the ESD inventory would not provide the necessary scientific information.

In support of the site assessment around the Superior Plastic Inc. facility an air sampling program was carried out. A total of 8 samples were collected. These were collected outside the property of the Superior Plastics Inc. facility and in the community of Beauharnois. The grab samples were manually collected and were either air samples collected in a stainless steel summa canister or surface wipe samples. Appropriate sample tracking initiatives were carried out that included a chain of custody form and laboratory sample submission letters.

The sampling program was limited by time and consisted of volatile organic compounds (VOCs) and soot samples. For VOCs emitted from the fire, a stainless steel summa canister (Restek Corp., Bellefonte PA) with post field operations laboratory analysis was selected to measure the low VOC concentrations. This detailed analysis identifies and quantifies approximately 150 volatile organic

compounds. A stainless steel summa canister is a vacuum-type sample collector designed to collect trace levels of volatile organic compounds. A restricted orifice can be used to control the flow of air into the canister but, in this incident they were not used. The sample was collected in approximately 30 seconds. Each 6 L summa generally collects approximately 5 to 6 L of sample. This sample volume was deemed to be the maximum while maintaining a constant flow through the valve since, as the canister fills up, it becomes impossible for the weaker vacuum to keep the same flow rate through the orifice. All summa canister samples were analyzed at the ETC by the Analysis and Air Quality Division (AAQD) following field operations. AAQD has extensive experience and expert knowledge in this type of analysis. A summary of the analysis method and detection limits are provided in Appendix A. Two summa canister samples were collected at each sampling location for a total of four samples. All were submitted for analysis.

To determine the potential concentrations of dioxin/furan generated by the fire and carried in the smoke plume, surface wipe samples were collected. A serialized gauze pad and the solvent isopropyl alcohol were used. A 1 m x 1 m surface area was sampled and the samples were collected from glass surfaces. The pad was stored in a clean 40 mL, amber vial until analyzed. As was the case for the summa canisters, the surface wipe samples were analyzed at the ETC by AAQD following field operations. AAQD has extensive experience and expert knowledge in this type of analysis. Two surface wipe samples were collected at each sampling location for a total of four samples. One surface wipe sample from each location was submitted for analysis. The remaining two samples, one from each location, has been archived at ESD.

Samples S6241208 and S6241210 were summa canister samples collected several hundred metres from the west entrance of the Superior Plastics Inc. facility on Rue St. Laurent. This location was in the smoke plume. The plume could be seen at ground level and physical evidence collected on site from the human senors (touch, taste and odour) of the ESD staff supported the conclusion that the plume was near surface level at this location. The ESD vehicle was parked along the side of the road directly across from the entrance to the neighbouring facility (Kruger Inc.). The grab sample was manually collected while standing several meters in front of the vehicle and holding the summa canister at approximately 2 m height. To collect a sample the screw cap was removed from the summa canister and a particulate filter attached. After turning a valve, an air sample is automatically drawn into the vacuum canister. Sampling time is approximately 30 seconds. Two summa canisters samples were collected at this location. Sampling took place between 0008 and 0010 hours, June 24th.

The surface wipe samples S6241226 and S6241233 were collected at the "security guard" building at the entrance to the same facility. Surface wipe sample S6241226 was collected from the glass door of the building while S6241233 was taken from the glass partition beside but perpendicular to the door. The sterile gauze pad is wetted with isopropyl alcohol solvent prior to use and then a 1 m^2 area of the surface was sampled. Isopropyl alcohol solvent was selected because of its low human health hazards, minimal transportation restrictions, availability and its satisfactory ability to remove particulate matter from a surface. Sampling took place between 0026 and 0033 hours, June 24th.

Samples S6241249 and S6241251 were summa canister samples collected outside a restaurant in the town of Beauharnois. The restaurant was located at the intersection of Rue St. Laurent and Rue St. Louis. This location was outside the smoke plume as supported by observations of physical evidence while on site. It was noted that numerous other vehicles were situated about the area with engines operating and may have been emitting exhaust (volatile organic compounds) into the air. The grab samples were manually collected while standing several metres away and attempting to remain upwind of the exhaust of the other vehicles, and holding the summa canister at approximately 2 m height. Sampling time is approximately 30 seconds. Two summa canisters samples were collected at this location. Sampling took place between 0049 and 0051 hours, June 24th.

The surface wipe samples S6241256 and S6240101 were collected from the two glass windows of the restaurant facing Rue St. Louis. Surface wipe sample S6241256 was collected from the upper right-hand corner of the window on the right-hand side, from the perspective of standing and facing the building from Rue St. Louis. Surface wipe sample S6240101 was collected from the lower left-hand corner of the window on the left-hand side. Sampling took place between 0056 and 0101 hours, June 24th.

4.0 Results

Four summa canister samples and two surface wipe samples were analyzed by AAQD, a certified laboratory at ETC.

The results for the 144 volatile organic compounds assessed from the four summa canister samples are presented in Table 1. Selected human health criteria has been added from the references ACGIH (1998), EC (1984) and USDHHS (1994a).

The criteria are often expressed as TLV, TWA and STEL. Definitions are presented in the reference ACGIH (1998). A number of chemical compounds with interesting results have been highlighted in bold and/or italics font. The AAQD analyst highlighted the concentrations of chemical compounds whose results were elevated above that normally noted in the day to day analysis of samples by AAQD. AAQD's normal samples include ambient air samples from numerous sampling stations located throughout Canada. Results were placed in italics font when there was a noticeable difference in the results for a particular compound in samples from different sampling locations.

The dioxin/furan results report from the laboratory is presented in Table 2. As the sampling area was 1 m x 1 m the results are presented in units of picograms/m^2. The laboratory analysis presented picograms (pg) and total equivalent (TEQ) results for 28 congener and homologues. In terms of the quality of the analysis, the detection limits for each of the homologues ranged from 1 to 8 pg and the recovery of the surrogate was equal to or greater than 70%. Information on the analytical methods can be found in the EC reports *A Method for the Analysis of Polychlorinated Dibenzo-para-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Polychlorinated Biphenyls (PCBs) in Samples from the Incineration of PCB Waste* (Environment Canada, 1990) and *Internal Quality Assurance Requirements for the Analysis of Dioxins in Environmental Samples* (Environment Canada, 1992). The second report provides detailed information on the method including detection limits.

The term "not detected R" used in Table 2 is described as the value was rejected due to incorrect isotope ratio.

A detailed report on dioxin and dioxin-like compounds can be found in the references (De Rose *et al.*, 1997a, 1997b). The following explanation is summarized from that reference. TEQ is the Toxic Equivalents as 2,3,7,8-TCDD using international toxic equivalency factors and this is a common way to present dioxin/furan results. TEQ is defined as the product of the concentration, C_i, of an individual "dioxin-like compound" in a complex environmental mixture and the corresponding TCDD toxicity equivalency factor (TEF_i) for that compound. The total TEQs is the sum of the TEQs for each of the congeners in a given mixture. TEFs are based on congener-specific data and the assumption that the toxicity of dioxin and dioxin-like compounds is mediated by the Ah receptor and is additive. The TEF scheme compares the relative toxicity of individual dioxin-like compounds to that of TCDD, which is the most toxic halogenated aromatic hydrocarbon.

5.0 Discussion

It is necessary to begin by commenting on the incident itself. The impact of the emissions on the health and environment was minimized by the conditions at the site. The fire broke out at a modern PVC production facility. There appeared to be a emergency response plan in place and appropriate measures were taken by the groups on site to stabilize the situation in a timely manner. This, along with the fact that the wind direction carried the plume out over an uninhabited area reduced the impact of the fire on the local community.

A review of literature was undertaken. Polyvinyl chloride, PVC (CAS# 9002-86-2), resin is a high-molecular-weight synthetic polymer. It is prepared by the polymerization of vinyl chloride polymer. PVC can contain a significant amount of additives. From literature, unplasticized PVC contained 56 percent by weight of chlorine while flexible polymer contains much less. The burning of PVC plastic may result in the release of numerous compounds including, in order of decreasing amount, carbon dioxide (CO_2), water, particulate and soot, hydrochloric acid (HCl), carbon monoxide (CO) and possibly phosgene (CCl_2O), volatile organic compound and dioxins/furans. HCl is the primary toxicant in PVC smoke. Concentrations of HCl will decrease rapidly with distance from fire if in the presence of absorptive surfaces (Harris *et al.*, 1994). The odour threshold for HCl is as low as 1 to 10 ppm (Environment Canada, 1984) and thus it is easily detected. It is interesting to note that Canadian national air quality criteria is not readily available for the majority of contaminants of concern at this incident (Environment Canada, 1996).

For volatile organic compounds, the concerns over the health and safety of the local population are minimal. The plume was not directly over the community for a significant portion of the incident and the concentrations of the VOCs, even in the smoke plume itself were well below established criteria for these compounds.

Following a review of the VOCs results several points are discussed. These points are presented based on the limited data set available. The two or duplicate samples collected at each location show relatively similar numeric values. Also, the relationship between the sampling locations is as expected. That is to say, the VOC concentrations were higher in the samples collected downwind of the fire and in the

plume than the VOC concentrations for the samples collected in the nearby community.

More specifically, a close examination of the VOC results highlights the following. There was no increase in the concentration of ozone depleting chlorinated substances such as the Freon compounds and carbon tetrachloride. Benzene and toluene concentrations were significantly higher in the smoke plume. Ethylbenzene as well as o-, m- and p-xylenes were also higher in the plume except in the case of sample S6241251. This sample was collected near a restaurant in the local community. At the time the sample was collected numerous vehicles were positioned about and engines were operating. Ethylbenzene and xylenes are commonly found in vehicle exhaust. This sample may have been contaminated. From a broad comparison of the VOC results of the samples collected in the smoke plume to those collected outside the plume it can be seen that with respect to the non-chlorinated hydrocarbons it would appear that the fire caused the PVC plastics to decompose into small molecules such as propene, butane, pentane and some slightly larger alkane complexes like 1,3-butadiene and the aromatic compound naphthalene. In regard to the chlorinated compounds, it appears that the PVC decomposition compounds were small chlorinated compounds, predominantly chloromethane and limited increases in single substituted compounds such as vinyl chloride, chloroethane and chlorobenzene. One did not see an increase in the concentration of large chlorinated compounds or compounds containing multiple substituted chlorines. Thus, it would appear that the PVC fire resulted in an small increase in a wide range of VOCs however, their individual concentrations were well below health criteria and should pose a minimal health concern.

A discussion on the dioxin/furan levels in the soot is presented. The results for the dioxin/furan results are in the low picograms/m^2 range and are well below criteria. According to the reference Socha *et al.* (1997) the acceptable cleanup value for Québec and New York is 25 ng TEQ/m^2 . Surface wipe samples collected during this incident showed concentrations 1000 times less than the criteria. This would indicate there is minimal long term threat to health and the environment.

Two surface wipe samples were collected, one in the smoke plume and the other outside the plume. Although the sample collected in the smoke plume showed higher concentrations than the second sample, the amount of dioxin/furan was of the same order of magnitude (0 to 0.027 ng TEQ/m^2) . For comparison purposes, the concentration of dioxin in soot samples ranged from 0.1 to 2.9 ng TEQ/m^2 at the Plasimet fire in Hamilton, Ontario, 1997. These samples were collected using surface wipe techniques at distances of 1 to 5 km from the incident (Socha *et al,* 1997).

The surface wipe samples would consist predominantly of soot from the fire which had been deposited downwind. It is a reasonable assumption that the surrounding downwind vegetation and water would contain similar concentrations and that the concentration would decrease with distance from the fire due to dilution of the soot in the plume with the surrounding air. It would be statistically incorrect to convert the pg/m^2 into other units such as μg/g, μg/L of μg/m^3 in order to calculate the concentration of dioxin/furan in soil, water and/or air. The references USDHHS (1994 and 1998) state that the persistence of dioxin/furans in the environment can be for long periods of time. Photodegradation and biodegradation have minimal impact

on the environmental fate of these compounds. Photolysis, by sunlight, has an impact however, it is slower when the compounds are absorbed on particulate as in this case in which soot is generated by the fire.

It is difficult to present the chemical compounds found in PVC emissions as a mass balance value of the original PVC. It is difficult to use the stoichiometry of a chemical equation to accurately determine the amount of the resulting compounds. This is because the degradation products for PVC are temperature dependent and a large fire has a highly variable temperature range. On the topic of laboratory studies on the decomposition of PVC, Wheatley *et al.* (1993) stated the following:

- that soot production increased with increasing fire temperatures;
- the total number of compounds detected decreased with increasing temperatures;
- PAH production, predominantly naphthalene, was greatest at 950 °C;
- at temperatures of approximately 500 °C it was observed that many conjugated aromatic compounds such as an abundance of benzene, notable styrene and biphenyls, toluene, etc. were present; and,
- at temperatures of 440 °C organic condensables such as heptene, pentene and pyrene and dodecane were detected.

In terms of applying the findings to real incidents it would seem that PVC fires produce a wide and unpredictable number of chemical compounds which require numerous different sampling and analysis techniques to accurately quantify. Generally, when the PVC is exposed to low temperature fires such as at the beginning and end of the fire and when portions of the flames are being extinguished the HCl concentrations will be highest. At temperatures nearer to 950 °C the production of PAHs and VOCs are also high. Sustained high temperatures, above 950 °C would result in the highest production of the elemental compound such as CO_2, water, CO and soot with a corresponding decrease in VOCs.

6.0 Conclusion

The Results for an air monitoring program carried out at a spill of opportunity involving a PVC fire are presented for VOC and dioxin/furans concentrations. In the limited on-site air monitoring activities and post-incident laboratory analysis, four summa canister samples were collected and analyzed for volatile organic compounds and surface wipe samples were collected and two were analyzed for dioxin/furans. The concentration values of all parameters analyzed were below established criteria indicating minimal long-term health and environmental impact to the surrounding community.

7.0 References

American Conference of Governmental Industrial Hygienists (ACGIH), *1998 TLVs and BEIs*, ACGIH, Cincinnati, OH, 184 p.,1998.

Bissonnette, M., M. Goldthorp, M.F. Fingas, J.M.R. Bélanger and J.R.J. Paré, "Design and Development of Person-Portable Instrumentation System for Emergency Response and Field Studies, *Proceedings of the Eleventh Technical Seminar on Chemical Spills*, Environment Canada, Ottawa, ON, pp. 109- 127, 1994.

De Rose, C. T., D. Brown, R. Dhara, W. Garrett, H. Hansen, J. Holler, D. Jones, D. Jordan-Izaguirre, R. O'Connor, H. Pohl and C. Xintaras, "Dioxin and Dioxon-like Compounds in Soil, Part I: ATSDR Interim Policy Guidelines", *Toxicology and Industrial Health*, Vol. 13, No.6, pp. 759-768, 1997a.

De Rose, C. T., D. Brown, R. Dhara, W. Garrett, H. Hansen, J. Holler, D. Jones, D. Jordan-Izaguirre, R. O'Connor, H. Pohl and C. Xintaras, "Dioxin and Dioxon-like Compounds in Soil, Part II: Technical Support Document for ATSDR Interim Policy Guidelines", *Toxicology and Industrial Health*, Vol. 13, No.6, pp. 769-804, 1997b

Environment Canada, *Manual for Spills of Hazardous Materials*, Environment Canada, Ottawa, ON, 516 p., 1984.

Environment Canada, *A Method for the Analysis of Polychlorinated Dibenzo-para-Dioxins (PCDDs), Polychlorinated Dibenzofurans (PCDFs) and Polychlorinated Biphenyls (PCBs) in Samples from the Incineration of PCB Waste*, Environment Canada Reference method 1/RM/3 (revised), Ottawa, ON, 36 p., 1990.

Environment Canada, *Internal Quality Assurance Requirements for the Analysis of Dioxins in Environmental Samples,* Environment Canada Report EPS 1/RM/23, Ottawa, ON, 26 p., 1992.

Environment Canada, *National Air pollution Surveillance (NAPS) Network Annual Summary for 1993,* Environment Canada Report EPS 7/AP/26, Ottawa, ON, 91 p., 1996.

Harris, L. and D. Sarvadi, *Synthetic Polymers*, Patty's Industrial Hygiene and Toxicology, Volume II, Part E, Chapter 37, John Wiley and Sons, New York, NY, 3673 p., 1994.

Lawuyi, R. and Fingas, "Environmental Impact of Polyvinyl Chloride and Vinyl Chloride (PVC/VC)", *Proceedings of the Fifteenth Technical Seminar on Chemical Spills*, Environment Canada, Ottawa, Ontario, pp. 51-73, 1998.

National Environmental Emergencies Centre (NEEC), *Pollution Incident Report # Que199906241453-Lambert*, Environment Canada, 3 p., Ottawa, ON, 1999.

Socha, A., S. Abernethy, B. Birmingham, R. Bloxam, S. Fleming, D. McLaughlin, D. Spry, F. Dobroff, L. Cornaccio, *Plasimet Inc. Fire, Hamilton, Ontario July 9-12, 1997*, Report prepared for the Ontario Ministry of the Environment, Queen's Printer for Ontario, 72 p., 1997.

U.S. Department of Health and Human Services (USDHHS), *NIOSH Pocket Guide to Chemical Hazards*, NIOSH Publications, Cincinnati, OH, 398 p.,1994.

U.S. Department of Health and Human Services (USDHHS), *Toxicological Profile for Chlorinated Dibenzo-p-dioxins (Update)*, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, 678 p., 1998.

U.S. Department of Health and Human Services (USDHHS), *Toxicological Profile for Chlorodibenzofurans*, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, 225 p., 1994.

Wheatley, L. Y.A. Levendis and P. Vouros, "Exploratory Study on the Combustion and PAH Emissions of Selected Municipal Waste Plastics", *Environmental Science and Technology*, Vol. 27, pp 2885-2895, 1993.

Table 1 Volatile Organic Compounds Assessed in Summa Canister Sample

Compounds	Sample Number S6241208 µg/m 3	S6241210 µg/m 3	S6241249 µg/m 3	S6241251 µg/m 3	Selected Human Health Data
Propene	43.17	50.67	1.56	1.31	
Propane	12.58	15.07	10.09	3.90	
Freon 22 (Chlorodifluoromethane)	0.55	0.57	0.46	0.48	
Freon 12 (Dichlorodifluoromethane)	3.09	3.17	3.77	3.55	
Propyne	1.78	2.34	0.00	0.00	
Chloromethane (Methylchloride)	*31.07*	*35.98*	**1.17**	**1.17**	**TLV/TWA 103,000 µg/m³ STEL 207,000 µg/m³**
Isobutane	1.03	1.43	1.94	1.40	
Freon 114 (1,2-Dichlorotetrafluoroethane)	0.29	0.26	0.17	0.18	
Vinylchloride	**1.96**	**2.26**	**0.00**	**0.00**	**TLV/TWA 13,000 µg/m³**
1-Butene/2-Methylbutene	*14.57*	*20.17*	1.59	1.24	
1,3-butadiene	*16.21*	*19.39*	**0.18**	**0.12**	**TLV/TWA 4,400 µg/m³**
Butane	6.78	9.24	3.22	2.67	
t-2-Butene	3.54	3.04	0.68	0.44	
2,2-Dimethylpropane	0.00	0.00	0.00	0.00	
Bromomethane	0.24	0.18	0.00	0.00	
1-Butyne	0.00	0.00	0.00	0.00	
c-2-Butene	2.95	3.27	0.72	0.54	
Chloroethane	1.49	1.70	0.00	0.00	
2-Methylbutane	2.34	4.54	6.54	5.82	
Freon 11 (trichlorofluoromethane)	1.65	1.32	1.57	1.57	
1-Pentene	2.75	4.83	0.52	0.41	
2-Methyl-1-Butene	0.93	1.15	0.77	0.67	
Pentane	5.77	8.37	2.02	2.00	
Isoprene (2-Methyl-1,3-Butadiene)	***3.27***	***7.20***	**0.28**	**0.57**	
Ethylbromide	0.00	0.00	0.00	0.00	
t-2-Pentene	0.91	0.64	0.43	0.27	
1,1-Dichloroethene	0.11	0.12	0.00	0.00	
c-2-Pentene	0.97	1.10	0.75	0.53	
Dichloromethane	1.23	1.16	0.49	0.49	
2-Methyl-2-Butene	2.20	2.80	1.51	1.02	
Freon 113 (1,1,2-Trichlrotrifluoroethane)	0.63	0.63	0.53	0.53	
2,2-Dimethylbutane	0.17	0.24	0.44	0.41	
Cyclopentene	1.14	1.26	0.14	0.10	
t-1,2-Dichloroethene	0.03	0.03	0.00	0.00	
4-Methyl-1-Pentene	0.10	0.00	0.00	0.00	
3-Methyl-1-Pentene	0.14	0.23	0.00	0.06	
Cyclopentane	0.65	0.47	0.29	0.18	
1,1-Dichloroethane	0.00	0.00	0.00	0.00	
2,3-Dimethylbutane	0.19	0.40	0.51	0.50	
t-4-Methyl-2-Pentene	0.00	0.00	0.00	0.00	
2-Methylpentane	0.99	2.53	1.96	1.66	
c-4-Methyl-2-Pentene	0.14	0.00	0.16	0.00	
3-Methylpentane	0.59	1.29	1.07	0.96	
1-Hexene/2-Methyl-1-Pentene	***3.00***	***7.58***	0.36	0.30	
c-1,2-Dichloroethene	0.04	0.00	0.09	0.14	
Hexane	2.23	3.35	1.59	0.83	
Chloroform	0.35	0.41	0.33	0.32	
t-2-Hexene	0.86	0.42	0.16	0.08	
2-Ethyl-1-Butene	0.13	0.15	0.08	0.05	
t-3-Methyl-2-Pentene	0.20	0.23	0.11	0.07	
c-2-Hexene	0.61	0.56	0.10	0.13	
c-3-Methyl-2-Pentene	0.23	0.29	0.13	0.09	
2,2-Dimethylpentane	0.00	0.07	0.05	0.04	
Methylcyclopentane	0.90	1.39	0.84	0.67	
1,2-Dichloroethane	0.21	0.00	0.04	0.00	
2,4-Dimethylpentane	0.11	0.18	0.18	0.15	
2,2,3-Trimethylbutane	0.30	0.00	0.00	0.00	
1,1,1-Trichloroethane	0.33	0.34	0.30	0.30	
1-Methylcyclopentene	1.56	1.91	0.22	0.14	
Benzene	*97.50*	*118.08*	**2.00**	**1.99**	**TLV/TWA (skin) 1,600 µg/m³ STEL 8,000 µg/m³**
Carbon tetrachloride	0.80	0.84	0.51	0.51	
Cyclohexane	0.90	0.00	0.45	0.45	

Table 1 (continued)

2-Methylhexane	0.39	0.82	0.58	0.55	
2,3-Dimethylpentane	0.14	0.28	0.23	0.22	
Cyclohexene	0.50	0.66	0.04	0.03	
3-Methylhexane	0.43	0.97	0.65	0.59	
Dibromomethane	0.11	0.00	0.05	0.04	
1,2-Dichloropropane	0.00	0.00	0.00	0.00	
Bromodichloromethane	0.00	0.00	0.00	0.00	
1-Heptene	1.22	5.93	0.41	0.00	
Trichloroethene	0.13	0.11	0.10	0.11	
2,2,4-Trimethylpentane	0.24	0.37	0.49	0.43	
c-3-Heptene	0.00	0.45	0.00	0.04	
Heptane	1.93	2.81	0.52	0.49	
t-3-Heptene	0.88	0.90	0.00	0.00	
t-2-Heptene	0.91	0.62	0.00	0.00	
c-2-Heptene	0.80	0.93	0.00	0.00	
2,2-Dimethylhexane	0.00	0.00	0.00	0.01	
c-1,3-Dichloropropene	0.00	0.00	0.00	0.00	
Methylcyclohexane	0.38	0.56	0.33	0.32	
2,5-Dimethylhexane	0.08	0.16	0.16	0.17	
2,4-Dimethylhexane	0.12	0.19	0.14	0.13	
t-1,3-Dichloropropene	0.00	0.10	0.00	0.00	
1,1,2-Trichloroethane	0.00	0.00	0.00	0.00	
Bromotrichloromethane	0.00	0.00	0.00	0.00	
2,3,4-Trimethylpentane	0.18	0.21	0.20	0.18	
Toluene	*25.16*	*31.08*	**4.52**	**4.82**	**TLV/TWA (skin) 188,000 µg/m³**
2-Methylheptane	0.26	0.43	0.26	0.25	
4-Methylheptane	0.12	0.00	0.10	0.08	
1-Methylcyclohexene	1.15	1.01	0.05	0.03	
3-Methylheptane	0.85	1.19	0.36	0.35	
Dibromochloromethane	0.00	0.00	0.00	0.00	
c-1,3-Dimethylcyclohexane	0.00	0.00	0.09	0.09	
t-1,4-Dimethylcyclohexane	0.00	0.13	0.05	0.04	
2,2,5-Trimethylhexane	0.00	0.00	0.04	0.04	
1,2-Dibromoethane	0.00	0.00	0.00	0.00	
1-Octene	0.00	0.00	0.00	0.00	
Octane	1.71	2.32	0.25	0.25	
t-1,2-Dimethylcyclohexane	0.00	0.00	0.00	0.00	
t-2-Octene	1.81	1.99	0.06	0.00	
Tetrachloroethene	0.20	0.19	0.24	0.15	
c-1,4/t-1,3-Dimethylcyclohexane	0.00	0.00	0.06	0.06	
c-2-Octene	0.44	0.76	0.00	0.10	
c-1,2-Dimethylcyclohexane	0.00	0.00	0.03	0.04	
Chlorobenzene	***4.66***	***5.53***	**0.00**	**0.00**	**TLV/TWA 46,000 µg/m³**
Ethylbenzene	*10.18*	*11.76*	**0.81**	*12.89*	**TLV-TWA 434,000 µg/m³, STEL 543 µg/m³**
m-/p-Xylene	**4.93**	**9.45**	**2.56**	*13.82*	**TLV-TWA 434,000 µg/m³, STEL 651 µg/m³**
Bromoform	0.00	0.00	0.00	0.00	
1,4-Dichlorobutane	0.00	0.00	0.00	0.00	
Styrene	2.13	24.54	0.20	0.00	
1,1,2,2-Tetrachloroethane	0.00	0.00	0.00	0.00	
o-Xylene	**6.10**	**8.52**	**0.99**	*13.91*	**TLV-TWA 434,000 µg/m³, STEL 651 µg/m³**
1-Nonene	0.00	0.00	0.00	0.00	
Nonane	1.09	1.50	0.17	0.24	
isopropylbenzene	1.88	2.23	0.05	0.10	
3,6-Dimethyloctane	0.00	0.00	0.00	0.00	
n-Propylbenzene	1.38	1.74	0.17	0.16	
3-Ethyltoluene	1.23	2.11	0.52	0.47	
4-Ethyltoluene	0.87	1.32	0.26	0.23	
1,3,5-Trimethylbenzene	0.42	0.75	0.22	0.20	
2-Ethyltoluene	1.84	2.53	0.20	0.17	
1-Decene	0.00	0.00	0.00	0.00	
tert-Butylbenzene	0.00	0.00	0.00	0.00	
1,2,4-Trimethylbenzene	1.78	3.14	0.91	0.78	
Decane	0.96	1.28	0.28	0.30	
Benzyl chloride	1.04	1.19	0.00	0.00	

Table 1 (continued)

1,3-Dichlorobenzene	0.30	0.28	0.04	0.02	
1,4-Dichlorobenzene	0.25	0.25	0.33	0.30	TLV/TWA 60,000 µg/m ^{3}
isobutylbenzene	0.07	0.07	0.02	0.00	
sec-Butylbenzene	0.11	0.12	0.02	0.02	
1,2,3-Trimethylbenzene	0.46	0.75	0.21	0.19	
p-Cymene (1-Methyl-4-isopropylbenzene)	0.14	0.14	0.00	0.00	
1,2-Dichlorobenzene	**0.67**	**0.69**	**0.05**	**0.02**	**TLV/TWA 150,000 µg/m ^{3}**
Indan (2,3-Dihydroindene)	1.80	1.98	0.11	0.09	
1,3-Diethylbenzene	0.18	0.23	0.05	0.05	
1,4-Diethylbenzene	0.49	0.72	0.19	0.19	
n-Butylbenzene	0.75	0.90	0.06	0.00	
1,2-Diethylbenzene	0.27	0.30	0.02	0.04	
Undecane	0.98	1.33	0.24	0.28	
1,2,4-Trichlorobenzene	0.54	0.35	0.00	0.00	
Naphthalene	*22.09*	*27.58*	**0.63**	**0.50**	**TLV/TWA 52,000 µg/m ^{3}, STEL 79,000 µg/m^3**
Dodecane	0.99	1.19	0.14	0.19	
Hexachlorobutadiene	0.00	0.00	0.00	0.00	
Hexylbenzene	4.13	4.90	0.08	0.00	

Table 2 Dioxin/Furan Results of Surface Wipe Samples

	Dioxin/Furan Description	Sample S6241226 Smoke plume (pg/m ^{2})	Sample S6241226 Smoke plume Maximum TEQ	Sample S6241256 Local community (pg/m ^{2})	Sample S6241256 Local community Maximum TEQ
Congener	2378-TCDD	4	4.40	not detected	not detected
Congener	12378-P5CDD	5	2.40	not detected	not detected
Congener	123478-H6CDD	not detected	not detected R	4	0.38
Congener	123678-H6CDD	not detected	not detected R	5	0.46
Congener	123789-H6CDD	not detected	not detected R	10	0.96
Congener	1234678-H7CDD	11	0.11	36	0.36
Congener	OCDD	39	0.04	117	0.12
Congener	2378-TCDF	277	27.68	111	11.08
Congener	12378-P5CDF	26	1.31	11	0.55
Congener	23478-P5CDF	31	15.50	17	8.7
Congener	123478-H6CDF	24	2.44	25	2.52
Congener	123678-H6CDF	12	1.16	14	1.36
Congener	234678-H6CDF	9	0.92	11	1.06
Congener	123789-H6CDF	not detected	not detected R	not detected	not detected R
Congener	1234678-H7CDF	21	0.21	29	0.29
Congener	1234789-H7CDF	4	0.04	not detected	not detected R
Congener	OCDF	13	0.01	18	0.02
	Total TEQ		56.22		27.86
Homologue	Total TCDD	276		5	
Homologue	Total P5CDD	67		11	
Homologue	Total H6CDD	8		40	
Homologue	Total H7CDD	23		68	
Homologue	OCDD	39		117	
Homologue	**Total PCDD**	414		241	
Homologue	Total TCDF	1408		336	
Homologue	Total P5CDF	490		228	
Homologue	Total H6CDF	122		169	
Homologue	Total H7CDF	41		55	
Homologue	OCDF	13		18	
Homologue	Total PCDF	2074		805	

Appendix A A summary of VOC Analysis

The summa canister analysis was performed using a cryogenic preconcentration technique with a high resolution gas chromatograph and quadrupole mass-selective detector (GC-MSD) as described in EPA Methods TO-14 and TO-15. An Entech Model 7000 preconcentrator with auto-sampler (Entech Instruments, Inc., Simi Valley, CA) was used for sample preconcentration. The instruments used for species identification and quantification were a Hewlett-Packard 5890 series II chromatograph with a Hewlett-Packard 5970 MSD. Volatile Organic Compounds (VOC) were separated on a 60 m, 0.32 mm I.D. fused silica capillary column with a 1.0 μm film thickness of J&W (J&W Scientific Inc., Folsom, CA) DB-1 bonded liquid phase.

All samples were diluted with clean, humidified air in order to provide sufficient positive canister pressure for proper operation of AAQD analytical systems. Air from each canister was drawn through the preconcentrator's multi-stage trapping system and sample volumes were measured with a mass flow controller. A gaseous mixture of internal standard was added in combination with 500 mL of the sample into a glass bead trap maintained at -170C. A three-stage concentration technique called Microscale Purge and Trap was used to separate water from the organic sample components. The sample with the internal standard was concentrated to approximately 0.5 mL in the cryogenic glass bead trap. The trap was then heated to 25C while slowly flushing with 50 mL of helium to transfer the organics to a secondary Tenax trap maintained at -50C. This process results in the transfer all of the VOCs with less than 1μL of water. Then, while heating to 180C, the VOCs were back-flushed to be further focussed on an open-tubular focussing trap at -160C. This cryofocussing trap was then ballistically heated to 100C, resulting in rapid injection of VOCs onto the analytical column.

Temperature programming of the GC column was used to obtain optimum results. Column temperature was held initially at -60C for 3 minutes, then raised to 250C at a rate of 8 degrees per minute. The GC-MSD was operated in the selected ion monitoring mode (SIM). Identification of target analytes by SIM analysis is based on a combination of chromatographic retention time and relative abundance of selected monitored ions. An instrument calibration standard was prepared using stock gas standards prepared in the laboratory of the AAQD from three multi-component liquid mixtures and Scott certified gas mixture cylinders (Scott Environmental Technology Inc., Plumsteadville, PA). Quantification was based on daily 3-point linear regression calibration curves obtained from analysis of this external standard mixture.

Table 3 Detection Limits for VOC Analysis

All results in µg / m3

		Detection Limit (µg/m 3)
		A
2	Propene	0.06
3	Propane	0.05
4	Freon 22 (Chlorodifluoromethane)	0.07
5	Freon 12 (Dichlorodifluoromethane)	0.07
6	Propyne	0.02
7	Chloromethane	0.06
8	Isobutane (2-Methylpropane)	0.06
9	Freon 114 (1,2-Dichlorotetrafluoroethane)	0.10
10	Vinylchloride (Chloroethene)	0.03
11	1-Butene/2-Methylpropene	0.13
12	1,3-Butadiene	0.04
13	Butane	0.12
14	t-2-Butene	0.03
15	2,2-Dimethylpropane	0.04
16	Bromomethane	0.08
17	1-Butyne	0.03
18	c-2-Butene	0.04
19	Chloroethane	0.04
20	2-Methylbutane	0.03
21	Freon 11 (Trichlorofluoromethane)	0.02
22	1-Pentene	0.05
23	2-Methyl-1-Butene	0.02
24	Pentane	0.05
25	Isoprene (2-Methyl-1,3-Butadiene)	0.02
26	Ethylbromide	0.03
27	t-2-Pentene	0.04
28	1,1-Dichloroethene	0.06
29	c-2-Pentene	0.05
30	Dichloromethane	0.05
31	2-Methyl-2-Butene	0.03
32	Freon 113 (1,1,2-Trichlorotrifluoroetha	0.04
33	2,2-Dimethylbutane	0.07
34	Cyclopentene	0.02
35	t-1,2-Dichloroethene	0.04
37	4-Methyl-1-Pentene	0.05
38	3-Methyl-1-Pentene	0.04
39	1,1-Dichloroethane	0.03
40	Cyclopentane	0.03
41	2,3-Dimethylbutane	0.02
42	t-4-Methyl-2-Pentene	0.01
43	2-Methylpentane	0.06
44	c-4-Methyl-2-Pentene	0.03
45	3-Methylpentane	0.04
46	1-Hexene/2-Methyl-1-Pentene	0.09
47	c-1,2-Dichloroethene	0.04
48	Hexane	0.06
49	Chloroform	0.04
50	t-2-Hexene	0.03
51	2-Ethyl-1-Butene	
52	t-3-Methyl-2-Pentene	0.05
53	c-2-Hexene	0.03
54	c-3-Methyl-2-Pentene	0.04

Table 3 Detection Limits for VOC Analysis

55	2,2-Dimethylpentane	0.04
56	1,2-Dichloroethane	0.04
57	Methylcyclopentane	0.03
58	2,4-Dimethylpentane	0.02
59	1,1,1-Trichloroethane	0.05
60	2,2,3-Trimethylbutane	0.01
61	1-Methylcyclopentene	0.05
62	Benzene	0.08
63	Carbontretrachloride	0.08
64	Cyclohexane	0.03
66	2-Methylhexane	0.02
67	2,3-Dimethylpentane	0.05
68	Cyclohexene	0.05
69	3-Methylhexane	0.03
70	Dibromomethane	0.12
71	1,2-Dichloropropane	0.07
72	Bromodichloromethane	0.08
73	Trichloroethene	0.09
74	1-Heptene	0.03
75	2,2,4-Trimethylpentane	0.03
76	t-3-Heptene	0.01
77	Heptane	0.10
78	c-3-Heptene	
79	t-2-Heptene	0.05
80	c-2-Heptene	0.07
81	c-1,3-Dichloropropene	0.01
82	2,2-Dimethylhexane	0.04
83	Methylcyclohexane	0.03
84	2,5-Dimethylhexane	0.02
85	2,4-Dimethylhexane	0.04
86	t-1,3-Dichloropropene	0.05
87	1,1,2-Trichloroethane	0.05
88	Bromotrichloromethane	0.14
89	2,3,4-Trimethylpentane	0.01
90	Toluene	0.09
91	2-Methylheptane	0.07
92	4-Methylheptane	0.02
93	1-Methylcyclohexene	0.06
94	3-Methylheptane	0.03
95	Dibromochloromethane	0.14
96	c-1,3-Dimethylcyclohexane	0.20
97	t-1,4-Dimethylcyclohexane	0.04
98	2,2,5-Trimethylhexane	0.01
99	1,2-Dibromoethane	0.10
100	1-Octene	0.03
101	Octane	0.05
102	t-2-Octene	0.07
104	t-1,2-Dimethylcyclohexane	0.02
105	Tetrachloroethene	0.07
106	c-1,4/t-1,3-Dimethylcyclohexane	0.01
107	c-2-Octene	0.04
108	c-1,2-Dimethylcyclohexane	0.03
110	Chlorobenzene	0.04
111	Ethylbenzene	0.02

Table 3 Detection Limits for VOC Analysis

112	m,p-Xylene	0.04
113	Bromoform	0.07
114	1,4-Dichlorobutane	0.04
115	Styrene	0.03
116	1,1,2,2-Tetrachloroethane	0.07
117	o-Xylene	0.02
118	1-Nonene	0.04
119	Nonane	0.02
121	iso-Propylbenzene	0.02
122	3,6-Dimethyloctane	0.02
123	n-Propylbenzene	0.02
124	3-Ethyltoluene	0.02
125	4-Ethyltoluene	0.05
126	1,3,5-Trimethylbenzene	0.02
127	2-Ethyltoluene	0.03
128	1-Decene	0.04
129	tert-Butylbenzene	0.02
130	1,2,4-Trimethylbenzene	0.03
131	Decane	0.02
132	Benzyl Chloride	0.07
133	1,3-Dichlorobenzene	0.03
134	1,4-Dichlorobenzene	0.02
135	iso-Butylbenzene	0.01
136	sec-Butylbenzene	0.02
137	1,2,3-Trimethylbenzene	0.02
138	p-Cymene (1-Methyl-4-iso-propylbenzene)	0.02
139	1,2-Dichlorobenzene	0.03
140	Indan (2,3-Dihydroindene)	0.01
141	1,3-Diethylbenzene	0.03
142	1,4-Diethylbenzene	0.03
143	n-Butylbenzene	0.01
144	1,2-Diethylbenzene	0.02
145	Undecane	0.02
146	1,2,4-Trichlorobenzene	0.04
147	Naphthalene	0.02
148	Dodecane	0.01
149	Hexachlorobutadiene	0.02
150	Hexylbenzene	0.02

Detection Limits calculated from standard deviations of peak areas for seven successive runs of dilute standard mixture, as per EPA Method TO-15.

Air Monitoring of Coal Tar Cleanup Using a Mobile Taga Ci/ms/ms

N.S. Karellas, Q.F. Chen, G.B. DeBrou and R.K. Milburn*
Environmental Monitoring & Reporting Branch, Air Monitoring Section
Ontario Ministry of the Environment
Toronto, Ontario, Canada
milburre@ene.gov.on.ca

Abstract

Real-time detection of air toxics is becoming increasingly important in air pollution monitoring. Detection of low levels of air toxics requires reliable sampling and calibration techniques, as well as sophisticated analytical instrumentation. Recently a new chemical ionization(CI) source was developed for ambient air monitoring of benzene, toluene, xylene (BTX) and polycyclic aromatic hydrocarbons (PAH) in real time. This ion source in conjunction with a triple quadrupole (Q1, Q2, Q3) mass spectrometer (TAGA IIe) has been proven highly useful for measuring selected air toxics. The ion chemistry under CI conditions involves charge transfer reactions yielding parent ions which are selected in Q1, dissociated in Q2 and, the resultant daughter ions are identified by Q3. Monitoring of parent/daughter ion pairs is used to measure concentrations of BTX and PAH. The response of the TAGA is characterized through multipoint calibration curves. Detection limits of 0.5 to 3 $\mu g/m^3$ for BTX and PAH were accomplished by optimization of various TAGA parameters. This unique method was applied in November 1999 to monitor emissions released during the cleanup of a coal tar site in Kingston, Ontario. Coal tar is a sticky, black liquid which contains toxic chemicals such as benzene and naphthalene. Odourous emissions from cleanup activities of a coal tar site involving excavation and removal of contaminated soil resulted in complaints and potential health concerns from local residents. The TAGA information was used by local officials for enhancing abatement activities or in some cases temporary halting the excavation when levels of air toxics were higher than allowable provincial guidelines.

1.0 Introduction

The ability to perform real-time, on-site chemical analysis is very important in the evaluation of emissions from sites containing hazardous chemical waste. Applications where fast response is critical include monitoring of chemical fires or chemical spills during emergency situations particularly at times when the public may be at risk due to exposure of high levels of toxic airborne contaminants. Information on the levels of toxic chemicals around an emergency site is requested usually immediately by medical officers of health, fire department personnel, police department, elected officials, for quick on-site assessment of the environment and, if necessary plan for evacuation of residents from the affected area. In such cases, the best approach is to bring a mobile air monitoring unit on-site for real time sampling and analysis. Collection of discrete air samples and analysis at a laboratory usually takes several days and such conventional methods are generally not useful for the minute-by-minute decisions that may have to be made at emergency site. The mobile TAGA (Trace Atmospheric Gas Analyzer) IIe has been used for on-site analysis of numerous contaminants from a variety of industrial sources in Ontario since 1998,

and during environmental emergencies such as the fire of a caulking and sealant plant in Toronto in April 2000. In this paper we describe the monitoring results including the Ministry's new mobile TAGA and the cleanup of remains of a historical coal gasification plant in Kingston, Ontario.

Coal tar contains mainly benzene, toluene, xylene (BTX), naphthalene and other polycyclic aromatic hydrocarbons (PAH). Naphthalene is a major constituent of coal tar containing up to 11% naphthalene (Budavari, 1989). A large area at a prime location in downtown Kingston, Ontario was contaminated by coal tar which had been buried in large underground tanks since the late 1950's. The Air Monitoring Section of Ontario's Ministry of Environment recently responded to a special request from the City of Kingston to monitor ambient air levels of pollutants released during cleanup of the coal tar site. This request stemmed from odour complaints and health concerns from local residents. The list of air toxics to be monitored included benzene, a known carcinogen, and naphthalene, an irritant, readily recognizable for its characteristic mothball odour.

2.0 The Mobile TAGA IIe

The TAGA IIe MS/MS is a real-time, direct-air sampling, analytical instrument which is mounted in a ten-meter "Orion" coach (SCIEX, 1999). It is a completely self-contained mobile air monitoring unit, capable of monitoring hundreds of different air contaminants "on the fly". The coach accommodates the TAGA IIe and other essential equipment: two computer stations for complete TAGA IIe automated control, data acquisition and data analysis, a fume hood, a refrigerator, various storage compartments and work benches. A telescopic 10-meter meteorological tower equipped with a combination anemometer/wind vane, is used for recording ambient air temperature, wind direction and wind speed. Meteorological data are recorded once every minute and displayed on real-time basis. Communication to other Ministry vehicles and home base offices is facilitated by two-way radios, cellular phone, digital phone and facsimile. Four roof-mounted air conditioners provide the necessary environmental control to the interior of the mobile unit. All power requirements of the mobile are supplied by an on-board 17.5 kilowatt diesel generator, interfaced with a four-cylinder water-cooled diesel engine, providing stable voltage and frequency. The mobile is equipped with an automated system to permit unattended generator and TAGA IIe start-up.

3.0 Experimental

3.1 TAGA IIe Mass Spectrometer

The main components of the TAGA IIe include an air inlet system, a chemical ionization source, a mass analyzer consisting of a series of mass filters and focusing elements, an ion detector, and a MAC-based computer system. The operation of the TAGA IIe is based on the principles of tandem MS/MS mass spectrometry. A triple quadrupole mass spectrometer is used to differentiate and quantitate thousands of different chemicals in gas phase (Figure 1). The analysis procedure involves multiple sequential steps: ambient air is sampled continuously at a flow rate of 90 liters/minute directly into the ion source. The high sampling rate, and the direct link to the heated ionization chamber, assures that sample adsorption or degradation is negligible.

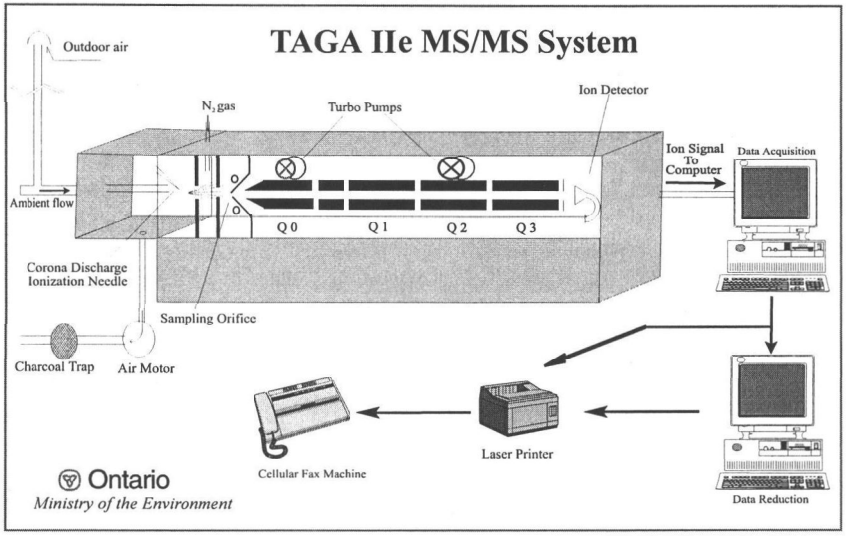


Figure 1: Schematic of the TAGA IIe tandem quadrupole mass spectrometer.

Earlier mass spectrometry methods for real-time detection of air pollutants used a well established atmospheric pressure chemical ionization (APCI) technique involving a corona discharge for ionization of chemicals. Chemical reagents such as water vapour are used for highlighting alcohols and ketones while ammonia highlights amines through proton transfer reactions and benzene focuses on some aromatics through charge transfer reactions. This method while excellent for polar compounds is not conclusive for monitoring benzene at low ppb levels. For several years, the Environmental Monitoring and Reporting Branch utilized a method involving cartridge sampling and analysis at a later time using GC/MS; this method is particularly useful for low levels (sub ppb) of volatile organic pollutants (VOCs). However, when VOC concentrations are higher than approximately 100 ppb, adsorbent cartridges become overloaded, breakthrough may occur and consequently ambient pollutant levels cannot be reliably quantified. With the assistance of SCIEX, the manufacture of the TAGA systems, a new Low Pressure Chemical Ionization (LPCI) source was developed and has been applied in several situations to measure aromatic air pollutants including BTX and naphthalene.

3.2 Low Pressure Chemical Ionization (LPCI)

Ionization of chemicals from coal tar is accomplished through a series of gas-kinetic, chemical ionization reactions, initiated in the LPCI source. The LPCI consists of a stainless steel rod to which a current is applied for glow discharge in a small volume of ambient air where positive and negative reagent ions are produced by donating or removing an electron. The LPCI source is nominally operated at 3 Torr and 100 microamps. The chemicals in the ambient air undergo charge transfer reactions with reagent ambient air ions (typically NO^+, N_2^+, and O_2^+) to yield parent

ions which are mass analyzed in the first quadruple (Q1). A Q1 only, or single MS spectrum obtained downwind of the coal tar cleanup site in Kingston, Ontario is shown in Figure 2. The major parent ions observed in Q1 were at 78, 92, 104, 106 116, 118, 120, 128, 134, 142 and 154 amu (atomic mass units). These are identified, operating the TAGA IIe in the MS/MS mode, as benzene, toluene, styrene, xylene isomers, indene, methyl styrene, C_3-benzene isomers, naphthalene, C_4-benzene isomers, methyl naphthalene and biphenyl. The parent ions are then subjected to collision activated dissociation (CAD) with an inert gas, nitrogen, and produce fragment ions better known as daughter ions in Q2. For example, the resultant daughter ions of 128 amu at 63, 78, and 102 amu are identified by Q3. Q1 and Q3 function as mass filters, where the Q2 operates in a non-resolving, radio frequency (RF) only, total ion mode.

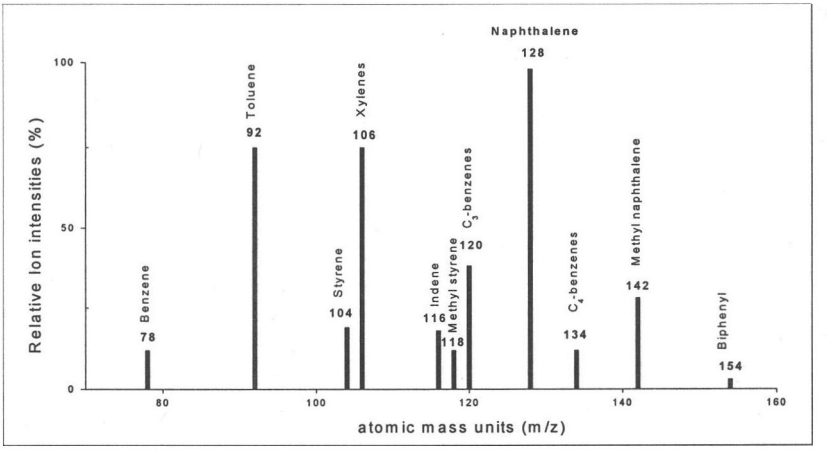


Figure 2: TAGA IIe single MS spectrum obtained downwind of the coal tar cleanup site.

3.3 Identification

A MS/MS library mass spectrum for naphthalene was created using 20 eV ion energy and nitrogen as collision gas for fragmentation of parent ions. The CAD fragmentation pattern of the "unknown" parent ion at 128 obtained downwind of the coal tar cleanup site, shown in Figure 3 (top left), is dominated by three daughter ions at 63, 78 and 102 amu. Figure 3 also shows daughter ion library spectra for m/z = 128 amu; one for naphthalene (bottom left) and one for chlorophenol (top right). The spectrum of the "unknown" is compared with the standard CAD library spectra; agreement between the "reverse" and "forward" library search results and their closeness to unity, indicate the degree of certainty for compound identification. In this case, the "best" search results match with naphthalene.

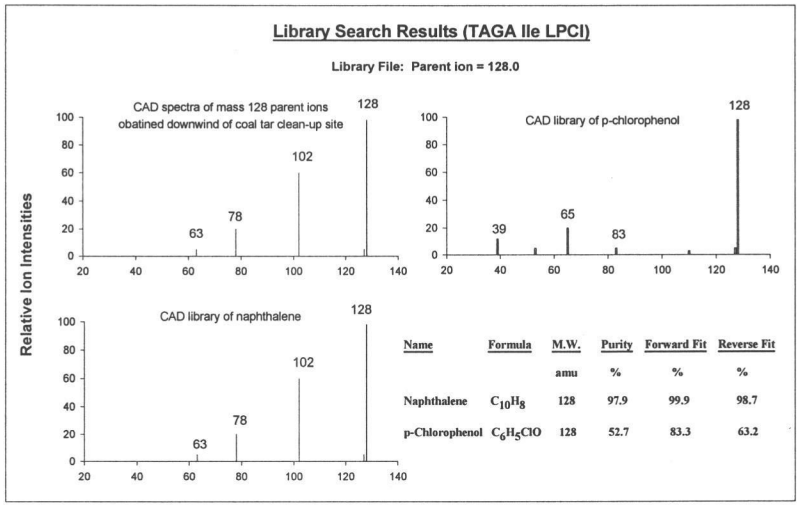


Figure 3: TAGA MS/MS library search of molecular ion at 128 amu.

3.4 Quantitation

Prior to quantitating levels of ambient air toxics, the response of the TAGA IIe is calibrated using known chemical standards. A calibration method developed by our group (Karellas *et al.*, 1991) involves injection of aqueous standards into the inlet air flow via a heated nebulizer. The nebulizer developed by the Air Monitoring Section consists of a capillary tube for liquid sample injections and two outer concentric stainless steel tubes for nebulizing and purging gases; this configuration ensures uniform sample atomisation thus providing for addition of controlled amounts of standards into TAGA IIe LPCI ion source. The standard solution is injected into the nebulizer with a 1 mL, 22s gauge Hamilton Gastight syringe mounted in a Harvard (model 22) syringe infusion pump. The flow rates of the liquid standard are controlled by the speed of the pump. For example, flow rates 0 to 20 μL/min allowed for naphthalene concentrations in the range 0 to 200 $\mu g/m^3$ to be generated in the LPCI source. Five-point calibrations of naphthalene were performed by simultaneously recording the responses of three parent/daughter ion pairs. An example of a calibration, in the concentration range 0 to 200 $\mu g/m^3$ is shown in Figure 4. Note that calibrations are performed in-situ that is, ambient air is used as the carrier gas. The slopes of the response curves are measures of the sensitivity of the LPCI/MS/MS system to naphthalene. A linear response was observed up to 400 $\mu g/m^3$. To avoid system contamination, the saturation points for response non-linearity was not determined. Another calibration method is achieved by introduction of a gas mixture of known concentration from a certified standard gas cylinder. For example, the linearity of the calibration curve was observed at least up to 2000 $\mu g/m^3$ for benzene.

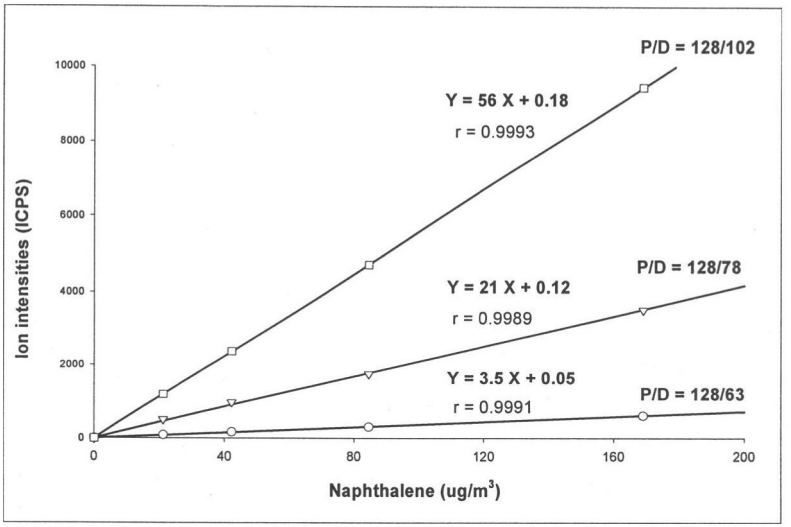


Figure 4: TAGA calibration plots of naphthalene.

3.5 Strategy of Mobile TAGA Air Monitoring

Upon arrival at the site to be investigated the TAGA crew acquires background data and performs calibrations of target chemicals (if they are known) upwind of the emission source. Following upwind measurements, "plume tracking" is conducted by driving the TAGA downwind of the source while monitoring for selected target compounds in real-time to get the highest levels of chemical emissions i.e., find the point of impingement. Downwind measurements include fingerprinting to identify as many chemicals as possible and concentration measurements of the most abundant chemicals or chemicals having high toxicity. Real time measurements are accomplished by multiple reaction monitoring (MRM) involving data acquisition of selected parent/daughter pairs, for example128/63, 128/78 and 128/102 are used to monitor ambient naphthalene levels. Depending on wind direction, monitoring is performed at several downwind locations usually for over a period of two weeks. During the survey period the Ministry's Air Quality and Weather Office provides updates of weather forecasts. The TAGA crew records monitoring locations, on-site activities and qualitative weather conditions. Information collected by the computer include minute-by-minute meteorological data, half-hour concentrations and instantaneous maximum levels of target compounds. At times when levels exceed provincial criteria, the TAGA crew immediately notify local on-site personnel such as environment and city officials. If there is some specific toxic chemicals detected without provincial criteria, the Ministry's Standards Development Branch provide additional information on toxicity and conversely the TAGA data is often used to generate guidelines or standards for those chemicals.

4.0 Results and Discussion

This method was field-tested in November of 1999 during a three-week air monitoring survey in the vicinity of a coal tar cleanup site. An area map of the coal tar contamination site in Kingston, Ontario is shown in Figure 5. A total of 168 half-hour concentrations were determined at several different locations upwind and downwind of the site. Figure 6 shows real time measurements of naphthalene recorded every 5 seconds for a period of 30 minutes at a fixed location downwind of the cleanup site. Rapid changes in naphthalene levels were mainly due to local air eddies or turbulence, as well as changes in wind directions. The downwind response profiles of the three parent /daughter ion pairs (128/63, 128/78 and 128/102) were similar indicating the presence of naphthalene. For simplicity the major parent/daughter ion pair 128/78 is shown in Figure 6. During this survey, calibration response factors and detection limits (DL) were determined twice daily at upwind locations for each of the BTX and PAH compounds. Detection limits are defined as 3 times the standard deviation of the background signal divided by the slope of the calibration curve. The variation in DL values from day to day was readily apparent; the DL's ranged from 0.5 to 3 $\mu g/m^3$ with a mean value of 2 $\mu g/m^3$ and a standard deviation of 0.3 $\mu g/m^3$.

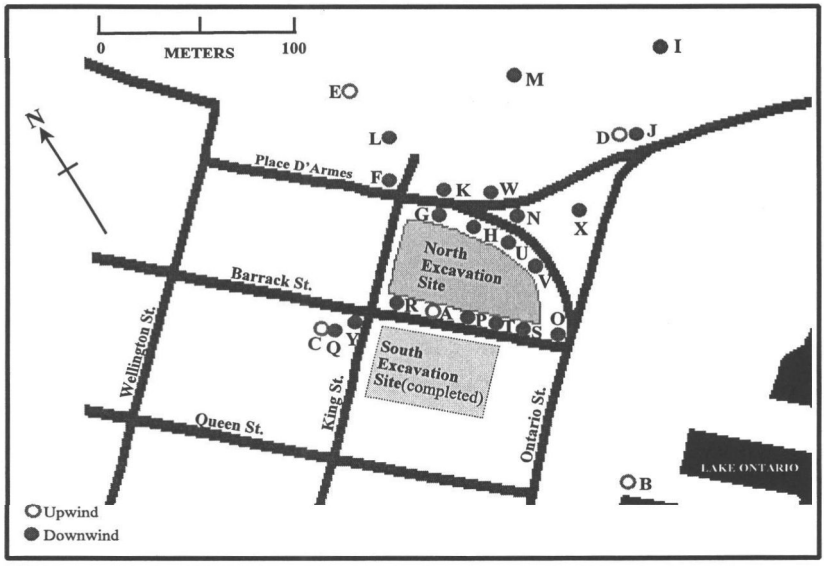


Figure 5: Coal tar cleanup site and the TAGA IIe monitoring locations, Kingston, November, 1999 (MOE, EMRB).

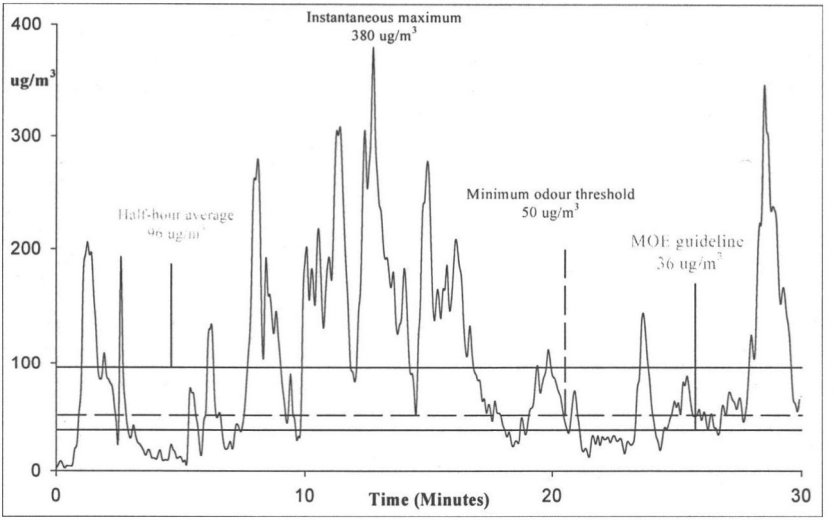


Figure 6: TAGA real time measurements downwind of the coal tar cleanup site, in Kingston, November, 1999 (MOE, EMRB).

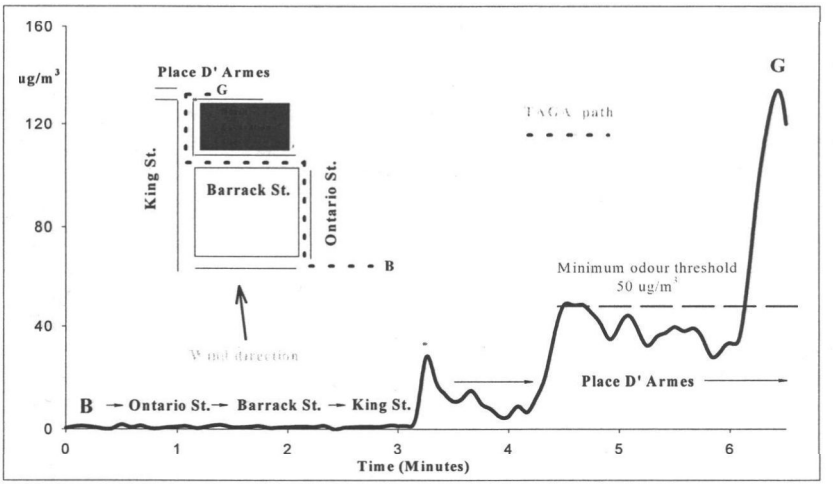


Figure 7: TAGA plume tracking for naphthalene around the coal tar cleanup site, Kingston, November, 1999 (MOE, EMRB).

BTX and PAH were measured concurrently while the mobile TAGA IIe was driven slowly along the streets downwind of the clean up site. Figure 7 shows an example of plume tracking; the concentration of naphthalene, varied with distance from the source. When the wind was from southwest, the mobile TAGA was driven from upwind (site B) to downwind, around the cleanup site to determine the highest ground-level concentration. The plume tracking technique showed the real-time concentrations of naphthalene peaking at site G. Plume tracking results were used in the selection of downwind monitoring locations and to isolate the target emission source.

4.1 Chemicals Detected

During cleanup activities eleven chemicals were identified by the TAGA IIe. Eight chemicals were selected for more comprehensive monitoring: naphthalene, methyl naphthalene, biphenyl, benzene, toluene, xylenes, trimethyl benzenes and styrene. In total, 168 half-hour concentrations were determined on 16 days.

4.2 Naphthalene

The highest half-hour average concentration for naphthalene was 250 $\mu g/m^3$. In 75 of the 168 half-hour samples (45%), concentrations of naphthalene were above the Ministry guideline of 36 $\mu g/m^3$. Figure 8 shows all half-hour concentrations for naphthalene measured during 16 days in November 1999. During the first few days only clean top soil was being removed hence levels were low and during the last few days coal tar was being removed from the bottom of the buried tanks and levels were high. On numerous occasions, during each half hour sampling period, instantaneous levels of naphthalene were as high as 380 $\mu g/m^3$ compared to the odour threshold of only 50 $\mu g/m^3$ (Van Gemert and Nettenbreijer, 1977).

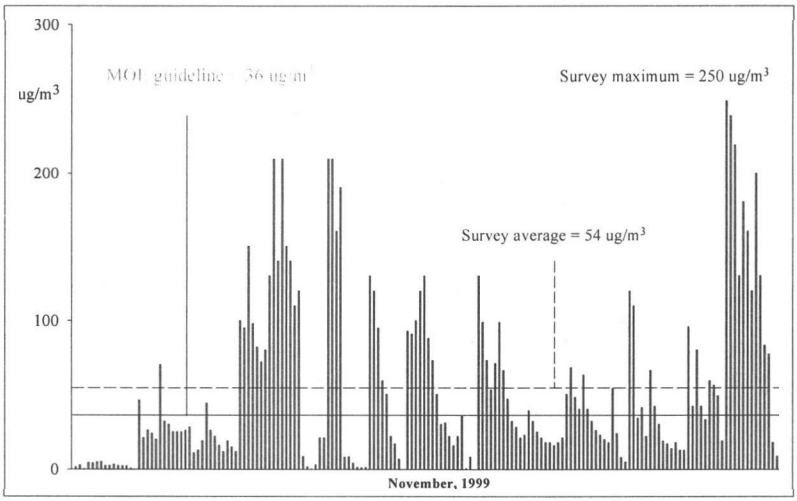


Figure 8: Naphthalene half-hour concentrations measured by the TAGA IIe downwind of the coal tar cleanup site, Kingston, November, 1999.

4.3 Benzene

Benzene is a known carcinogen and its emissions to the environment are to be prevented or limited to the greatest extent possible (Standards Development Branch, 1999). Figure 9 shows all the half-hour concentrations for benzene downwind of the cleanup site during the 16 days in November 1999. Typical urban levels of benzene are about 1 to 5 $\mu g/m^3$ (Air Quality in Ontario, 1997). The highest half-hour average concentration for benzene measured during the cleanup of coal tar was 51 $\mu g/m^3$. Only a few times during the removal of liquid coal tar and transferring it to trucks, were the ambient benzene levels above 5 $\mu g/m^3$. The overall average half-hour concentration of benzene was 3.6 $\mu g/m^3$.

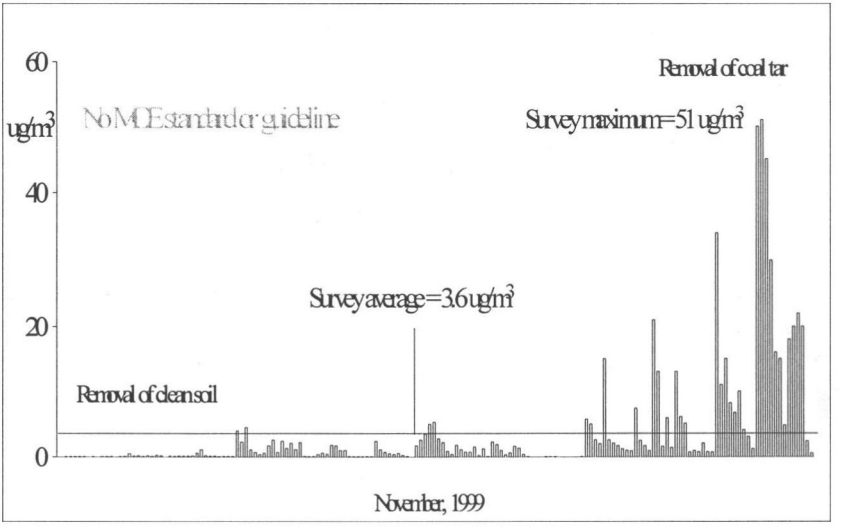


Figure 9: Benzene half-hour concentrations measured by the TAGA IIe downwind of the coal tar cleanup site, Kingston, November, 1999 (MOE, EMRB).

4.4 Concentration Versus Distance

The mobile capability of the TAGA unit was also utilized in determining BTX and PAH concentrations versus distance. Concentrations of the target chemicals were highest around the perimeter of the cleanup site, less than 25 meters from the excavation area containing the tanks. Concentrations dropped off rapidly at distance up to 100 meters, reaching background levels further away (Figure 5).

4.5 Action Taken

The TAGA information was used by local MOE environmental officers and the engineers of the City of Kingston, on daily basis, for assessing the effectiveness of the abatement activities, i.e., more odour suppressing foaming and wood chips were applied continuously to the excavation site following soil transfer. Also, the information was used by the local Medical Officer of Health to temporary halt the

cleanup activities, i.e., stoppage of soil excavation and loading contaminated materials onto trucks.

5.0 Summary

The Air Monitoring Section of Ontario's Ministry of Environment monitored, in real time, several chemicals emitted during the cleanup of a coal tar site in Kingston, Ontario. For this, a new LPCI/MS/MS based on the Ministry's new mobile TAGA IIe technology method was used; it gave relatively low "background" levels, lower detection limits than previous methods and long monitoring range. This unique technique, proved very useful in real time measurements of ambient BTX and naphthalene. Benzene levels as high as 51$\mu g/m^3$ and naphthalene levels as high as 250 $\mu g/m^3$ were recorded during this survey. Levels of emitted chemicals were monitored daily for 3 weeks during cleanup activities. The information was given to local environment and health officials for altering or halting cleanup activities in order to minimize exposure to the public. The information is currently being used for validating theoretical models which may be used in predicting ground-level emissions rates from chemically contaminated sites in Ontario.

6.0 Acknowledgements

The authors express their appreciation to TAGA staff (Mr. John Merritt, Mr. George Rioual), local Ministry of Environment staff : Mr. Robert Michea and Mr. Vic Huggard.

7.0 References

Air Quality in Ontario - A Concise Report on the State of Air Quality in the province of Ontario, 1997.

Budavari, S., *The Merck Index: An Encyclopedia of Chemicals, Drugs, and Biologicals*, 11th ed., Merck & Co. Inc., Rahway, New Jersey, 1989.

Karellas, N.S., De Brou, G.B., Ng, A.C.W., "Application of a Mobile MS/MS Air Monitoring System During PCB Incineration in Smithville, Ontario", *Proceedings of the eighth technical seminar on chemical spills*, Environment Canada, Vancouver, BC., pp189-198,1991.

SCIEX, *TAGA Model TAGA IIe MS/MS System Operators Manual*, October, 1999.

Standards Development Branch, *Summary Point of Impingement Standards, Point of Impingement Guidelines, and Ambient Air Quality Criteria (AAQCs)*, Ontario Ministry of the Environment, November, 1999.

Van Gemert, L.J. and Nettenbreijer, A.H., *Compilation of Odour Threshold Values in Air and Water*, Netherlands, 1977.

Putting the New MSD Through the Pace: Evaluating the HP 6890/5973

Ken Li and Merv Fingas
Emergencies Science Division, Environment Canada,
Environmental Technology Centre, Ottawa, Ontario, Canada
Li.ken@etc.ec.gc.ca

Abstract

Introduced in 1996, the Hewlett Packard HP 6890/5973 GC/MSD system is the latest of the GC/mass spectrometry (MS) from HP. The benchtop GC/MSD, started with the HP 5970 MSD introduced in the mid-1980's has provided small/medium size laboratories with the power of a true MS that provides selectively and library-searchable capability. This paper presents results of studies on instrumental sensitivity achieved with the new MSD, with examples illustrated by trace-level analysis of semi-volatile compounds such as PCB and Dioxins. Optimisation to the system such as ionisation energy, dynode voltages and dwell time were carried out. In the standard electron impact selected ion monitoring (SIM) mode, the new MSD can provide sub-picogram level sensitivity for chlorinated hydrocarbons. In scan mode, under optimal condition, the system can generate library-searchable spectra from sub-nanogram quantity of analytes. This sensitivity level rivals traditional GC with selective detectors such as electron capture detector but has the added advantage of an onboard database of over 75 thousand spectra which makes the system an essential tool in spill emergencies analyses.

1.0 Introduction

Gas chromatography/mass spectrometry (GC/MS) has generally been recognised as one of the most powerful analytical tool for separation, identification and quantitation of organic compounds in a complex mixture. In the respect, GC/MS has been a mainstay of analytical tool for environmental analysis, where detection and quantitation of trace level of contaminants are often sought after in the presence of a myriad of background materials.

One of the most significant developments in the GC/MS instrumentation field in recent years is the introduction of relatively low cost benchtop GC/MS systems. Part of the impetus came from the space exploratory program in the 60's, plus the advent of inexpensive personal computer technology. Bench- top MS is characterised by a relatively compact chassis which houses the ion source, analyser and detector assembly. For cost consideration, the majority of them operate by electron impact ionisation mode only. The analyser is the active component that separates the fragment ions by mass/charge ratio. This is achieved inexpensively by quadrupole or ion cyclotron. Detector technology is invariably the electron photo multiplier type. Because of the relatively small manifold volume, vacuum is readily achieved by low cost air-cooled diffusion or turbo pumps and backed by rotary pump. In contrast, traditional research grade stand alone GC/MS systems require ancillary equipment for their operation; for example, their large diffusion pumps require temperature controlled cooling water to condense the diffusion pump oil. Another example is the bearing of turbo pumps requiring cooling due to the high rotation speed. They have high initial purchase price and relatively more expensive to operate, but offers more

sample introductory device such as liquid chromatography interface, solid probe and a more comprehensive sample ionisation technique such as chemical ionisation, which might not be required to most environmental analytical labs.

The Mass Selective Detector (MSD), first introduced by Hewlett Packard (HP) in the early 80's as the HP 5970 was one of the first generation of legitimate low cost MS used as dedicated GC detectors (the other one being Varian's Ion Trap Detector). To keep the cost down, the MSD did not have other sample introduction devices. Electron impact was the standard mode of ionisation. No other interface other than a simple direct interface was available, and column flow was restricted to 1 mL/min or less. Higher column flow rate was possible through an open-split interface which bled off excess column flow via a 3-way union open to the atmosphere, with a restrictor limiting the flow to a nominal 0.7 mL/min. No enrichment or other separation device was available to keep the design simple. Solely used with an attaching GC, it nevertheless provides a lot of small or medium size labs the unique power of mass spectral identification

The MSD has evolved through 3 updates to the present 5973, bringing improvements in sensitivity and capability with each changes. The current MSD has an optional chemical ionisation: the higher pressure is achieved by a specially designed ion chamber that allows operation within to limited pumping capacity of the vacuum system. In additional, there is an increase in mass range to 800 amu, a high capacity turbo pump which provides a cleaner background and faster pump down, plus ability to handle flow up to 4 mL/min from a 0.32 mm wide-bore column. The ion source and analyser are now independently heated, an improvement over the previous designs which rely on conductive heat from the interface heater, requiring a 4- hour stabilising time. The vacuum manifold can now be kept cleaner in the presence of matrix rich sample and allows for much faster thermal equilibrium during pump down. The MSD is equipped with a high-energy dynode (HED) detector that improves sensitivity by increasing the efficiency of the ion detector.

In this work we will present our experience with the new MSD. We have carried out optimisation and studied the various parameters that can affect sensitivity. Examples include the analyses of semi-volatiles such as PCB, pesticides and dioxin/furans in environmental samples. Results of past performance evaluation exercise, conducted by CAEL (Canadian Association of Environmental Laboratories) were used to illustrate the performance of the system.

2.0 Instrumentation and Methodology

The system consists of the HP 6890 GC/5973 MSD with a HP 7683 ALS (automated liquid sampler). Vacuum system is the upgraded 250-L tubo pump. System control is by a HP ChemStation with a Kayak pentium-based PC running under Windows-NT. The software includes autotune programs for EI, as well as programs for data acquisition, data editing, reporting, quantitaion and library searching. Several columns were used in the course of this study. Due to the restriction of the vacuum system, column up to 0.32 mm i.d. is allowable.

All semi-volatile analyses were carried out using a 30-m HP-5 MS capillary column (0.25-mm id, 0.25-mm film) was used. Experimental parameters were: injector temperature 270 ^{0}C, capillary interface temperature 300 ^{0}C; automated injection of 1 μL; MSD operated in Selected Ion Monitoring (SIM) mode. Tuning

was performed by autotuning and the electron multiplier was at a nominal value of 1400 V. The GC column flow was a constant 1 mL per min controlled via the electronic pressure programming (EPP) constant flow mode. The oven temperature program for PCB analysis was: 120 ^{0}C for 1 min heated to a final temperature of 310 ^{0}C at 10 ^{0}C/min, and held at this temperature for 5 min. Prior to injection, an internal standard of d14-Terphenyl was added to give a final concentration of 1 μg/mL. In actual analysis, quantitation was based on the internal standard method.

For dioxin/furan analysis, the oven temperature was 100 ^{0}C for 1 min and heated to 200 ^{0}C at the rate of 35 ^{0}C/min, then to 280 ^{0}C at the rate of 2.5 ^{0}C/min and held at the final temperature for 3 min. One μL was injected via an auto-sampler using the splitless mode . Injector and detector temperature was 270 ^{0}C and 280 ^{0}C respectively. For the purpose of evaluation, a simplified one-step SIM acquisition program was carried out. Ion source was held at 220 °C.

2.1 Performance Evaluation (CAEAL): PCB in Water

Liquid-Liquid Extraction. Liquid-liquid extraction was performed on a 1- L aliquot of the received water sample, fortified with known amounts of Aroclor mixtures by a contract lab of CAEL. A mixture of isotopically labelled surrogates (C-13 tetrachlorobiphenyl to heptachlorobiphenyl) was added to the sample in the separatory funnel just before the extraction. Extraction was carried out with a 50 mL aliquot of dichloromethane and the process was repeated two more times with fresh solvent. The extracts were combined, and were filtered and dried over Na_2SO_4.After the addition of 1 mL of iso-octane, the volume was reduced by evaporation to ~ 1 mL using a roto-evaporator. The extract was transferred quantitatively to a calibrated test tube blown down to less than 1 mL under nitrogen. The extract was finally made up to 1 mL in iso-octane and an internal standard of d14-Terphenyl added at 1 ng/μL. One μL of the extracts was injected in the GC/MSD for analysis.

3.0 Results and Discussions

3.1 Analysis of Dioxin/Furan (PCDD/PCDF)

Within a family of 75 congeners of PCDD and 135 PCDF, TCDD (2,3,7,8-Tetrachlorodibenzo-p-dioxin) and the corresponding furan are among the most toxic substances known to Man. Their presence in the environment, even at trace levels of parts-per-billion or trillion is of great concern due to it propensity to bio-accumulate similarly to most persistent chlorinated substances. Mass spectrometry techniques play a key role in monitoring environmental samples for this substance and its isomers because of the sensitivity and unique conformational power of GC/MS, important because in actual samples, trace levels of TCDD/F is often present in a myriad of background organic compounds. Traditionally, trace analysis of PCDD/F are mostly carried out on research grade GC/MS for its high sensitivity and specificity (in case of high resolution MS). For large scale monitoring exercises such as air quality survey in the picogram level of target compounds, where perhaps reliable and consistent analytical data is more useful as in trend analysis, rather than absolutely sensitivity in the femtogram level. Another example is the chemical or transformer fires in which relatively high levels of such contaminants are encountered. For these

scenarios, the need for MS may be met with bench-top MS such as the MSD. Within the last 10 years, such instrumentation has made great strife in terms of sensitivity and ease of operation such that it has become a common GC detector in most labs. The following presents the finding of the new MSD in this application.

A stock solution of EPA 1613 PCDD/F standard solutions (0.4-4 ppm) obtained from Wellington Lab, Guelph was serially diluted to give mixtures down to 0.4-4 ppb. This mixture contains all of the 2, 3, 7, 8-substituted chlorinated dioxins/furans, noted for their enhanced toxicity due to the coplanar nature of the molecule.

3.1.1 Optimisation

There are several ways to improve the detection limit, one can introducing more sample onto the column, or set up the MS to increase analyte response. To inject more samples onto the column, one can us make use of EPP on the HP 6890 GC for pulse splitless injection. The column pressure at injection was programmed to step up to a high value, thereby squeezing the larger vapour cloud in point of large liquid volume injection. A series of injections (1 to 5 μL) were made in a EPP pulse mode 3 times the normal value (45 psi) during the initial 0.5 min. There was a more or less linear increase in analyte response, however the peak shape was extremely poor, with a broadening base indicating there was band broadening even at a pulsed pressure of 45 psi.

At the ion source, it has been estimated the ionisation efficiency is in the order of 1 in a million. An obvious path of improving the sensitivity therefore lies with improving the ionisation process. The electron energy is the amount of energy on the ionising electrons. The energy is determined by the bias voltage; -70 V dc bias on the filament causes emitted electrons to possess -70 eV (electron volts). Normal operation sets this parameter to 70, which gives classical mass spectrum for library searches. As known to PCDD/F analysts, reducing the electron energy from the normal 70 eV in the ion source causes less fragmentation, thereby increasing the abundance of the parent ion and enhancing the detection limit. A series of runs were made to lower the ionisation energy by 10 eV steps from 70 eV to 40 eV. No changes in the resulting chromatograms were noted, indeed at 40 eV, baseline noise became excessive. Emission current was also lowered by 50 % of tune value to reduce the extent of ionisation, but again no improvement was observed.

The dynode voltage of the electron multiplier (EM) was varied by steps of 200 V relative to the autotune value to study the effect on the response. Started with a tune value of 1000 V (nominal), a series of injections were made at -200, +200, +400 and +600V. Results are shown in Figure 1. The log function of the EM was closely reflected in the observed response curve. While greatly increasing the analyte response, the life of EM is shortened by operating the EM in high voltages.

Dwell time was also varied from 25 to 200 msec for each monitored ion in the SIM mode. There were no significant difference in response but 100 msec appears to give a slight enhancement in OCDF (Figure 2). Longer dwell time usually improves the signal to noise ratio but this is offset by missing the fast changing profile of capillary peaks. In general a minimum 15-20 points are required to construct a peak accurately (HP 5970A Workstation Operation Manual).

3.1.2 Calibration

Figure 3 shows a calibration curve created by using various amounts of the 2,3,7,8-TCDD congener and a fixed amount (40 pg) of a carbon-13 enriched sample of 2,3,7,8-congener. The ordinate of the curve is the ratio of the measured area of the 322 m/z ion to the measured area of the 334 m/z ion from the carbon-13 enriched congener. The areas of these two ions fragments were measured in SIM mode, each ratio was calculated from a single area measurement for each of the two m/z ions. The abscissa is the ratio of the amount of the 2,3,7,8-congener (0.4, 4, 40, 100 and 400 pg) to the fixed amount of the carbon-13 enriched 2,3,7,8-congener internal standard. The calibration curve is linear up to 400 pg of TCDD/F injected, and the lowest amount detectable appears in the 0.1 pg range.

3.1.3 Detection Limit and Repeatability for Quantitative Analysis of TCDD

Five replicate injection of a 0.4-4 ppb mixture were made at a EM voltage of 1600 V (+600 V over tune value). At 0.4 pg TCDD/F injected on the column, we obtained RSD of 4.7 and 9.8 % respectively. For identification purpose, an instrument detection limit down to 0.1-pg is ready achievable. For a 1- L water sample, extracted and concentrated to a final volume of 0.1 mL, a total of 10 pg is detectable in the final extract. This translated to a method detection limit of 10 pg/L or 10 ppt, which is more than sufficient to determine whether a spill or discharge poses any health risk to the population at large, and compared favourably with free-standing research grade GC/MS system but at only a fraction of the cost. Figure 4 illustrates a total ion chromatogram (TIC) of a 4-40 ppb standard at the normal tune values.

3.2 Pesticide Analysis

The dwell time study was repeated using a mixture of chlorinated pesticides at 1 ppm. Again there appears to be no significant difference in response from a dwell time of 25 to 200 msec. A calibration curve was generated by injecting a series of solutions ranging from 0.2 to 50 ppm and shown to be linear (Figure 5).

3.3 PCB Analysis

Performance evaluation was carried out using Aroclor mixtures of 1242, 1254 and 1260. Calibration runs from 0.01 to 0.2 ppm of each Aroclor were made and found to be linear at this extreme low level (Figure 6). It was interesting to note the performance of the new MSD actually surpassed the sensitivity of electron capture detector which is around 0.05 ppm. In this regard, the sensitivity improvement over the previous generation of MSD is at least 10 times. In extraction of PCB from soil, a 0.4 ppm carbon-13 surrogate mixtures were generally used to monitor PCB sample workup loss, thus accurate determination of the surrogate standards affects the quality of data. Five replicate injections were made and RSD was found to be from 11 to 14 %.

3.3.1 CAEAL Performance Evaluation

As part of the accreditation program, ESD has joined the performance evaluation exercise conducted twice a year. The analysis of PCB in water is among a number of environmental analytical protocols ESD has been accredited. In each round, four water fortified with Aroclor mixtures were received and extracted in

accordance to the protocol. Analysis was carried out on the MSD, using a multi-stepped SIM program. Results of the past two rounds are shown in Figure 7. In each of the two rounds, PCB was measured in the ppb level. ESD were credited with the maximum points assigned in each sample, thus scoring a perfect 100 %.

4.0 Conclusion

The HP MSD has been a mainstay in ESD's analytical instrumentation, the new 5973 MSD proves to be a very capable performer. A number of new features has brought increased performance to an already versatile analytical system. In this study, we have optimised the system for analysing a variety of semi-volatile contaminants, and the system was shown to perform admirably well in all aspects of environmental testing.

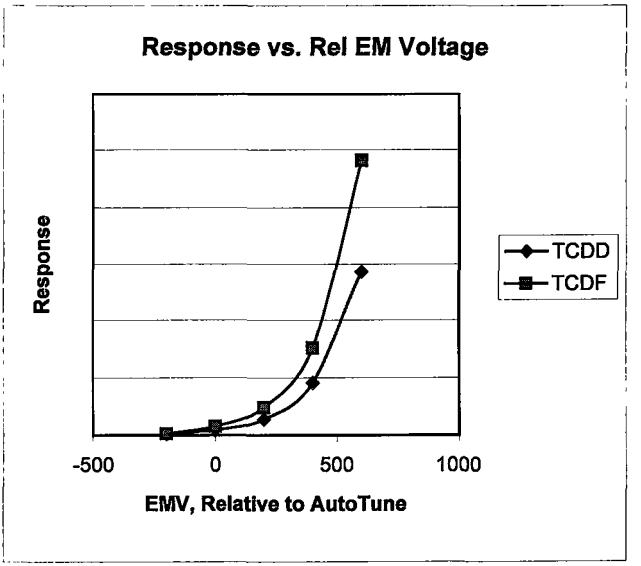


Figure 1: Response vs. EM Voltage, Dioxin Analysis

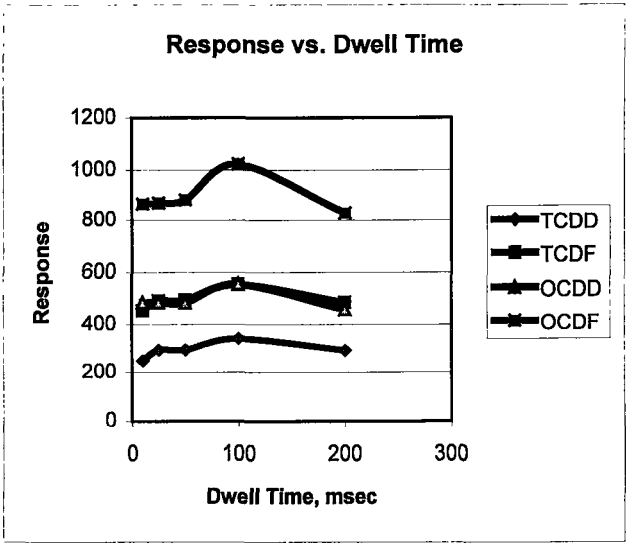


Figure 2: Response vs. Dwell Time, Dioxin Analysis

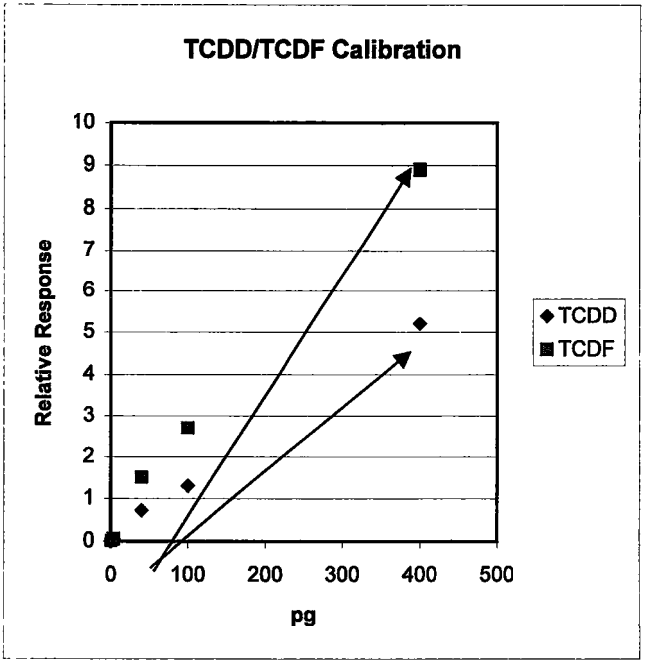


Figure 3: Trace Level PCDD/F Calibration, SIM method

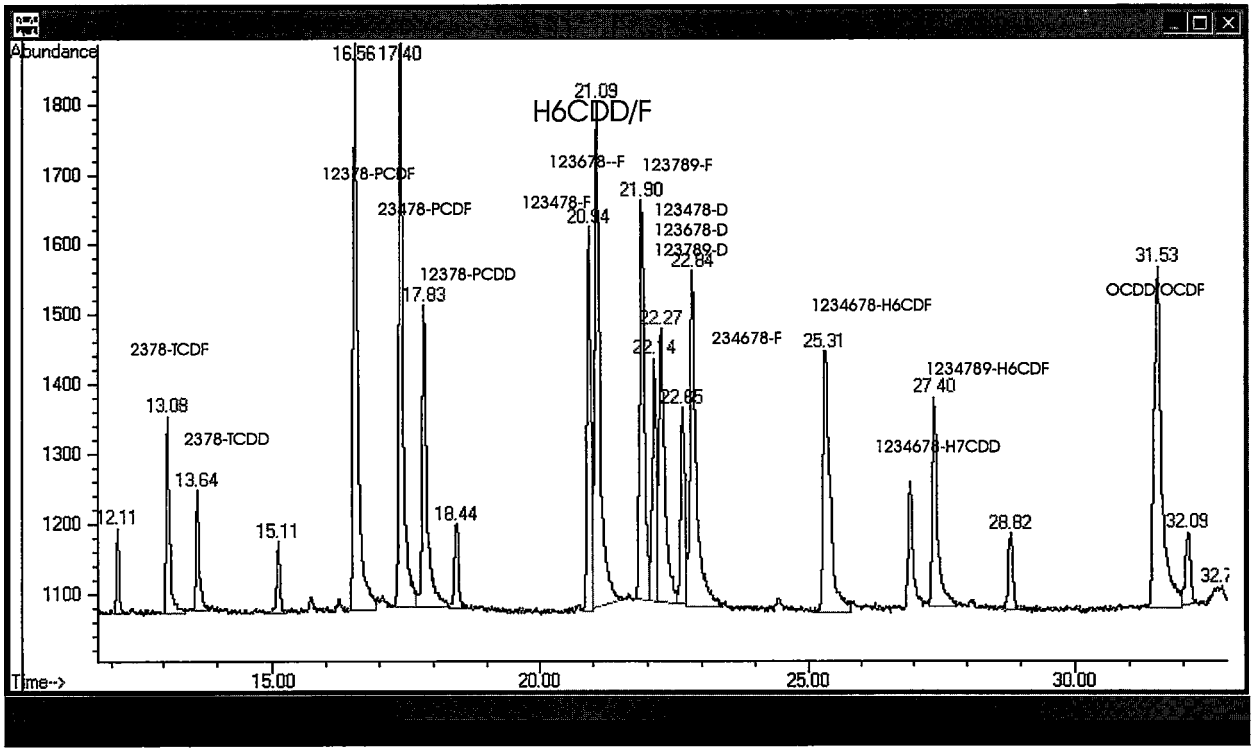


Figure 4: Total Ion Chromatogram of PCDD/PCDF, 4-40 ppb

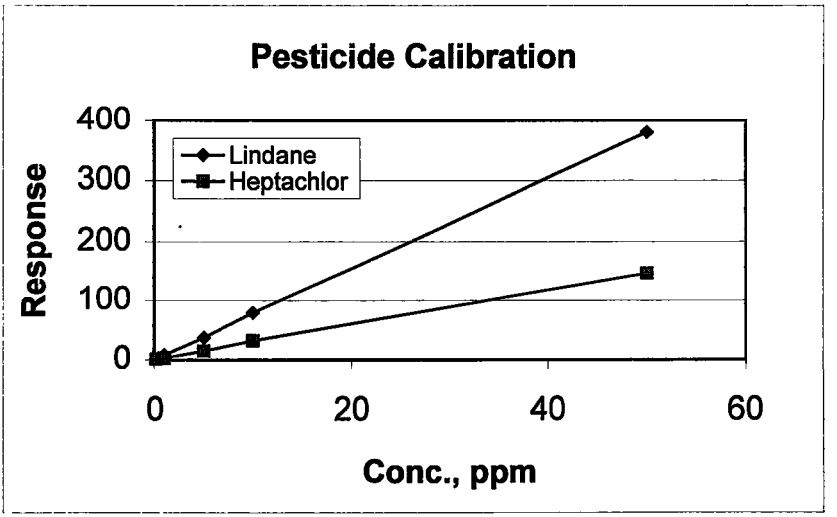


Figure 5: Pesticides Calibration, SIM Mode

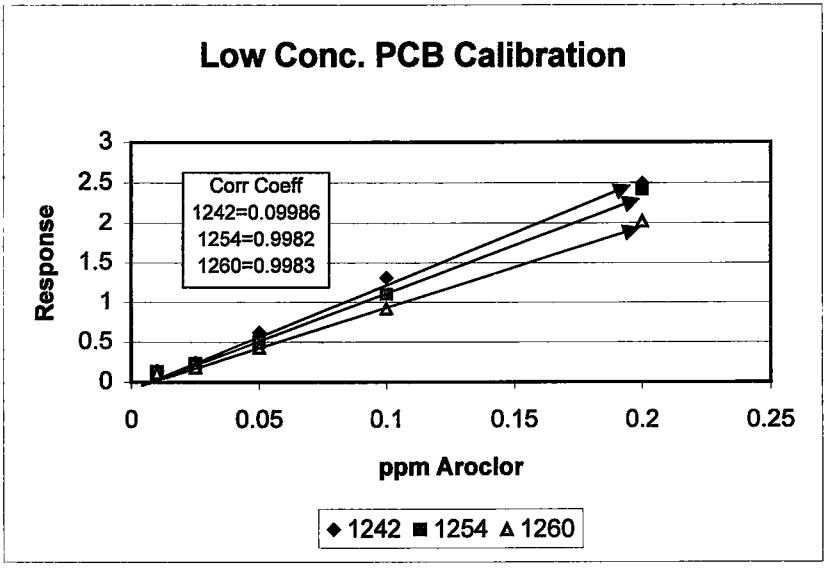
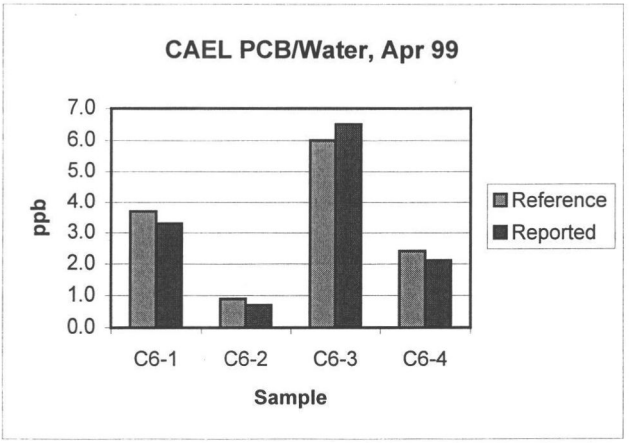


Figure 6: Very low level PCB Calibration, PCB SIM method



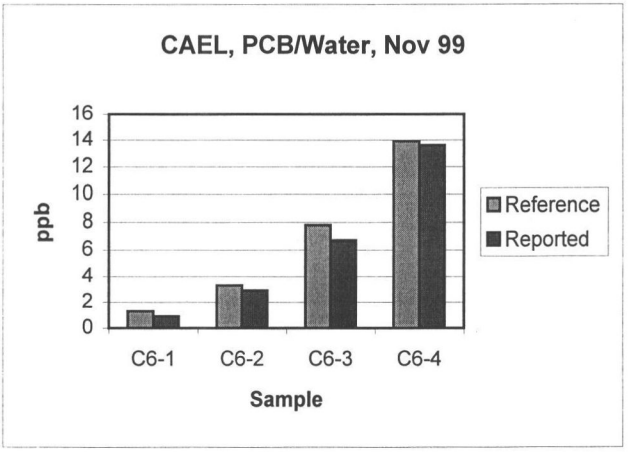


Figure 7: CAEAL Performance Evaluation Samples, PCB in Water [First (April) and Second (Nov.) Rounds]

Review of Personal Protective Equipment for Spill Situations

Merv Fingas
Emergencies Science Division
Environmental Technology Centre
Environment Canada
Ottawa, Ontario, Canada
Fingas.Merv@etc.ec.gc.ca

Abstract

This paper is a review of the types of personal protective equipment best used by those who respond to accidental chemical spills, particularly such spills that occur outside the workplace. It looks at factors to consider in selecting protective clothing and respirators, the different levels of response for chemical spills, the most often spilled chemicals, and the basic components of a chemical spill response program.

1.0 Introduction

The use of personal protective equipment is very important in spill situations because response personnel face exposure to chemicals that could cause serious injury or illness. The hazards are accentuated by the unknown physical environment of the spill site and the random nature of spills. The multiple hazards of spill sites distinguish such incidents from spills in the laboratory or exposure in the workplace. Spill responders entering a site cannot always predict what chemicals or concentrations they will encounter and what other hazards may be present. There is also a lack of standards and guidelines for selecting and operating of personal protection equipment. Most standards are written for use in the workplace and may not be fully applicable to emergency situations.

Preventing exposure to toxic chemicals is a primary concern at spill sites. Substances can enter the unprotected body by inhalation, ingestion and skin absorption or permeation. Ingestion can occur by transferring absorbed contaminant during eating or smoking or by other forms of contact with the mouth. Some chemicals readily pass through the skin in a process known as permeation.

The most common categories of protection equipment necessary for spill response are clothing and respirators. Totally encapsulated chemical protection suits (TECPS) or gas-tight suits are used when the contaminant is unknown or when a skin-permeating or skin-attacking chemical is present. The self-contained breathing apparatus (SCBA) provides the highest protection against the inhalation of chemical contaminants is the most commonly-used form of respiratory protection in the initial phases of a spill. The response levels used in North America are described below. The levels are commonly accepted among spill response organizations including Environment Canada, United States Environmental Protection Agency and the United States Coast Guard.

Level A is the first-response or entry level. The SCBA and totally encapsulated suit are used to protect against high or unknown levels of chemicals. Chemical substances that permeate or otherwise attack the skin may be present and the totally encapsulated suit must protect against these.

Level B involves the use of the SCBA with liquid-tight chemical-protection clothing or "splash" gear as it is sometimes known. Level B gear is used to enter a site where it is known that no skin-penetrating or damaging chemicals are present, or where high levels of contaminant may be present that a standard air-purifying device would not protect against. There is a variety of acceptable options, but the clothing usually consists of a special water-tight suit or water-tight rain gear.

Level C includes respirators and standard clothing, which most typically consists of liquid-repellant coveralls. These coveralls are often made of polypropylene or Tyvek. This level of response is very commonly used by cleanup crews when the situation has stabilized and concentrations are known and are not likely to rise above the capability of the respirator. No skin-penetrating materials are present. Gloves are used throughout the first three protection levels.

Level D is applicable to spills where there are no airborne contaminants of concern and where the likelihood of harm by contact with the spilled material is minimal. Many organizations provide treated cotton coveralls or similar garb for working in such frequently occurring situations.

2.0 The Spill Situation

The most important consideration when selecting protection equipment is the target chemical. While it is not possible to be prepared for all types of chemical spills, it is possible to be prepared for the most frequent ones.

Canada has had a national data base for a number of years (Beach, 1982; Fingas, 1987). Such a database is useful in assessing priorities. Table 1 is a list of some common chemicals spilled from 1984 to 1997 and their frequency and volume (Fingas *et al.*,1991; 1996). Only about 40 materials have been spilled more than 10 times and about 150 materials have been spilled more than 3 times. The data show that about 5% of the incidents are single or one-time incidents with a low probability of repeat. According to the database, about 90% of the incidents are spills of common industrial materials. Fifty substances account for about 80 % of the spills and 100 substances for about 90% of the spills. The spill situation is that most spills are of high-volume production industrial chemicals. Less common chemicals account for only a small number of spills.

A priority list of spill substances has been prepared using spill and toxicity data. A summary of the protection requirements necessary for the highest priority materials is provided in the appendix. The assessments are given in terms of whether SCBA's or encapsulated suits are required or not. It is important to stress that the protection levels listed are for typical spill situations. Where chemicals and/or their concentrations are unknown SCBAs and totally encapsulated suits must be worn. The same is true for enclosed or confined spaces. On the other hand, once chemical concentrations are known and the situation is under control, lower levels of protection might be applicable.

3.0 Equipment Overview

A wide variety of respirators is available on the market. Respirators are common and are of two basics types, air-supplied and air-purifying. Air-purifying respirators are used when oxygen levels are in question as well as when contaminant levels are unknown and expected to be high. Air-purifying respirators are used when

Table 1 Frequently-spilled Substances

Chemical	Numbers of Spills	Spill Volume (t)
PCBs	334	89
Sulphuric acid	155	13000
Hydrochloric acid	123	3300
Ammonia	107	470
Sodium hydroxide	92	8200
Sulphur	68	70000
Ammonium nitrate	63	4200
Fenitrothion	49	100
Nitric acid	48	140
2,4-dichlorophenoxyacetic acid (2,4-D)	37	130
Chlorine	36	120
Potassium chloride	31	12000
Ethylene glycol	31	590
Vinyl chloride	31	180
Styrene	24	5000
Sodium chlorate	23	7700
Calcium chloride	20	3700

contaminant levels are relatively known and are certainly below the maximum capacity of the respirator.

Protective clothing is quite diverse, but the most common items used for spill response are boots, gloves, totally encapsulated suits, splash gear or firefighters bunker suits, and coveralls. Hearing protection and hard hats are used where necessary.

4.0 Selection of Respirators

Selecting respiratory protection equipment for use in the workplace has been the topic of several well-known references (NIOSH, 1985; OE, 1991, CSA, 1993). Some publications have dealt with selecting respirators for spill situations (EPA, 1992; Fingas, 1987). The differences between selecting a respirator for the workplace and selecting a respirator for use in spills hinges on the certainty with which both the substances present and their concentrations, are known. In spill situations maximum protection must often be used because of the possible presence of high chemical concentrations.

Respirators provide protection from three dangers: chemical contaminants, particulate matter and oxygen deficiency. Chemical contaminants include a wide variety of materials such as listed in the appendix. Particulate matter consists of small matter that can be inhaled. 'Respirable' particulate matter has particulate sizes less than 10 μm. This size is below which particulates lodge in the lungs and can cause permanent damage. Particulates are also important in view of chemical spill response because many chemicals can be absorbed or adsorbed to particulate matter. A special type of filter, known as the HEPA or High Efficiency Particulate filter, removes the small particulates and is a part of many air-purifying devices. Oxygen deficiency is a common danger associated with chemical contamination, particularly in confined spaces where the air is displaced by the chemical. Oxygen deficiency can only be protected against using air-supplied respirators.

Respiratory protective devices consist of a facepiece connected to either an air-source or an air-purifying device. Facepieces for respirators are available in two basic configurations, half facepieces and full facepieces. The half facepieces fit around the nose and do not have an integrated eye-shield. A wide variety of devices are available on the market, some of which are listed in Table 2. This table also lists a protection factor which is the ratio of the concentration of the contaminant outside the facepiece to the concentration of the contaminant inside the facepiece. The protection factors presented in the table represent an average value for a large number of individuals. Such values can be much lower however if the facepiece does not fit properly. Beards, for example, can cause leakage around a facepiece, reducing the protection factor by as much as a factor of 10.

Protection factors are important criteria for selecting respiratory protection equipment. The protection factor must be sufficiently high to reduce the contaminant inside the facepiece to an acceptable level, usually taken as the TLV or Threshold Limit Value. The Appendix lists the TLV values for commonly-spilled materials. These data are used in the following manner (ACGIH, 1999; NIOSH, 1994). A spill of a substance with a TLV of 5 ppm which according to calculations could rise as high as 5000 ppm, would require a respirator with a protection factor of at least 1000. For a safety factor of 2, a protection factor of 2000. Pressure-demand SCBA's, which

Table 2 Respiratory Protection Equipment and Associated Protection Factors

Respirator	Protection Factor[1]
Air-Purifying Respirators - Dust Masks	
Single-use dust mask	5
Quarter mask	5
Half mask	10
Full facepiece dust mask	50
Powered dust mask	1,000
Air-Purifying Respirators - Chemical Cartridge	
Half facepiece mask	10
Full facepiece mask	50
Supplied-air Respirators	
Demand half facepiece mask	10
Demand full facepiece mask	50
Pressure-demand half facepiece mask	1,000
Pressure-demand full facepiece mask	2,000
Continuous-flow helmet or suit	2,000
SCBA's *(Self-Contained Breathing Apparatus)*	
Open-circuit demand	50
Open-circuit pressure demand	10,000
Closed-circuit, oxygen cylinder type *(all are full facepiece)*	50

1 Protection factor is the ratio of the contaminant concentration outside the facepiece versus inside

have a protection factor of about 10,000, they represent the ultimate in safety and are generally used at spill scenes because the exact substance and the level of the contaminants is not known for certain until measurements have been made.

Air-purifying respirators are limited in the concentrations that they can handle or absorb. The top level at which an air-purifying respirator is useful is the "Immediately Dangerous to Life and Health" (IDLH) level. This is also the level at which a chemical can cause severe damage. The IDLH value represents the level at which one must either switch from an air-purifying respirator to an air-supplying respirator, or escape from the environment. The IDLH values for commonly-spilled chemicals are listed in the Appendix. Another requirement for air-purifying respirators is that they be used at contaminant concentrations less than the specified Maximum Use Concentration (MUC). The MUC is based on the capability of the sorbent in air-purifying respirators to deal with high concentrations of materials.

Figure 1 shows the selection process for a respirator. The following guidelines can simplify the selection process for respiratory protection devices for use at a spill scene;

- The SCBA should be used for entry into an unknown situation, where unknown or high levels of a toxic chemical are present or if there is any possibility of an oxygen shortage.
- The air-purifying respirator can be used when the situation is stable and when the levels of chemicals are below the IDLH with very little possibility of them rising.
- In both cases, the selection should be verified by taking measurements and calculating concentrations inside the facepiece.

The protection factor can now be measured for a given mask and a given person. This is called 'fit testing' and refers to the fit of the mask to a person. In the past, a number of qualitative measures using indicators such as banana oil and smoke were used which provided a rough indication of mask fit. In the past 10 years, many quantitative fit-testing apparatuses have come onto the market. These directly measure the protection factor for a given mask by measuring the concentration of ambient particulate inside and outside a mask or by measuring the ingress of air using sensitive pressure transducers. The measurement devices now include computers or built-in computing devices to directly calculate protection factors and the percentage of facepiece leakage. Fit testing should be done for new users as well as on an ongoing basis to ensure adequate protection. Sometimes, certain facial features, such as a scar or a very thin face, result in a lack of proper protection and such individuals should not be put in a position that requires respiratory protection.

Problems can arise when respirators are used in extreme cold or hot weather. In cold weather, there are two concerns: the icing of the regulator and fogging of the facepiece window. Icing of the regulator becomes serious because the decompression of the air can cause the moisture to precipitate and then freeze. The amount of water in the starting air is usually measured by the dew-point, which is the temperature at which moisture begins to form droplets of water. Table 3 shows the dew point and water content of air. The CSA standard requires extensive filtration to remove the moisture (CSA, 1985). When using supplied-air respirators in cold weather a number of precautions are taken, including as leaving tanks in heated vehicles before use. The

Table 3 **Approximate Moisture Content in Compressed Breathing Air***

Atmospheric Dew Point (°C)		**Pressure dew-point (°C)**	
30 or 60-minute apparatus	Water content at atmospheric pressure (ppm)	30-minute apparatus at 2216 psig	60-minute apparatus at 4500 psig
-45.5	68	7	18
-48.5	48	2	12
-51	34	-2	8
-53 (CSA standard)	27	-5	4
-54	24	-6	3
-56.5	17	-10	-2
-59.5	11.5	-14	-6
-62	8	-18	-10
-65	5.5	-22	-15
-68	3.5	-27	-20
-70.5	2.3	-31	-24
-73	1.5	-34	-27

* data adapted from CSA, 1985

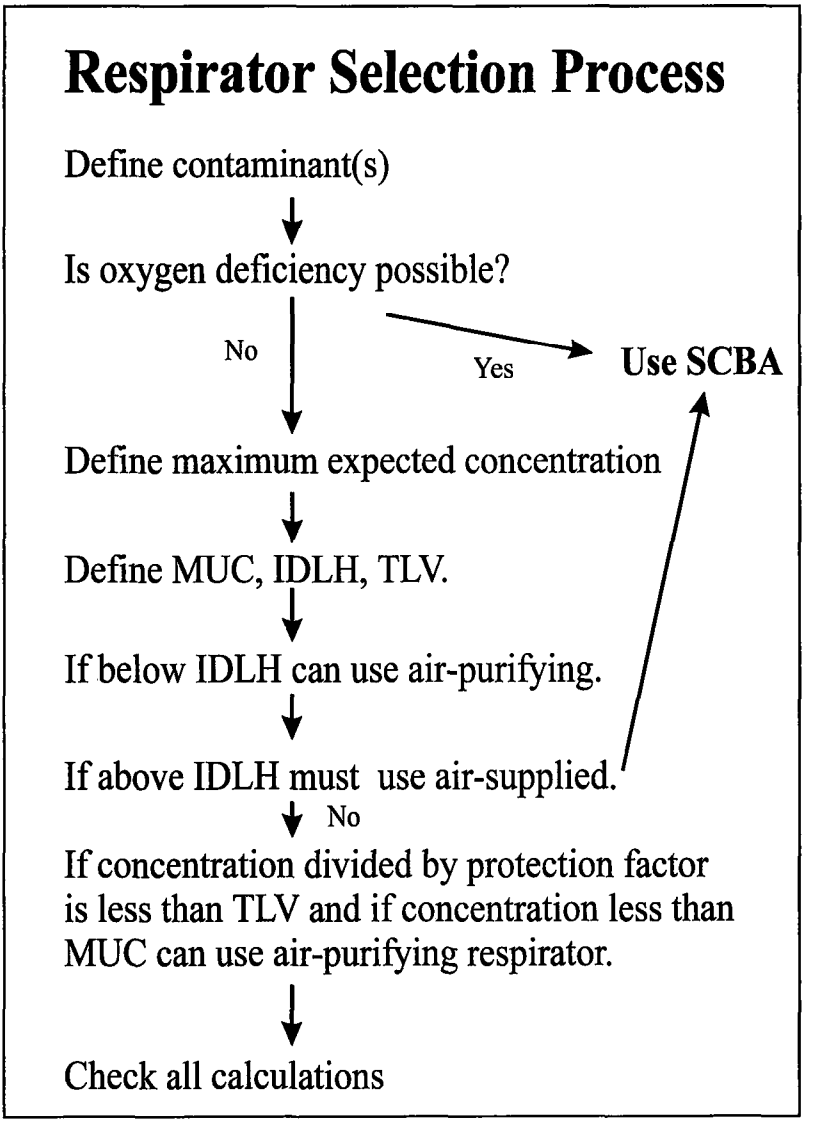


Figure 1 Respirator Selection

fogging of lenses by exhaled moisture is readily prevented by using a device known as a 'nose cup' which directs moist air to the exhalation valve and away from the lens.

The use of respirators in very hot conditions does not cause life-threatening events, but the user can tire quickly and excessive sweating can cause face-seal problems with the mask.

Another issue when using respirators is the need for prescription glasses in the facepiece. Regular glasses cannot be worn because anything that interferes with the face piece seal is dangerous and illegal. Special lens holders are available that fit into the face piece. Contact lenses, once not recommended for use in a respirator, can now be used, as new contact lenses allow for gas exchange and thus do dry out and stick to the eyeball.

For air-supplied respirators, the quality of the air is also an issue. Standards exist for the minimum air purity (CSA, 1985). The moisture content in the air is also an issue, especially when operating in cold climates, as this can cause the respirator to freeze.

5.0 Clothing

Clothing, gloves, goggles, boots and other such items are required to prevent the chemical from contacting the skin or eyes. In the case of vapours that can permeate the skin, gas-tight protection is required. In the case of chemicals that are corrosive or absorbed as liquids through the skin, protection is required to prevent contact with the substance itself. Some chemicals pose both dangers.

Chemicals can gain access to the wearer or can affect clothing material in three ways.

1. Permeation: This is the process by which liquid or gaseous chemicals move through clothing material on a molecular basis. It is the most important indicator of the usefulness of a particular clothing material. Some chemicals can permeate through clothing material in only a few seconds. If these chemicals are toxic, then the clothing material is not useful for chemical protection.

2. Penetration: This occurs when liquid or gaseous chemical flows through closures, seams, pin holes or other similar openings in the clothing. Penetration does not pertain to the type of material selected, although certain types of materials are more or less resistant to puncture mechanisms (such as abrasion, pin-holing), depending on the conditions the clothing is subjected to.

3. Degradation: This is the deterioration of clothing material caused by the action of the chemical. Degradation may change bulk properties such as tensile strength or small areas of the material to dissolve. In the past, most data on a material's resistance to a chemical related to degradation as there were no standards for the measurement of other types of chemical intrusion. Many different measurements were known as "chemical compatibility". As will be shown later, degradation data, although important, are not usually as crucial as permeation data.

Permeation is the most important of the entry mechanisms in terms of spill response. It is chemical dependent and changes with material thickness, temperature and the presence of other solvents. It has been found that mixtures of chemicals can sometimes permeate the clothing material much faster than any of the chemicals alone.

Existing data on permeation are primarily measured using the ASTM (American Society for Testing and Materials) procedure or the ISO (International Standards Organization) procedure. These prescribe the use of a standard test cell which consists of two spherical halves. The clothing material to be tested is placed as a divider between these two halves. The challenge liquid is placed on one side, with air in the other side. The air is then monitored for the presence of the chemical. Breakthrough is said to occur when the chemical can be measured in the air space. As the clothing material is completely immersed in the challenge liquid, the test does provide a conservative measure.

Permeation data in the form of the time a chemical permeates a specific material, for commonly spilled chemicals are presented in Table 4. Data are compiled from Forsberg and Keith, 1995. The clothing materials presented here are those commonly-used for totally encapsulated suits or gloves. In both cases, permeation data is very important for selection. Permeation times of less than 30 minutes imply that the material has little application to spills as this is the time usually spent in an encapsulated suit. In some cases, however, there is no material with a long permeation time and the material with the best permeation time would be used.

Specific permeation data on the clothing material actually used in the manufacture of the clothing item should be obtained whenever possible. As already noted, permeation data vary greatly, even with similar materials. Some of the variance may be due to the thickness of the material. The thicker the material, the longer the permeation time. In fact, thickness is so important that materials, such as used in light clothing, that show significant permeation in thin sheets of typically 0.05 cm, can have no or little permeability at thicknesses of about 0.5 cm thick. Thus permeation through very thick synthetic materials, such as on SCBA facepieces, may not be a serious concern. Permeation times also vary with material fabrication and other differences may be due to erroneous data. It is important to verify the permeation data for a given material with more than one source.

Boots and gloves are the most important two pieces of protective clothing, because they most often come into contact with contaminated materials. Glove technology has progressed immensely in the past few years and many companies have good selection charts based on permeation data for their specific materials. The manufacture of boots has not progressed much and very few specific permeation data are available for these clothing items.

For chemical spills, an important piece of clothing is the totally encapsulated chemical protection suit (TECPS) which is used if the materials encountered will be unknown or known to be skin-permeating. A few cautions should be noted in selecting totally encapsulated suits:

1. There are few standards governing the design and manufacture of such equipment and those that do exist are applicable primarily to firefighters. The buyer must therefore be careful to ensure that the suit purchased is appropriate for use in a chemical spill response.

2. Any permeation data provided by the manufacturer must have been measured for the actual suit material and are generated by a standard method, preferably the ASTM method.

3. Suits that interfere with the face-seal of the SCBA should not be purchased. Such practice is dangerous and contravenes most occupational health laws.

Table 4 **Permeation Times Through Clothing Materials**
(in minutes)

Chemical	BETEX	Butyl	Rubber	Neoprene	Nitrile	PVC	Teflon	Viton
Acetic acid	>360	180	120	360	360	180	>480	120
Acetic anhydride	>360	>240	60	210	180	90	>180	60
Ammonia,anhydrous	>360	>480	2V	>180	250V	15V	>300	
Ammonium hydroxide	>360	>480	120	360	360	180		>60
Benzene	15	30V	3V	12V	15V	1V	>200	9V
Chlorine	>360	>480	>480	>480	>480	30	>300	>480
Ethylene glycol	>360	>480	360	360	360	360	>480	
Formaldehyde	>360	>480	60	120	>360	70V	>180	>480
Hexane	5	15V	5	50V	360	30	>300	>480
Hydrogen peroxide	>360		>360	6	>360	>360		
Hydrochloric acid	300	>480	360	>360	360	360	>480	>480
Hydrofluoric acid	>480	>480	150V	360	120V	360	>480	>480
Methanol	100	>480	15	10V	180V	2V	>480	60
Nitric acid	>360	>480	360	150	100V	240		60
Pentachlorophenol			150	6-360V	>360	180		>480
Perchloroethylene	20	4V	0	15V	40V	15V	>180	>480
Phenol	>480	>480	60V	180	60	20V	>180	>480
PCB's		>480	60	>480	150V		>480	>480
Sodium hydroxide	>360	>480	360	360	360	>360	>480	>480
Sodium nypochlorite	>360	>360	360	360	360	360		
Styrene	10	30V	1V	12	30	30	>240	>180
Sulphuric acid	>360	>480	80	>360	10V	10V		>240
Toluene	<10	10V	5V	10V	20V	10V	>180	>180
Toluene diisocyanate		>480	7V	0-240V	240	480	>480	>480
Vinyl chloride					300			260
Xylenes	10	30V	2V	4V	60V	1V	>180	>60

Legend
* all permeation times are in minutes
* blank indicates no testing performed
* BETEX=Butyl on neoprene
* Rubber=natural rubber
* V Indicates highly variable data
* PVC = Polyvinyl chloride
* 0 indicates no service , usually because material degrades

4. Gas-tight suits sometimes are made of several materials. Permeation of the weakest material is the limiting factor. Permeation of each material should be measured, as well as the joint between each material. It may be wise to avoid suits made of more than one material.

5. The suits should allow access to the controls of the SCBA, whether the SCBA is worn inside or outside the suit. Many responders prefer that the SCBA be worn outside the suit so that they have unrestricted access to the controls.

6. Caution should be observed when dealing with sales staff for totally encapsulated suits. Many sales staff are not aware of the intricacies of spill response, the respiratory protection required, safety at spill scenes and permeation data for the clothing needed and thus may provide incorrect information.

7. The question of whether a SCBA should (or can be) worn inside or outside the suit is still controversial. Sales staff may indicated that suits with built-in face masks are not safe or legal, but this is not correct.

8. Any prospective suits should be tested for application in different weather conditions. Many suits cannot be used in cold weather because they are too stiff and some suits do not allow enough movement to perform many tasks.

9. Other users should be surveyed, to ensure that the suit has performed in actual spill situations.

The use of Totally-Encapsulated Chemical Protection Suits (TECPS) is an extensive topic. Wearing TECPS is often physically and mentally stressful. In hot weather, a person wearing such a suit can lose as much as 2 kg of water through perspiration. Organizations such as EPA have suggested that TECPS not be worn more than for one hour per day and then for two half-hour sessions.

The selection of other clothing material is less critical. Coveralls and such clothing are not worn when there is a skin-penetrating material spilled. Disposable coveralls are now frequently used at spill scenes and are very useful for minimizing contact with chemicals. Treated cellulose fabrics are now more popular than Tyvek because of their greater comfort. Goggles are used occasionally at the spill scene if there is a danger of material getting into eyes and if respirators with full facepiece masks are not worn. Splash guards are also occasionally used, but their use is not recommended, as they were originally designed to protect construction workers from spark and projectiles projected directly at the guard. In the case of liquids spills, the materials are often at ground level and the open area at the bottom of the device can actually be direct liquids to the face. Hard hats and ear protectors should be used as required in any hazardous situation. Some types of protective clothing, such as totally encapsulated suits do not readily allow for the use of hard hats, but most responders would not require both forms of protection at once.

Decontamination of clothing and breathing apparatus has been a controversial issue. There has been too much fixation on this task and far too complicated procedures have been proposed in the past. Totally encapsulated suits rarely need decontamination unless contact with a material has been made, then specific chemical procedures should be consulted. Generally, if the contaminant is a gas, the suit should be hung in a well-ventilated area, away from the sun and away from people, for about two weeks. If the material is a liquid that permeates, the suit may have to be destroyed or special procedures followed in consultation with the manufacturer. Non-permeating liquids or solids can be washed from the suit by placing the person in the

suit under a specially-designed shower or other water spray. If the material is oily or can be removed easier with a detergent, this can be used. Only dish-washing detergents are mild enough to not affect the suit material. More damage could be caused to the suit if a harsh decontaminating mixture is used, than if the suit is simply washed with water. Special detergents are available for decontaminating for bacteria and viruses, however, mild chlorine and peroxide solutions have also been used.

Boots must almost always be decontaminated after leaving a chemical spill incident. A child's wading pool with a mild detergent is a suitable solution for many situations. The water must often be treated as contaminated waste, just as the water from the suit decontaminations noted above. Gloves can be washed separately in a bucket in a manner similar to boots.

If it is suspected that equipment is contaminated, it is far better to dispose of it or put it into secure containers for further assessment, than to try to reuse it without the certainty that it is in good condition. Management will certainly be sympathetic and replace any equipment. For many organizations, this occurs so infrequently that the occasional loss is not a serious economic problem.

6.0 Confined Spaces

Confined spaces are those areas with poor air circulation where gas concentrations can rise far beyond danger levels, thus there is a high potential for oxygen deficiency. There is also the danger of entrapment and fire. Confined spaces include such locations as sewers, closed rooms, silos. Special occupational health and safety rules govern entry and working in confined spaces because they pose a high hazard. In many jurisdiction, recording of the entry into confined spaces is required and details of activities and safety procedures must be recorded.

7.0 The Personal Protection Program

Response to chemical spills requires a complete program that includes medical testing, training, retraining, and practice. Purchasing, maintaining, upgrading and replacing equipment are also part of the program. One or more persons in the organization should be responsible for supervising, coordinating and developing the program. A body of literature is available to help with establishing a recognized and systematic program (EPA, 1992; OE, 1991). The program should be based on a carefully developed policy concerning spill-site entry procedures and minimum requirements for training and equipment. Organizations such as Environment Canada and the U.S. Environmental Protection Agency have had such programs and policies for many years. For example, anyone entering a spill site must have a minimum of one week of training in using the equipment and a refresher course of at least two days must be taken every year. Environment Canada has issued their spill responders with an SCBA and a totally encapsulated suit with all the accessories. This equipment is signed out by the employees and kept until they leave the program. The equipment is repaired and replaced on a regular basis.

Training at regular intervals is very important. In the United States, 40 hours of training are required before an individual can enter a site. Annual refresher courses are also required. Similar requirements should be put into place by any response organization. It is also important to recognize that first-responders are generally like first-aiders. They perform limited emergency duties at the site but refer to specialists

for further advice and follow-up action. Just as the first-aider does not perform surgery at the site, those who respond to chemical spills should not be required to perform task beyond their training and capability. Professionals in the fields of chemistry and site remediation should be consulted and a network of information sources be built up by any response organization.

In conclusion, There are many requirements for a thorough chemical spill response program. This includes recording-keeping, the developing check lists for equipment testing, donning and doffing of equipment and site entry procedures. Detailed site safety plans and standard operating procedures must be developed. A specification should be in place to ensure that persons required to respond are fit to do so and this should include regular medical checkups. A regular practice program and a regular technical refresher program are essential.

8.0 References

ACGIH, *1999 TLVs and BEIs*, American Conference of Governmental Industrial Hygienists, Cinncinnati, OH, 1999.

Beach, R.A., "Information Systems and Reporting - Canadian Systems", in *Hazardous Materials Spills Handbook*, G.F. Bennett, F.S. Feates and I. Wilder, Eds, McGraw-Hill, New York, NY, pp. 3-45 to 3-54, 1982.

CSA (Canadian Standards Association), *Compressed Breathing Air and Systems*, Canadian Standards Association, CAN3-Z180.1-M85, Toronto, ON, 1985.

CSA (Canadian Standards Association), *Selection, Care and Use of Respirators*, Canadian Standards Association, Z94.4-93, Toronto, ON, 1993.

EPA, *Standard Operating Safety Guides*, U.S. Environmental Protection Agency, Washington, D.C., 1992.

Fingas, M.F. and C. Lau, "Recent Chemical Spill Data", in *Proceedings of the Thirteenth Technical Seminar on Chemical Spills*, Environment Canada, Ottawa, Ontario, pp. 327-369, 1996.

Fingas, M.F., "Personal Protection at Spill Scenes", *Spill Technology Newsletter*, Vol. 12, No. 2, 1987.

Fingas, M.F., N. Laroche, G. Sergy, B. Mansfield, G. Cloutier and P. Mazerolle, "A New Chemical Spill Priority List", in *Proceedings of the Eighth Technical Seminar on Chemical Spills*, Environment Canada, Ottawa, ON, pp. 223-332, 1991.

Forsberg, K. and L.H. Keith, *Chemical Protective Clothing*, Lewis Publishers, Boca Raton, 1995.

NIOSH, *Occupational Safety and Health Guidance Manual for Hazardous Waste Site Activities*, National Institute for Occupational Safety and Health (NIOSH), Occupational Safety and Health Administration (OSHA), U.S. Coast Guard (USCG) and U.S. Environmental Protection Agency (EPA), U.S. Government Printing Office, Washington, D.C., 1985.

NIOSH, *NIOSH Pocket Guide to Chemical Hazards*, National Institute for Occupational Safety and Health (NIOSH), U.S. Government Printing Office, Washington, D.C., 1994.

OE, *Occupational Health and Safety Guidance Manual for Contaminated Site Activities*, Operating Engineers Local 115, Joint Apprenticeship and Training Program, Burnaby, BC, 1991.

Appendix -1 *Table of Protective Considerations for Frequently-Spilled Substances*

		Health Exposure Limits							Maximum Use Capacity for Respirators[1] (PPM)				
Name	**Significant Vapour at Normal Temperature**	**TLV (ppm)**	**TLV (mg/m³)**	**STEL (ppm)**	**STEL (mg/m³)**	**IDLH (PPM)**	**IDLH (mg/m³)**	**Concern with Skin Contact**	**Canister half-face**	**Regular Canister**	**Gas Mask**	**SCBA**	**Need TECPS under Normal Conditions?[2]**
Acetic acid	✔	10		15		50		corrosive	10	25	50	unlimited	c
Acetic anhydride	✔	5				200		corrosive	50	125	200	unlimited	c
Acetaldehyde	✔	100		150		2000			400	1000	2000	unlimited	
Acetone	✔	500		750		2500			500	1000	2500	unlimited	
Acrylonitrile	✔	2		10		85			20	50	85	unlimited	
Aldrin		0.02	0.25	0.05	0.75	2	25	absorbed	0.5	1	2	unlimited	
Aluminum sulfate													
Aminocarb													
Ammonia	✔	25		35		300			50	150	300	unlimited	
Ammonium chloride	*as fume*	5	10	9	20				10	25	50	unlimited	
Ammonium hydroxide	*as ammonia*								50	150	300	unlimited	
Ammonium nitrate													
Ammonium phosphates													
Ammonium sulfate													
Aniline		2				100		permeation	20	50	100	unlimited	
Atrazine		0.6	5						2	5	10	unlimited	
Azinphosmethyl		0.02	0.2			0.8	10	absorbed	0.2	0.4	0.8	unlimited	
Benzene	✔	0.5		2.5		500		*permeation*	10	50	200	*unlimited*	c
Benzene hexachloride (Lindane)		0.04	0.5	0.1	1.5	4	50	absorbed	0.4	2	4	unlimited	
Benzoic acid													
Biphenyl		0.2		0.6		16			2	8	16	unlimited	
2-Butanol		100		150		2000			200	1000	2000	unlimited	
Butyl Acetate		150		200		1700			200	1000	1700	unlimited	
Butyl alcohol				25		1400			150	750	1400	unlimited	
Calcium chloride													
Calcium cyanide													
Calcium hydroxide		1.6	5						dust only	dust only	11	unlimited	
Calcium hypochlorite													
Calcium oxide		0.9	2	2	5	11	25		dust only	dust only	11	unlimited	
Calcium phosphate													
Carbon dioxide	✔	5000		30000		40000			asphyxiant			unlimited	
Carbon monoxide	✔	25		200		1200			100	500	1200	unlimited	
Carbaryl		0.6	5	1.2	10	12	100		1	6	12	unlimited	

Appendix -2 Table of Protective Considerations for Frequently-Spilled Substances

		Health Exposure Limits							Maximum Use Capacity for Respirators[1] (PPM)				
Name	Significant Vapour at Normal Temperature	TLV (ppm)	TLV (mg/m³)	STEL (ppm)	STEL (mg/m³)	IDLH (PPM)	IDLH (mg/m³)	Concern with Skin Contact	Canister half-face	Regular Canister	Gas Mask	SCBA	Need TECPS under Normal Conditions? [2]
Carbon tetrachloride	✔	5		10		200		permeation	20	100	200	unlimited	
Chlorpyrifos		0.01		0.03		10		permeation	1	5	10	unlimited	
Chlordane		0.03	0.5	0.1	2	6	100	absorbed	1	3	6	unlimited	
Chlorine	✔	0.5		1		10		corrosive	5	5	10	unlimited	✔
Chlorodifluoromethane	✔	1000		1250		2500			500	1500	2500	unlimited	
Chromic acid								corrosive					c
Cobaltous nitrate													
Copper sulfate													
Cresol		5		10		250			25	125	250	unlimited	
Cyclohexane	✔	200		400		1300			250	700	1300	unlimited	
Demeton		0.1		0.3		0.9		absorbed	0.5	0.5	0.9	unlimited	
Diazinon		0.01	0.1	0.02	0.3			absorbed	0.2	0.5	1	unlimited	
Dicamba													
1,2-dichlorobenzene		25		50		200			50	100	200	unlimited	
1,2-dichlorotetrafluoroethar	✔	1000		1250		15000			asphyxiant			unlimited	
Dichlorvos		0.10	0.9	0.3		11	100	absorbed	2	5	10	unlimited	
Dieldrin		0.016	0.25	0.05	0.75	3.16	50	absorbed	1	2	3	unlimited	
Diethylamine	✔	5		15		200		irritation	50	100	200	unlimited	c
Dimethylamine	✔	5		15		500		irritation	100	250	500	unlimited	c
Dinoseb													
Diquat		0.03	0.5					absorbed					
Ethyl alcohol	✔	1000		5000		3300			400	2000	3300	unlimited	
Ethyl acetate	✔	400		1000		2000			1000	1500	2000	unlimited	
Ethyl acrylate	✔	5		15		300			50	150	300	unlimited	
Ethylbenzene	✔	100		125		800			150	400	800	unlimited	
Ethylene	✔	10000							asphyxiant only			unlimited	
Ethylene dichloride	✔	10		20		50			5	25	50	unlimited	
Ethylene glycol		10							5	25	50	unlimited	
Ethylhexanol													
Fenitrothion													
Ferric chloride													
Formaldehyde	✔	0.75		2		20			5	10	20	unlimited	
Formic acid	✔	5		10		30			5	15	30	unlimited	

Appendix -3 Table of Protective Considerations for Frequently-Spilled Substances

		Health Exposure Limits							Maximum Use Capacity for Respirators[1] (PPM)				
Name	Significant Vapour at Normal Temperature	TLV (ppm)	TLV (mg/m³)	STEL (ppm)	STEL (mg/m³)	IDLH (PPM)	IDLH (mg/m³)	Concern with Skin Contact	Canister half-face	Regular Canister	Gas Mask	SCBA	Need TECPS under Normal Conditions?[2]
Hexane	✔	50		100		1100			not effective			unlimited	
Hydrazine	✔	0.02		0.1		50			limited usefullness		2.5	unlimited	
Hydrochloric acid	✔	5		10		50		corrosive	10	25	50	unlimited	c
Hydrofluoric acid	✔	3		6		30		corrosive	5	15	30	unlimited	c
Hydrogen peroxide	✔	1		2		75		corrosive	limited usefullness		75	unlimited	c
Isopropyl alcohol		200		400		2000			500	1000	2000	unlimited	
Malathion		0.7	10	1.5	20	18	250	absorbed	5	10	18	unlimited	
Maleic anhydride		0.25		0.75		2.5	10		limited usefullness		2.5	unlimited	
Mercury		0.006	0.05	0.06	0.5	1,2	10	absorbed	0.2	0.5	1.2	unlimited	
Methoxychlor		0.70	10	1.4	20	350	5000		70	200	350	unlimited	
Methyl alcohol	✔	200		250		6000		permeation	not effective			unlimited	
Methyl chloride	✔	50		100		2000		permeation	not effective			unlimited	
Methyl ethyl ketone	✔	200		300		3000		de-fatting	600	1500	3000	unlimited	
Methyl methacrylate		50		100		1000			200	500	1000	unlimited	
Methylene chloride	✔	100		300		2300		de-fatting	limited usefullness			unlimited	
Naphthalene		10		15		250			50	150	250	unlimited	
Nitric acid	✔	2		4		25		corrosive	limited	15	25	unlimited	c
Nitrogen (liquefied)	✔							freezing	asphyxiant only			unlimited	
Nonylphenol													
Oxygen (liquefied)	✔							freezing				unlimited	
Paraquat		0.05	0.5			0.09	1	absorbed	0.09	0.09	0.09	unlimited	
Parathion		0.01	0.1	0.02	0.3	0.8	10	absorbed	0.2	0.4	0.8	unlimited	
PCBs		0.01	0.1					absorbed	2	5	10	unlimited	
Pentachlorophenol		0.05	0.5	0.14	1.5	0.2	2.5	absorbed	0.2	0.2	0.2	unlimited	
Perchloroethylene	✔	25		100		150		defatting	limited usefullness		150	unlimited	
Phenol	✔	5		15.6		250		absorbed	50	125	250	unlimited	
Phosphamidon												unlimited	
Phosphoric acid		0.25	1	0.7	3	245	1000	corrosive	50	125	245	unlimited	c
Phosphorus		0.02				1	5		not effective			unlimited	
Phthalic anhydride		1		4		10	60	sensitizer	2	5	10	unlimited	
Picloram		1	10	2	20				20	50	100	unlimited	
Potassium chloride													
Potassium cyanide													

Appendix -4 Table of Protective Considerations for Frequently-Spilled Substances

		Health Exposure Limits							Maximum Use Capacity for Respirators[1] (PPM)				
Name	Significant Vapour at Normal Temperature	TLV (ppm)	TLV (mg/m^3)	STEL (ppm)	STEL (mg/m^3)	IDLH (PPM)	IDLH (mg/m^3)	Concern with Skin Contact	Canister half-face	Regular Canister	Gas Mask	SCBA	Need TECPS under Normal Conditions? [2]
Potassium hydroxide		0.9	2					corrosive	20	40	80	unlimited	
Potassium permanganate													
Propylene glycol													
Propylene oxide	✔	5		10		400		irritation	not effective		400	unlimited	
Pyridine	✔	5		10		1000		irritation	50	250	1000	unlimited	
Sodium carbonate													
Sodium chlorate													
Sodium chloride													
Sodium cyanide (as CN^-)						11	25	moisture produces toxic CN^-			11	unlimited	
Sodium hydroxide		1.2	2	2.4	4	6	10	corrosive	6	6	6	unlimited	
Sodium hypochlorite								corrosive					
Sodium silicate													
Styrene	✔	20		40		700		irritation	100	200	700	unlimited	
Sulfur													
Sulfur dioxide	✔	2		5		100			20	50	100	unlimited	
Sulfuric acid	✔	0.2	1	0.7	3	4	15	corrosive	2	2	4	unlimited	
Tetraethyl lead		0.007	0.1	0.02		3	40	absorbed			3	unlimited	
Thallium sulfate													
Toluene	✔	50		150		500		permeation	100	250	500	unlimited	
Toluene-2,4-diisocyanate	✔	0.005		0.02		2.5		sensitization	escape only		2.5	unlimited	
Trichloroethane	✔	10		20		100		permeation	escape only		100	unlimited	
Trichloroethylene	✔	50		100		1000		de-fatting	escape only		1000	unlimited	
Trichlorofon								absorbed					
Trifluralin								absorbed					
Trinitrotoluene		0.01	0.1	0.02		53	500	permeation	escape only		50	unlimited	
Vinyl acetate		10		15					20	50	100	unlimited	
Vinyl chloride	✔	1		2.3				hazardous	escape only		25	unlimited	
Xylene	✔	100		150		900			200	450	900	unlimited	
Zinc chloride (fumes)		0.2	1	0.4	2	9	50		2	5	9	unlimited	
Zinc cyanide													
Zinc oxide (dust/fumes)		1.5	5	2.955	10	150	500		50	75	150	unlimited	
Zinc sulfate													

		Health Exposure Limits							Maximum Use Capacity for Respirators[1] (PPM)				
Name	Significant Vapour at Normal Temperature	TLV (ppm)	TLV (mg/m^3)	STEL (ppm)	STEL (mg/m^3)	IDLH (PPM)	IDLH (mg/m^3)	Concern with Skin Contact	Canister half-face	Regular Canister	Gas Mask	SCBA	Need TECPS under Normal Conditions?[2]

1 - Maximum Use Concentration is taken from commercial literature or is generally taken that MUC for a gas mask is equal to IDLH, for a full-face piece respirator is half of IDLH and for a half-face piece air purifying respirator is 1/5 IDLH. It is important to note that MUC may vary with manufacturer and model, It is important to consult with the manufacturer for specific data.

2 - Entry into spill situations where the substance and its concentrations are unknown should always be done with a TECPS or Totally-encapsulated Chemical Protective Suit

c is conditional on potentially high vapour concentrations

Ammonia Gas Releases: Some Recent Prevention, Preparedness and Response Activities of Public Health Agencies in Quebec

P. Guerrier, S. Sebez, M. Rhainds
Environmental Health Service
Regional Public Health Department - Quebec City Region
Beauport, Québec, Canada
pguerrier@cspq.qc.ca

Abstract

In Quebec, accidents involving ammonia, such as a pipe rupture in a Montreal meat processing plant causing the death of one worker, have contributed to the awareness of the public, industry and governments of the potential impacts of ammonia gas releases. As there are no ammonia producers in Quebec, accidents may take place further in the product life-cycle at the transportation level, despite stringent regulations, and at the user level where lack of training and financial constraints may facilitate the occurrence of such events. This paper deals with some recent prevention, preparedness and response activities related to ammonia gas releases and undertaken by Regional Public Health Departments in Quebec.

1.0 Introduction

In the last two decades, spectacular accidents involving hazardous substances (such as fires, explosions and spills) have contributed to public, industry and government awareness of the possible health, environmental and financial impacts of chemical accidents. In Quebec, the 1988 PCB fire in a Saint-Basile-le-Grand storage site (Montérégie), which received broad media coverage, led fortunately to no casualties but required a major evacuation as well as considerable involvement, especially from public health officials (Godon et al., 1990).

In 1997, a propane explosion in Warwick (Centre du Québec) had more dramatic consequences for responders: it caused the death of four firefighters and led health and safety officials to look more closely at the preparedness (training) activities required for responders (CSST, 1995). Spills may also have severe impacts. Releases of toxic gases such as ammonia, chlorine or sulphur dioxide are particularly important as these substances might affect not only workers and responders but even the public which, in certain circumstances, must be protected from potential or actual hazardous vapours. While most toxic gases releases are minor, some presenting potential risks to the population or causing health consequences have occurred, in particular during transportation and use. In Canada, derailments of freight trains carrying chlorine in Mississauga (Ontario) in 1979 and St-Léonard-d'Aston (Québec) in 1989 received also much coverage by the media. Despite the lack of casualties, 217,000 and 1,000 civilians were respectively evacuated (Denis, 1993).

Despite the strong debate surrounding chlorine (Guerrier et al., 1996), data on chemical spills indicate that ammonia, especially anhydrous ammonia, must also be a concern for health and safety personnel and the emergency community. In Quebec, an accidental ammonia release in a meat processing plant in Montreal in 1997 causing one death was a reminder that this chemical must be a priority for emergency planning activities (CSST, 1997).

This paper will focus on ammonia gas releases and will present some recent prevention, preparedness and response activities of Regional Public Health Departments in Quebec.

2.0 Background on Ammonia

2.1 Ammonia: a toxic gas and a hazardous substance priority.

Ammonia is a colourless, acrid-smelling, low density gas at ambient temperature and normal atmospheric pressure (WHO, 1990). In the international classification system, (anhydrous) ammonia belongs to Class 2 (gases) in the subdivision 2.4 (Corrosive gas). Its 4-digit PIN (Product Identification Number) is UN 1005 (Transport Canada, 1996).

Table 1: Product Identification Number of Various Commercial Forms of Ammonia

PIN	Form
1005	• Anhydrous ammonia • Liquid anhydrous ammonia • Aqueous solution containing more than 50% ammonia
3318	• Aqueous solution containing more than 50% ammonia
2672	• Aqueous solution containing between 10 and 35% ammonia
2073	• Aqueous solution containing between 35 and 50% ammonia

Ammonia is among the five most abundantly produced chemicals in the world. About 80% of ammonia produced is used in fertilizers. It is also used as a refrigerant and in the manufacture of plastics, explosives, pesticides, and other chemicals. It is found in many household and industrial-strength cleaning solutions. It easily dissolves in water to form a caustic solution called ammonium hydroxide (ATSDR, 1995). The impact of ammonia on the environment has been described extensively (Lawuyi and Fingas, 1993).

In the emergency response community, ammonia is a relatively well-known hazardous material (table 2). Nevertheless, responders must be advised that ammonia gas is a very volatile compound that may ignite if its concentration is between 16 and 25 % in air. It has a relatively high autoignition point (651°C). Moreover, as the density of ammonia in a gaseous form is inferior to air density (0,6), ammonia vapours tend to rise in the atmosphere but in certain conditions, anhydrous ammonia vapours may behave like a heavy gas (Environment Canada, 1985).

In Canada, a Chemical Spill Priority List was established by Environment Canada in 1991. This list was developed by a simple ranking of reported spill frequency, supply volumes, historical spill volumes, toxicity data, stability and persistence. Ammonia is at the top of this list (Fingas et al, 1991). Ammonia was also identified in other documents such as the MIACC List 1 of Priority Hazardous Substances in 1994 (MIACC, 1994).

Table 2: Summary of Physical and other Properties of Ammonia

Characteristics		Source
Molecular Formula	NH_3	Leblanc et al. (1978)
Molecular Weight	17,03	Leblanc et al. (1978)
Melting Point	$-77,7^{o}C$	WHO (1990)
Boiling Point	$-33,35^{o}C$	WHO (1990)
Autoignition point	$651^{o}C$	WHO (1990)
Lower and upper explosion limits	16 - 25%	WHO (1990)
Relative vapour density ($25^{o}C$)	0,6	WHO (1990)
Detection levels	In water: 1,5 ppm In air: 35 mg/m^3	WHO (1986)

2.2 Ammonia: a Toxic Gas with Potential Major Health Effects

Ammonia is absorbed readily through mucous membranes and the intestinal tract, but not through the skin. Most exposures to ammonia are by breathing the gas. About 80% of inhaled ammonia dissolves in the mucous lining of the upper respiratory tract and does not reach the alveoli (WHO, 1990).

Even with very short or low-level exposures, most people will notice the pungent odour and experience burning of the eyes, nose and throat. With higher doses, coughing or chocking may occur. Severe exposure can cause death from throat swelling or from chemical burns to the lungs. There are many reports in the literature of human deaths resulting generally from acute accidental exposure to concentrated aerosols of anhydrous ammonia. Short-term exposure to 5 000-10 000 ppm is considered to being rapidly fatal in humans (ATSDR, 1990).

Eye exposure to concentrated gas or liquid can cause serious corneal burns or blindness. Skin contact with ammonia containing liquids may cause burns. Contact with rapidly escaping ammonia gas from a leaking pressurized cylinder can cause frostbite injury. There is no antidote for ammonia poisoning, but its effects can be treated and most people do recover fully. Persons who have experienced serious signs and symptoms (such as severe or persistent coughing, tearing eyes or running nose) may require close medical observation for several hours. After a severe exposure, symptoms may progress over 18 hours (ATSDR, 1995).

Exposure to high concentrations of ammonia is believed to cause an asthma-like syndrome in some subjects. It was first described by Brooks et al. in 1985 and termed RADS (Reactive Airways Dysfunction Syndrome) (Brooks et al., 1985). This condition, referred to as irritant induced asthma in subjects who had no history of asthma, is characterized by the presence of non-specific bronchial hyper-

responsiveness. There is no latency period. The physiopathology reactions involved in RADS are still unknown. A recent study suggests that lymphocytic infiltration of the bronchial layers, denudation of the mucosa, and thickening of the basement membrane are key pathological features (Bhérer et al., 1994).

2.3 Ammonia: Guidelines to Assist in the Control of Health Hazards.

Several guidelines have been developed to assist in the control of health hazards associated with toxic gases such as ammonia, chlorine and sulphur dioxide. Threshold Limit Values (TLVs™) are intended for use in the practice of industrial hygiene. Immediately Dangerous to Life and Health Concentrations (IDLHs) have been established to ensure that a worker can escape without injury or irreversible health effects from an IDLH exposure in the event of the failure of respiratory protection equipment. Emergency Response Planning Guidelines (ERPGs) are intended for use in community emergency planning efforts, where there is concern for exposure to sensitive members of the population, such as the young, the old, and pregnant women. ERPGs (levels 1,2,3) are used to evaluate the health significance of the estimated concentrations (Cavender et al., 1993).

Table 3 TLV™, IDLH and ERPGs for Ammonia (Compared to the Guidelines for Chlorine and Sulphur Dioxide) (Bhérer et al, 1999)

	Ammonia	Chlorine	Sulphur Dioxide
TLV-TWA: (ACGIH)	25	0,5	2
IDLH: (NIOSH)	500	25	100
ERPG-1: (AIHA) (*)	25	1	0,3
ERPG-2: (AIHA) (**)	200	3	3
ERPG-3: (AIHA) (***)	1000	20	15
Immediate death	5000	1000	400

(*) ERPG-1: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odor.

(**) ERPG-2: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

(***) ERPG-3: The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

3.0 Ammonia in Quebec

3.1. Ammonia Life-cycle

In Quebec, public health activities related to emergency planning must be undertaken by public health agencies called *Directions régionales de santé publique* (DRSPs). In most regions, environmental emergencies such as chemical spills have been identified as events for which DRSPs have to undertake prevention, preparedness and response activities.

The life-cycle management process is an interesting approach for emergency planners such as DRSPs to improve their prevention, preparedness and response activities to accidental releases of hazardous substances. With regard to ammonia in Quebec, transportation, distribution and use stages constitute the most important stages to study. "Transportation" is the physical movement of chemicals by rail, truck and ship. Businesses which supply, handle or sell chemicals, i.e. packagers, processors, reformulators and importers, constitute the "Distribution" phase. The "Use" stage applies to commercial enterprises and institutions or which consumer use is a secondary consideration (Shrives, 1993).

3.1.1 Production and Transportation of Ammonia in Quebec

In Canada, the production of ammonia has doubled from 2,6 million tons in 1983 to more than 5 million tons in 1996 (Agriculture Canada, 1997). In 1997, more than 72 % of anhydrous ammonia was produced in Alberta. There are no manufacturing ammonia plants operating in Quebec. Anhydrous ammonia is shipped as compressed gas by railroad tank cars usually containing from 75 to 80 tons of product. In 1996, the CN transported nearly 700 000 tons of anhydrous ammonia during 9263 deliveries (CN, 1997). Anhydrous ammonia is also transported by truck in cylinders (in general, containing 45,4 or 68 kg of ammonia) or in pressurized tanks (mainly from 5 to 25 tons, up to 30 tons) (Stanchem, 1993).

3.1.2 Storage and use of Ammonia in Canada

Anhydrous ammonia is usually liquefied for storage in pressurized or refrigerated tanks. The storage mode is summarized in Table 4.

Table 4: Storage Modes of Anhydrous Ammonia

Characteristics	Storage mode		
	Pressurized	Semi-pressurized	Refrigerated
Tank type	Cylindrical and horizontal	Spherical	Cylindrical and vertical
Storage capacity	10 to 100 tons	500 to 5000 tons	5000 to 40 000 tons
Storage temperature	Ambient	-10 to 10°C	≤ -33,3°C
Internal pressure in tank	@ 900 kPa	170 to 520 kPa	Ambient

In Quebec, ammonia is mainly used in agriculture but many other users, such as pulp and paper or mining companies also exist. Table 5 summarizes the ammonia volumes used in Canada (CPI, 1990).

Table 5 Ammonia Volumes Used in Canada (1990)

Use	Volume (tons)
Manufacturing of Urea	1 242 000
Manufacturing of Nitric Acid	300 000
Manufacturing of Ammonium Nitrate	235 000
Manufacturing of Ammonium Sulphate	86 000
Manufacturing of Ammonium Phosphate	170 000
Other agricultural use	435 000
Pulp and paper	19 000
Mines and metallurgy	35 000
Manufacturing of diamine hexamethylene	5 000
Manufacturing of thanolamines	4 000
Manufacturing of amines and nitriles	5 000
Other uses	16 000
Exports	1 200 000
Total production	**3 752 000**

3.2 Ammonia Spills in Quebec

3.2.1 Prevention and Preparedness Activities of the Public Health Agencies

DRSPs frequently collaborate with industry and municipalities to prevent accidents involving hazardous substances: their activities may be linked to existing industries where hazards have been identified or to industrial regulated projects where hazardous materials are expected to be manufactured, transported, stored or used.

At the provincial level, the DRSPs work closely with various agencies, such as the ministère de l'Environnement (MENV). The MENV's mandate is to:

- enforce legal requirements or regulations aimed at minimizing the frequency and severity of technological and natural disasters;
- cooperate with various partners working in prevention notably with regard to spills.

The DRSPs also benefit from their close relationship with the Quebec Occupational Health and Safety Commission, the CSST (Commission pour la santé et la sécurité du travail). The CSST's duties with regard to prevention are to:

- promote occupational health and safety;
- assist workers and employers in their efforts to achieve a healthier, risk-free work environment;
- inspect work premises.

In the Quebec City area (Region 03), industrial accident prevention activities set out by the DRSP-03 began in 1990. The activities involved several users of

hazardous materials, in particular a liquid storage company in the Port of Quebec and a major pulp and paper company located between the Port and downtown Quebec City. The collaboration produced detailed databases of these industries' hazardous chemicals. These databases could be used on computerized or hard-copy formats by the local responders. After these information management activities, the DRSP-03 collaborated in 1994 in the development of a full scale exercise simulating a toxic gas release (Rhainds et al., 1994).

In 1997, the DRSP-03 decided to offer training workshops on hazardous chemicals to first responders (firefighters, emergency medical staff, etc.) from inside and outside the region and to other persons interested in emergency response. The first training workshop dealt with ammonia (considered a chemical spill priority) and carbon monoxide (known as a residential and workplace hazard. This workshop, held in the Port of Quebec, was a success as more than 100 persons attended the activity. The program included particularly a presentation on ammonia life cycle (Tremblay, 1999) and a case story report by the Montreal Fire Department personnel that had responded to the ammonia release in a meat processing plant (Centre de santé publique de Québec, 1997).

Just a few months after this workshop, a real spill occurred in 1998 in Quebec City at the pulp and paper company. Following this spill, the DRSP-03 and the other response organizations met with the supplier and the company. The company decided to shut down the use of ammonia and to switch instead to urea, a more expensive product, for its secondary water treatment, thus making the neighbouring community much safer.

The DRSP-03 continued its efforts concerning ammonia, collaborating with cold storage facilities, food processing and beverage plants using ammonia as a refrigerant. Activities (inspections, training sessions) were based on the FRIGO program described in a guide published by the CSST and dealing with preventive measures for cooling systems using ammonia (CSST, 1998). The Montreal-Centre DRSP collaborated in the preparation of this guide, which was published after the Montreal accident in a meat processing plant.

The DRSP-04 (Mauricie-Centre du Québec) is also concerned by the potential impact of industrial accidents on public health. The pulp and paper industry is highly developed in this region with fourteen pulp and paper plants generating 20% of the jobs in the manufacturing sector. Monitoring of the pulp and paper sector is a high priority for the DRSP. In 1999, the DRSP-04 selected this sector to undertake a study concerning ammonia as well as five (5) other hazardous substances transported and used by pulp and paper plants in the region: chlorine (UN 1017), sulphur dioxide (UN 1079), hydrogen peroxide (UN 2015), sodium hypochlorite (UN 1791) and caustic soda (UN 1823).

Table 6: Ammonia and Other Chemicals Used in the Pulp and Paper Industry: Their Importance in Terms of Spills in Canada.

Hazardous substance	Rank	Number of spills (1985-1994)	Spilled volume (in tons)
Ammonia	1	107	470
Chlorine	2	36	120
Sodium Hydroxide	18	92	8200
Sulfur Dioxide	44	16	90
Hydrogen Peroxide	92	7	0,71
Sodium Hypochlorite	93	11	58

The main objectives of this study were to:

1. Identify the pulp and paper plants operating in this region
2. Identify the major hazardous chemicals used by these pulp and paper plants
- Identify how these chemicals are shipped to the plants
- Identify the main distributors and transporters
- Evaluate the quantities of hazardous chemicals stored and used
- Identify protection measures and emergency plans carried out by the plants
3. Evaluate the transportation frequency and the quantities of chemicals transported to the plants
- Identify transportation corridors used for these chemicals
- Identify the inhabited zones crossed by these transportation corridors
4. Present the main characteristics of these zones (amount and density of population, presence of hospital centres, schools and other sites of population at risk, etc.)
- Identify the regional protection measures and emergency plans
5. Evaluate the risk potential and identify the main areas at risk
   - Carry out preventive measures and activities to undertake in public health

The results of this recent study should provide the public health response staff and other regional emergency responders valuable data and insight to the transportation and use of the selected hazardous materials in the Mauricie and Centre du Québec regions (Sebez, 1999).

3.2.2 Response Activities of Public Health Agencies related to Ammonia Releases

Several events involving ammonia have led to catastrophic consequences for public health and the environment: in Potchefstroom, South Africa (1973, 18 deaths, hundreds of injured), in Houston, Texas (1976, 5 deaths, 178 injured) and in Dakar, Senegal (1992, 116 deaths, 1150 injured) (Olive, M. et al., 1992).

In Canada, 241 accidental spills of anhydrous ammonia and ammonium hydroxide were reported between 1981 and 1993 in the NATES database (*National Analysis of Trends in Emergencies System*). Among these spills, 138 involved

anhydrous ammonia and 103 hydroxide ammonium solutions. According to Environment Canada, spills are more frequent in fixed installations. Nevertheless, spills associated with transportation are also frequent.

Table 7: Accidents involving Anhydrous Ammonia and Solutions According to the Life-cycle Stages (Environment Canada, 1999)

Life-cycle stages	Accident rates	
	Anhydrous ammonia	Ammonia solutions
Use	51,6 %	45,3 %
Road transportation	27,4 %	28,1 %
Rail transportation	8,9 %	9,4 %
Ship	0,8 %	0,0 %
Storage	7,3 %	10,1 %
Other	4,0 %	7,2 %

Ammonia spills may be linked to causes such as fires and explosions, equipment failure, human error and natural elements. Equipment failure and human errors are the main causes of ammonia spills.

Table 8: Main Causes of Ammonia Release

Cause of Accident	Percentages	
	Anhydrous Ammonia	Ammonia Solutions
Equipment failure	58,9 %	58,9 %
Human error	31,8 %	27,9 %
Natural elements (Including earthquakes and weather conditions)	4,7 %	1,6 %
Fires and explosions	2,8 %	0,8 %
Other	1,9 %	10,9 %

In 1978, Baldock calculated that the highest probability of an accident in a fixed installation involved a pipe rupture between a truck and a storing tank ($p = 1{,}00 \times 10^{-3}$ per terminal per year) and activities linked with ammonia synthesis ($p = 5{,}00 \times 10^{-4}$ per plant per year). The annual accident probability for transportation is relatively high: 1 / 3000 units for the main four transportation modes. Spills associated with transportation by truck are the most serious as they may lead in general to three deaths per accident (Baldock, 1978).

In Quebec, 60 incidents involving ammonia were reported to the CSST (Commission pour la santé et la sécurité du travail), between 1991 and 1995. To justify being reported, these incidents must have caused injuries resulting in the payment of compensation (CSST, 1998). Several major events involving anhydrous ammonia have occurred in a recent past.

In 1997, the Montreal meat processing plant accident caused 1 death and 22 wounded (including 5 firefighters) after a pipe ruptured when a box was accidentally dropped on it (CSST, 1997).

In the Quebec City region, a tank truck carrying several tons of anhydrous ammonia was hit by a car on the same year. No ammonia was released but the content had to be transferred to another truck. An accident also took place in 1998 in a pulp and paper plant. As a result of human error, ammonia was released from a horizontal pressurized cylindrical tank (20 metric tons, 32,6 m^3) during a truck delivery. The Quebec City Fire Department hazmat team was called. One firefighter and several employees (from the plant and a nearby liquid storage company) were exposed to ammonia vapours. The population in the neighbourhood noticed nothing more than the particular smell of ammonia. In recent years, minor spills have also occurred in a curling club and in food and beverage plants.

After this last accident, two meetings were set up with the pulp and paper company to evaluate and identity ways of improving the response of organizations involved (company, distributor, firefighters, EMS and public health, 911 dispatch centre and hospital facilities). Several recommendations were made to the various organizations regarding communications, emergency plans, maps locating hazardous materials, respiratory protection equipment, the role of hospital centres, media access to information and training.

4.0 Concluding remarks

Since there are no ammonia manufacturing plants in Quebec, major accidents involving ammonia release will occur during transportation or use of this hazardous material. Recent events in Quebec should serve as a reminder that, although this product is frequently used without problem, exposure to high concentration levels can cause, in certain circumstances, the death of workers and may pose a serious threat to responders, such as firefighters. Moreover, this toxic gas can also put the general public at risk, particularly in the event of a transportation accident or a fixed installation accident near a densely populated area.

Joint municipal-governmental-industrial prevention and preparedness activities are crucial to reduce the risks in the different stages of this product life-cycle or to effectively respond to an accidental release, if one occurs despite all preventive measures.

In the province of Quebec, several DRSPs are investing time and human resources to train public health responders and other emergency personnel on toxic gases and on the risks related to the transportation and use of such gases in their regions. All these activities do not prevent accidental releases. However, these activities help responders react more effectively, protect workers and the public and may save lives. In certain cases, to substitute a toxic gas with a less dangerous (but often more costly) product remains the best decision to improve the safety of a neighbourhood.

5.0 Acknowledgment

The authors would like to thank all their colleagues involved in environmental emergencies in the DRSPs. Special thanks also to Thierry Tremblay, now with the Department of National Defence for his research and to Daniel Houle for his valuable suggestions concerning the English version. Thanks also to Lucie Murphy for her contribution to the final version. The opinions expressed herein are those of the

authors alone, and do not necessarily represent the official positions of agencies with which they are affiliated.

The authors are not responsible for errors and omissions, and are not liable for any direct, indirect, or consequential damages flowing from the use of the information contained in this text.

M. Sebez now works for DRSP-Mauricie-Centre du Québec in Trois-Rivières, Québec.

6.0 References

Agriculture et Agro-Alimentaire Canada, *Canadian Fertilizer Consumption, Shipments and Trade 1995 / 96. Farm Income Policy and Programs Directorate*, Agriculture and Agri-Food Canada, Ottawa, 32 p, 1997.

AIHA, *Emergency Response Planning Guidelines*, American Industrial Hygiene Association, Fairfax, VA, 1988.

ATSDR, *Toxicological Profile for Ammonia.* Agency for Toxic Substances and Disease Registry, U.S. Department of Health and Human Services, TP-90-03, 125 p., 1990.

ATSDR, http:// www.atsdr.cdc.gov/mmg2.html, Agency for Toxic Substances and Disease Registry, 1995.

Baldock, P.J., *Accidental Releases of Ammonia: An Analysis of Reported Incidents,* Loss Prevention, vol.13, 1979, p.35-42.

Bhérer, L., Cushman, R., Courteau, J.P., Quévillon, M., Côté, G., Bourbeau, J., L'Archevêque, J., Cartier, A., Malo, J-L., *Survey of construction workers repeatedly exposed to chlorine over a three to six month period in a pulpmill: III. Follow up of affected workers by questionnaire, spirometry, and assessment of bronchial responsiveness 18 to 24 months after exposure ended*, Occupational and Environmental Medecine, 51:225-228, 1994.

Bhérer, L., Guerrier, P., Lévesque, B., Rhainds, M., Roy, L.A., Sanfaçon, G. *Critères d'une intoxication et d'une exposition significative : les gaz irritants* , Comité de santé environnementale du Québec, Beauport (Québec) 1999.

Brooks, S.M., Weiss, M.A., Berstein, I.L., *Reactive Airways Dysfunction Syndrome (RADS). Persistent Asthma Syndrome after High Level Irritant Exposures,* Chest, 88:376-84, 1985.

Brooks, S.M., Weiss, M.A., Berstein, I.L., *Reactive Airways Dysfunction Syndrome. Case Reports of Persistent Airways Hyperreactivity Following High-Level Irritant Exposures*, J. Occup Med, 27:473-6, 1985.

Canadian Fertilizer Institute, *Fertilizer Production Capacity Data Canada,* Canadian Fertilizer Institute, Ottawa, Ontario, 10 p, 1997.

Canadien National, *Personal communication*, Canadien National, John L'Espérance, September 1997.

Cavender, Finis L., Gephart, Larry A., *Emergency Response Planning*, "The Practical Approach to Hazardous Substances Accidents", Conference Proceedings, Major Industrial Accidents Council of Canada (MIACC-CCAIM), Ottawa, 1993.

Centre de santé publique de Québec, *Atelier de formation sur les risques à la santé liés au monoxyde de carbone et à l'ammoniac*, Beauport (Québec), 30 octobre 1997.

CSST, *Accident entraînant un décès et vingt-deux blessés, le 21 mars 1997, vers 17h00, à l'usine Montpak située au 4293, rue Hogan à Montréal.* Direction régionale de l'île de Montréal - 5, Commission de la santé et de la sécurité du travail du Québec, Rapport d'enquête d'accident R773182, 24 p. + annexes, 1997.

CSST, Direction régionale Mauricie-Bois-Francs, *Accident mortel survenu à quatre pompiers volontaires de la Ville de Warwick le 27 juin 1993, rapport d'enquête d'accident*, Montréal, Québec, janvier 1995.

CSST, *Systèmes de réfrigération fonctionnant à l'ammoniac, Mesures de prévention*, Québec, DC 200-16280, 58 p., 1998.

Denis, Hélène, *Gérer les catastrophes, L'incertitude à apprivoiser*, Les Presses de l'Université de Montréal, Montréal, Québec, p.236, 1993.

Environnement Canada, *L'ammoniac*, Collection Enviroguide, Ministre des approvisionnements et Services Canada, En 48-10/16-1985F, Ottawa, Ontario, 136 p., 1985.

Environnement Canada, *Rapport statistique sur les déversements survenus au Canada 1984-1995*, Programme des urgences environnementales, Environnement Canada, En 49-14/5-3F, 88p., 1999.

Fingas, M., Laroche, N., Sergy, B., Mansfield, B., Cloutier, G., Mazerolle, P., *A New Chemical Spill Priority List*, Proceedings of the Eighth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, pp. 223-332, 1991.

Guerrier, P., Rhainds, M., Auger, P., Prud'homme, H., Leroux, R., *Chlorine Gas Releases: some recent prevention, preparedness and response activities of public agencies in Quebec,* Proceedings of the Tenth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, pp. 53-66, 1996.

Godon, D. , Guerrier, P., Leroux, R., *Project PIGES : A Geographic Information System Designed to Reduce the Risks to Health and the Environment due to Major Technological Disasters*, Proceedings of the Fourth International on Medical Geography, Norwich, UK, 16-19 July 1990, pp. 343-362, 1990.

Lawuyi, R., Fingas, M., *The Impact of Ammonia on the Environment*, Proceedings of the Tenth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, pp. 161-202, 1993.

Leblanc, J.R. Jr, Maohovon, S., Porter, R.E., "Ammonia" in Kirk-Ohtmer, *Encyclopedia Chemical Technology*, Vol. 2., John Wiley and Sons Inc., New-York, New-York, pp. 470-515, 1978.

Major Industrial Accidents Council of Canada, *MIACC Lists of Hazardous Substances, MIACC List 1, Priority Hazardous Substances*, Ottawa, 1994.

Olive, M., M. Vitris, S. Karoutsos, B. Diatta et J.M. Saissy , *Exemple d'une intoxication collective massive par l'ammoniaque : la catastrophe de la SONACOS à Dakar, mars 1992.* Résumés des communications et des affiches, 8e congrès national des SAMU, Elsevier, Paris, 1992.

Rhainds, M., Auger, P., Guerrier, P., Prud'homme, H., Exercice de simulation PIABS 1994, "Alerte jaune", Rapport d'évaluation de la participation de la Direction régionale de la Santé publique de Québec, Service Santé et Environnement, Beauport (Québec), Septembre 1994.

Sebez, S, *Corridors de transport utilisés dans l'approvisionnement en matières dangereuses des usines de pâtes et papiers: évaluation du potentiel de risque. Région Mauricie-Centre du Québec*, Essai de maîtrise, Département de médecine sociale et préventive, Faculté de médecine, Université Laval, 1999.

Shrives, J.S., *A Generic Framework for Life-Cycle Management of Hazardous Substances*, Chlorine Life-Cycle Accident Prevention Workshop Report, CCAIM-MIACC, Ottawa, Ontario, November 1993.

Stanchem, *Bulletin technique: L'ammoniac anhydre*, Stanchem Inc., Etobicoke, Ontario, 43 p., 1993.

Transport Canada, *Guide Nord-Américain des mesures d'urgence*, Ottawa, Ontario, 342 p., 1996.

Tremblay, T., *Risques à la santé, à la sécurité et pour l'environnement associés à la fabrication, à l'utilisation, au transport, à la manutention et à l'entreposage de l'ammoniac anhydre*, Essai, Faculté des lettres et des sciences humaines, Université de Sherbrooke, Québec, mars 2000.

WHO - International Programme on Chemical Safety, *Ammonia Health and Safety Guide,* Health and Safety Guide N°37, World Health Organization, Geneva, 1990.

A Pilot Study to Investigate the Causes of Spontaneous Combustion of Tire Chips Material

N. Barnea, J.K. Farr
National Oceanic and Atmospheric Administration
Seattle, Washington USA
D.E.B. Nightingale
Washington Department of Ecology
Olympia, WA USA

Abstract

A pilot study was conducted to investigate why tire chips used as road fill material spontaneously combust. Three 55-gallon plastic drums were insulated with thermal blankets wrapped around each drum to simulate the insulation provided by approximately three meters of tire chips. A layer of dirt was placed at the bottom of each drum and the rest of the space was filled with tire chips containing steel wires. Water was poured into the drum to saturate the soil and tire chip layer, and the drums were sealed. An air sampling tube and temperature probes were placed inside each drum. Temperature measurements and air samples were taken over a period of two months.

Over the duration of the experiment, the maximum temperature rose less than 3°C. Gas sampling indicated a decrease in oxygen level from 21% to 5-10%, depending on the drum; increase in carbon monoxide and carbon dioxide levels; and presence of hydrocarbon compounds. Inside drum temperature remained largely unaffected by the fluctuation of the ambient temperature.

1.0 Background

Tire chips have been used as road fill material in 70 locations around the United States. In two locations in Washington state, tire chips road fill spontaneously ignited (Nightingale and Green, 1997). The combustion of tire chips underneath the road surface generated toxic gases, vapors, and liquid pyrolysis product, and required extensive, costly response and remediation actions (Barnea *et al.*, 1997).

Spontaneous combustion of organic material, mostly coal, has been reported by the U.S. Bureau of Mines, which mentioned spontaneous combustion as the most significant coal storage problem (Goodman *et al.*, 1946)

The U.S. Department of Energy listed spontaneous combustion of coal as a frequent and serious hazard, and noted that the fire begins in hot spots deep within the coal pile. The coal absorbs oxygen from the air, heat generated from the oxidation increases the temperature in the pile, which in turn increases the rate of reaction, until

a critical temperature is reached and a fire is ignited (Environment Safety and Health Bulletin, 1993).

A fire igniting spontaneously in a large, above-ground pile of tire chips occurred in Japan. In December 1991, fire broke out at a used tire shredding facility near the city of Nakatsu, Oita Prefecture. The pile, measuring 60 by 70 meters by 10-12 meters high contained an estimated 30,000 cubic meters of used tire chips. Smoke was first seen coming out of the pile on December 3. Extensive fire fighting efforts were used, with little success. The fire was then allowed to burn itself out, and finally was self extinguished after three months, on March 11, 1992. About a third of the pile was burned (Sugawa, 1993).

Following this fire, a study was commissioned by Japan's Tire Recycling Committee to investigate the possible causes of tire chips igniting spontaneously. Dr. Sugawa suggested that the organic components of the tires undergo oxidation, which increases over time as antioxidants, added to the tire in the manufacturing process, age and become less effective. This oxidation generates heat, which, if captured and retained within the system, increases the rate of reaction until the gases present self-ignite.

Dr. Sugawa also simulated the spontaneous combustion, using the Kamenetskii Heat-Ignition Theory. He placed a small amount of tire chips in an oven and measured the temperatures in which it ignited. Based on these simulations he generated a curve for the diameter of the tire chips pile required for spontaneous ignition. This curve suggests that a tire chip pile 10 meters in diameter may ignite spontaneously when the temperature is 10°C. Furthermore, Dr. Sugawa suggested that if insulating conditions occurred during storage, the heat generated during oxidation would build up over time, and an accelerated oxidation reaction could occur (Sugawa, 1993).

When discussing the tire chips fires in Washington State, David Nightingale noted that in both cases the depth of the fill material was greater than 8 meters, and water was present. Using the ignition curve that Dr. Sugawa generated, Nightingale showed that the fill material pile in Garfield County, Eastern Washington fell on the edge of the spontaneous combustion zone. For the Ilwaco fire, the point was in the transition zone, where spontaneous combustion is possible, but not certain to occur (Nightingale and Green, 1997). Nightingale proposed an experiment to test several parameters that may lead to spontaneous combustion, using several well-insulated cells filled with tire chips. This suggestion was the basis for the pilot study.

The main purpose of this pilot study was to investigate possible causes for spontaneous ignition of tire chip road fill material, by creating a model that includes several of the factors found in both road bed fires: Moisture, tire chips with steel wires, and insulation to trap the heat of the reaction.

2.0 Pilot Study Design

This simple and inexpensive pilot study used three open-head polyethylene 55-gallon drums (Lab Safety Supply Cat# OA-3973*) with a snap-on lids that could be sealed. The drums were filled as follows:

A 15 cm layer of moist dirt was placed at the bottom of each drum (Figure 1). The dirt from Garfield County, Washington, was brought from where one of the tire chips fires occurred. It was used to provide the bacteria prevalent in that site.

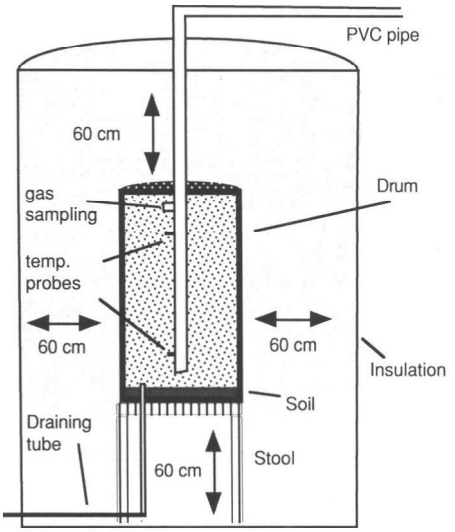


Figure 1 A Cross-Section of the Drum and Insulation

Tire chips were placed over the dirt, to the top of the drum. In drum 1 and 2 the tire chips were two parts 5 cm chips, 1 part 2.5 cm chips, and 1/4 part steel wires, to compensate for the lack of steel wires in the 2.5 cm parts. Drum 3 was filled with three parts 2.5 cm chips and one half part steel wires. The weight of tire chips in each of the three drums was approximately 120 kg.

Water was added from the top to moisten the tire chips and saturate the soil. Excess water was allowed to drain.

A 2.3 cm I.D. PVC pipe was placed vertically in the center of each drum before the tire chips were placed, with the bottom of the pipe approximately 10 cm above the soil layer, and its top extruding outside the drum lid and its insulation. The pipe served as a conduit to the temperature probes and the sampling tube. Two

---

* The use of trade names does not imply support or endorsement

temperature probes protruded through the PVC pipe, at 40 and 76 cm below the surface, with their wires leading through the pipe and connected to the data logger. A Teflon gas sampling tube, 0.5 cm I.D., was also be inserted in the pipe, to collect gas samples from the drum, 10 cm below the surface.

A PVC drainage pipe was placed inside the drum through a hole drilled at the bottom, extending 15 cm high, to the top of the soil layer. The open end of the pipe extended past the insulation layer.

The tire chips were compacted manually as much as possible as they were placed in the drum, the lid was placed on the drums, and the drums sealed. Each drum was placed on a stool 60 cm high, and when the filling of the drums was completed, they were insulated with R-19 commercial insulation rolls to a thickness of at least 60 cm in all directions, including the bottom. Insulation was placed inside the stool.

The temperature probes were connected to a data logger, which was programmed to log the readings every hour. Data from the data logger were transcribed at least once daily. Gas sampling for screening purposes was conducted using a real-time instrument combining an oxygen meter, lower explosive limit, carbon monoxide, and hydrogen sulfide. Gas samples were also sent for laboratory analysis by GC/MS

3.0 Results

The pilot study provided useful information on reactor design, temperature increase, and gas measurements and identification.

3.1 Reactor Design

The polyethylene drum retained moisture well. When the drums were opened two months after the experiment began, the tire chips were still moist in all three drums, and the dirt at the bottom was wet. The insulation provided an effective heat retention layer. Despite significant fluctuations in the temperature of the large, unheated warehouse in which the reactors were placed, the temperature inside the drums was steady. The drums did not support free air exchange with the environment. In all the drums the levels of oxygen dropped from 21% to 5-10%. When fresh air was introduced either by pumping it in or by creating a vacuum through air sampling, the level of oxygen rose temporarily, then dropped again.

3.2 Temperature Measurements

The results of the temperature measurements in drum 1 are presented in Figure 2. The temperatures measured in the other two drums followed the same pattern: a gradual, but slight increase after the beginning of the experiment that peaks after approximately two weeks, then a gradual decline in temperatures. The

temperatures inside the drums did not seem to be affected by the fluctuations of the ambient temperature. The highest temperature rise in any of the three drums was less than 3°C.

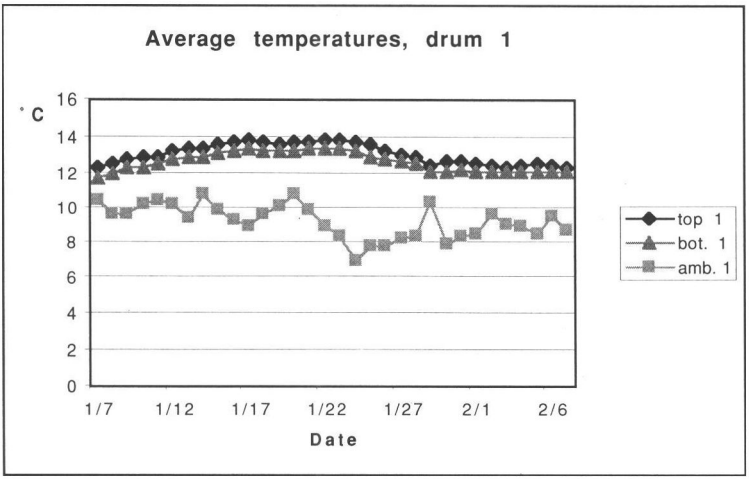


Figure 2 Temperatures Recorded Inside Drum 1 at the Top and Bottom, and the Ambient Temperatures in the Warehouse

3.3 Air Sampling

Percent oxygen levels in drum 3 are presented in Figure 3. Initially, air sampling was planned to be triggered by temperature rise. However, when it became apparent that the temperature will not rise as expected, air sampling was conducted on a routine basis.

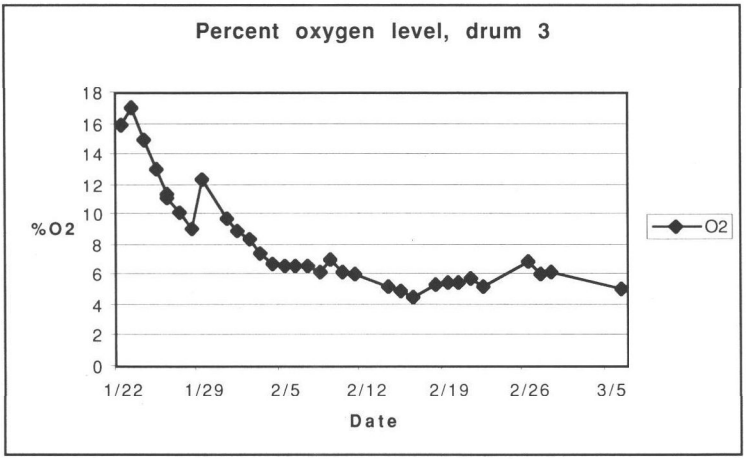


Figure 3 Percent Oxygen Level in Drum 3

Using a multi-gas detector (Biosystems PhD5), air samples were taken from each drum by drawing air through the air sampling tubes. Using a vacuum pump, air was drawn until readings stabilized, and the concentrations of oxygen, carbon monoxide, the lower explosive level, and hydrogen sulfide were recorded. Of these four, only the oxygen reading was deemed reliable, because the carbon monoxide and hydrogen sulfide sensors were sensitive to cross-contaminants, and the lower explosive limit sensor was affected because of the low oxygen present.

Sampling to screen for the presence of volatile organic compounds was done with a flame ionization detector (Foxboro Organic Vapor Analyzer model 128). Reading up to 380 instrument units suggested that organic vapors are present in substantial concentrations.

Air samples were also taken for laboratory analysis. The results are presented in Table 1. Several samples were collected both on Carbosieves S-III tubes and in a SUMA canister. All samples for laboratory analysis were collected from drum 3. In addition, a sample of tire chips from a stock used for the drum was heated to 80°C, and the compounds in the head space analyzed.

Table 1. Results of Laboratory Analysis for SUMA Air Sampling from Drum 3 and Heated Tire Chips.

Compounds in drum 3	**Compounds from heated tire chips**
Ethene	2,3-Dimethylpentane?
Ethane	Heptane?
Propene	Methylcyclohexane
Propane	1,3-Dimethylcyclohexane
Isobutane	Ethylcyclohexane
1-Butene	Trichloroethylene
Butane and *cis*-2-Butene	Tetrachloroethylene
Trans-2-Butene	Toluene
2-Methylbutene	Ethylbenzene
1-Pentene	*p*-Xylene
Pentane and 2-Pentene	2-Methyl-2-isocyanopropane
	m-Xylene
	o-Xylene
	Propylbenzene
	Trimethylbenzene (3 isomers)
	1-Methylstyrene

Most of the compounds identified in drum 3 were C2 to C5 hydrocarbons. The compounds emitted from the heated tire chips were a mixture of aliphatic and aromatic hydrocarbon, some chlorinated.

4.0 Discussion

This pilot study was a precursor to a possible more thorough and involved investigation. It is important to remember that its scope was limited and so were the means to measure and analyze the information it provided. However, the study did provide insight on several points, the most interesting of which is the lack of temperature rise.

The reasons for the spontaneous combustion of tire chips are not fully understood. One way to investigate the possible cause was to create a small scale model of the real conditions using insulation (to trap the heat of reaction inside the system) instead of a thick layer of tire chips. This design, however did not lead to temperature rise in the drums, possibly for several reasons: Lack of pressure, too much water, insufficient amount of oxygen, and not enough tire chip mass.

4.1 Pressure

The scope and design of this experiment prevented the use of more pressure. The drums could not be compressed without an elaborate apparatus, and the need to conduct the experiment under the pressure that would typically be found at the bottom of a pile eight meter high was not seen as necessary. The thickness of the tire chip layer above the hot spots was viewed in terms of its insulation ability, not for its ability to exert pressure. It is possible that the reactions that cause temperature rise are pressure dependant, especially if they are dominated by interaction of gases. A study to test this possibility is planned for the future.

4.2 Water

One of the factors common to the two spontaneous combustion in Washington state was the presence of water. Water was added liberally to the three reactors tested, and definitely brought about some reaction: The steel tire wires some of which were shiny before the experiment started, were covered with rust when the drums were opened and the chips inspected. On the other hand, it is possible that water was present at an excess. In Ilwaco and Garfield water may have been present to begin with, may have initiated a reaction, but then drained to the point that it did not serve as a heat sink and barrier to the reaction taking place. Indeed, when storage of coal is discussed, one of the recommendation is to keep the pile saturated with water at all time to prevent spontaneous combustion. It is possible that the presence of too much water prevented the reaction from proceeding further.

4.3 Oxygen Level

Initially, air samples were to be triggered by a substantial temperature rise. However, when it became apparent that significant temperature rise would not occur, air sampling was done nevertheless, and low oxygen level was detected in all the drums. The low level of oxygen is a strong indication that an oxidation reaction indeed was taking place, but it is not clear if the oxygen was consumed by the oxidation of the steel wires, or by oxidation of the tire material itself. It is possible that inadequate supply of oxygen prevented the oxidation reaction from taking off. On the other hand, pumping air into the drums did not seem to have produced any temperature rise that we could detect.

The laboratory analysis suggests that several processes may take place in the spontaneous combustion of tire chips. Analysis of air samples taken from drum 3 identified light unsaturated aliphatic hydrocarbons, which are natural degradation products of the tire rubber material. The analysis of gases emitted from the heated tire chips in the lab identified aromatic gases closely resembling the gases identified escaping from the crack in the road near Ilwaco. It is possible then that these aromatic products (alkyl benzene compounds) were formed by the reaction of the initial degradation products catalyzed by metal wires present in the tire chips and further accelerated by the combustion of these products as sufficient heat was generated to ignite the gases.

4.4 Tire Chip Mass

The pilot study used small quantities of tire chips, much smaller than the 10 meters diameter mass suggested by Sugawa as necessary for providing the needed conditions for spontaneous combustion. The insulation layer may have kept at least some of the heat of the reaction in the system, but if the heat generated is dependent on the total mass of tire chips, the mass present was too small. An open-air experiment with sufficient mass (10 meter diameter) may provide the conditions needed to simulate what has happened in the two road beds that spontaneously ignited in Washington State.

5.0 Acknowledgements

This study was funded in part by a grant from the Weyerhaeuser company. Drums and other supplies were provided by Washington State Department of Ecology. Many thanks to Mark Hope, Waste Recovery Inc. for providing tire chips; the University of Washington and NOAA-WASC for loaning instrumentation; Steve Scordino, intern, for valuable assistance; and NOAA-OR&R Technical Support group for editorial assistance.

6.0 References

Barnea, N., J.K. Farr and C.B. Henry, "The Ilwaco Tire Fire and Spill: Chemistry and Health and Safety Aspects" in *Proceedings of the Fourteenth Technical Seminar on Chemical Spills, June 9-10, 1997,* Environment Canada, Ottawa, ONT., pp. 29-40. 1997.

U.S. Department of Energy, Environment, Safety, and Health Bulletin, *The Fire Below: Spontaneous Combustion in Coal*, Issue No. 93-4, http://tis-nt.eh.doe.gov/docs/bull/bull0094.html , 2000.

Goodman, J.B., V.F. Parry, and W.S. Landers. *Storage of Subbituminous Slack Coal in Open Pits*, Report of Investigation R.I. 3915. Bureau of Mines, U.S. Department of the Interior, 1946.

Nightingale, D.E.B. and W.P. Green, "An Unsolved Riddle: Tire Chips. Tow Road Beds, and Spontaneous Reactions" *Testing Soil Mixed with Waste or Recycled Material: ASTM STP 1275.* American Society for Testing and Material, 1997.

Sugawa, N, *An investigation of the Possibility of Spontaneous Combustion of Used Tire Chips* (translated by the US Federal Highway Administration) Fire Sciences Institute, Science College of Tokyo, 1993.

Development of a New Chemical Spill Priority List

Merv Fingas, Kerry Ketcheson, Nanci Laroche, and Natalie Jones
Emergencies Science Division
Environment Canada, Ottawa, Ontario

Carol Lau, Gilles Cloutier and Mary-Ann Spicer
Environmental Emergencies Branch
Environment Canada, Hull, Quebec

Abstract

Priority lists for spills of chemicals have been developed since 1980 to focus research and development efforts to the most frequently spilled and most harmful chemicals. The development of analytical techniques have been focussed on the top priority chemicals as well as the preparation of chemical-specific response manuals.

This paper presents a summary of the development of a new spill priority list based on a 10-year spill data set from 1987 to 1997. This new list is compared to older lists and to other priority chemical lists.

1.0 Introduction

In 1979, the Environmental Emergencies Branch embarked on an accelerated program to improve the response and countermeasures technology for spills of materials other than oil. As an essential part of this program, a methodology was devised to develop a priority list of chemicals. A list of 150 chemicals was compiled of hazardous materials that had significant potential as spills in Canada. This list was then used to develop specialized countermeasures, analytical techniques and spill manuals. Individual manuals called EnviroTIPS were prepared for the first 50 priority substances. Tests of the utility of the priority list showed that a large portion of the spills were those of the higher priority substances.

Statistical spill data are extremely useful for setting priorities and identifying project needs for spill prevention and preparedness. This was recognized in 1972 and a database was developed to consolidate all Canadian spill data. This database is known as NATES, short for National Analysis of Trends in Emergencies System. The NATES database now contains data on over 200,000 spill events. About 70% of these spill events are related to oil and petroleum products. About 20% involve wastes and aggregate materials. Only about 10% involve the spillage of "pure" chemicals.

The first spill priority list was developed in 1980 (Fingas, 1984). Lists of the top 10, 50 and 150 were developed. . Several mathematical approaches to the development of the priority list were tried, however it was found that a simple ranking of supply volume, reported spill frequency, historical spill volumes and toxicity could result in a satisfactory list. The main objective was to identify the minimum number of chemicals that would account for the maximum number of spills. The use of the list would be as noted above, to act as a focus for the development of countermeasures, analytical methods and spill manuals.

The first priority list was successful in that a few number of chemicals could account for many spills. The first 10 chemicals accounted for 37% of the reported spill events by number, 83% of the spill volume, and 50% of the volume of chemical supply in Canada. Figure 1 shows the utility of the list as applied to the spill history

of 1980. The "utility" is a mathematical term to describe the usefulness or applicability of a particular formula or in this case the results of a mathematical exercise.

A new list was developed in 1990 (Fingas *et al.*, 1990, 1991a, 1991b). This list used a similar procedure, however more extensive toxicity data was used. The utility of this new list was analyzed like the 1980 list. The first 10 priority substances account for 43% of spill numbers, 25% of spill volume and 15% of supply volume. The first 50 substances account for 80% of spill numbers, 97% of spill volume and 65% of supply volume. The 150 top priority chemicals account for 97% of spill numbers, 98% of spill volume and 82% of supply volume. This utility was much higher than the previous priority list.

This paper presents the third update of the spill priority list based on chemical spill data over a 10 year period of 1987 to 1997.

2.0 Development of a New Priority List

There are a number of motivations to developing a new priority list:

1. There may be a change in spill statistics due to a change in chemical use and transportation patterns, a prime example of this is the presence of tetraethyl lead near the top of the second list and this chemical has nearly disappeared from chemical commerce,
2. There is a need to examine the priority of chemicals in view of improved availability of toxicity data, and
3. Ten years is an appropriate time to re-evaluate the list.

The objectives and principles for the new list development were set as the following:

1. The list should be developed in a systematic and mechanical fashion- that is the placement of individual compounds will only be due to the algorithm used and not on the basis of human judgement,
2. The high volume and frequently spilled chemicals should appear at the top of the list, but toxicity should affect their relative placement,
3. Toxicity will be divided into two considerations, mammalian and aquatic, encompassing both environmental and health concerns,
4. As in the first two lists, one of the prime objectives is to produce a list that contains as few chemicals as possible to deal with the largest number and volume of spills,
5. All possible candidates will be evaluated, but only materials with a spill history will be in the top lists,
6. Completely innocuous materials will be removed from consideration to ensure that they do not appear in any final priority lists, and
7. Several sizes of groupings (eg. 10, 25, 50, etc.) will be prepared to allow use for a variety of purposes.

The procedure employed for developing the new list is different from previous methods. Candidate chemicals and hazardous substances other than oil, were not taken from all known spill priority lists but only from materials known to have been spilled in the past 15-year period.

Table 1 Aggregate Materials Spilled (1987 to 1997)

	Number	Mass (tons)
Acid, unspecified	52	89.06
Acrylic materials	22	0.29
Adhesives	44	127.14
Alcohols	10	0.61
Alkylamines	2	0.03
Aluminum	3	15.25
Bases, unspecified	29	982.41
Burn emissions	40	0.00
Calcium lignosulfonate	7	34.80
Chromium materials	71	65.43
Clay	20	3.85
Cleaners	69	454.60
Coal and clinker	4	0.02
Cobalt	3	3.72
Construction materials	58	813.07
Consumer products	11	0.03
Copper and concentrates of copper	17	4802.74
Copper/nickel concentrates	8	44.55
Drilling muds	17	662.00
Dyes	118	94.36
Explosives	2	0.01
Fatty acids	4	6.33
Fertilizers, unspecified	151	1674.86
Firefighting foam	12	12.25
Food	64	66.92
Fungicides, unspecified	5	0.00
Gas releases	51	45.00
Gasoline additives	20	0.50
Herbicides, unspecified	77	2.09
Industrial materials, various	158	149.37
Iron and iron oxide	11	32908.71
Latex	43	33.55
Lead ore and concentrates	12	1099.74
Lead/zinc concentrates	1	48.00
Manure	27	137.59
Mercaptan liquid	4	0.00
Metals, unspecified	19	306.21
Mine material	6	64.29
Molybdates	11	33.47
Natural materials	13	0.00
Nickel and nickel concentrates	21	4738.58
Oil additives	9	8.74
Paints	401	312.00
Pesticides, unspecified	134	128.33
phenolic resins	29	39.44
phosphates	7	124.50
phossy water	24	188.70
Plastics and plastic materials	37	95.88
Polymers, miscellaneous	18	8.85
Polyols	6	2.06
Radioactives	5	0.30

Table 1 Aggregate Materials Spilled (1987 to 1997)

	Number	Mass (tons)
Resins	82	15.30
Sewage	171	4424.59
Silicone materials	12	29.57
Silver concentrate	1	17.00
Soils and sediments	62	100.03
Solvents, unspecified	94	80.02
Steel mill liquors	6	0.17
Surfactants	74	314.99
Tin and tin concentrates	7	2.36
Tire fires	8	0.00
Unknown or not clearly specified	777	134046.28
Waste materials	143	642.82
Waste water	62	11481.56
Wood waste and products	37	61.02
Total	**3523**	**201645.95**

After the potential candidates were accumulated, they were reviewed for synonyms and substances that were just different forms of each other. This reduced the list by about 25%.

Materials that could not be classified and include many forms of environmental emergencies were separated. They are presented in this paper as Table 1. Table 1 shows that many materials which could be specified as a pure chemical, are not. Examples of this include 'pesticides' and 'unknown'. There are also a large number of materials which are best listed on a table such as this such as the metal concentrates, construction materials and food. Because some of these materials do not pose a simple chemical hazard, they are best considered as aggregate materials as noted in Table 1. Table 1 shows the diversity of incidents that are typically dealt with by emergency crews and environmental concerns. Materials which may appear to be innocuous to the public may pose a serious environmental threat. Examples of this include soil spilled into a salmon spawning area may have serious consequences.

Data on aquatic and mammalian toxicity were collected from standard reference sources. Aquatic data included the results of acute lethal toxicity testing on Rainbow Trout, Blue Gill, Fathead minnow and to Daphnia Magna. Aquatic data on similar species was collected if none of the above were available. Data was found for over 50% of the named compounds. Oral and inhalation toxicity to the rat were collected for the mammalian toxicity along with some human data. Data were available for over 70% of substances on the list. These data on the substances and the remaining priority substances are shown in Table 2. Values in Table where the toxicity data was for a slightly different species or time range are shows in gray.

Similarly, the spill numbers and spill amount of the chemicals were ranked by simple numbers. The sum of the ranking for each of the five categories (spill numbers, spill volume, aquatic toxicity and mammalian toxicity) were simply added to yield an overall value. These overall values are then directly related to the order of priority, lowest number first.

The top priority chemicals are listed in Table 3.

The utility of this new list was analyzed like the previous list and a graph of this is shown in Figure 1. The first 10 priority substances account for 45% of spill numbers, and 24% of spill volume. The first 50 substances account for 80% of spill numbers, and 79% of spill volume. The 150 top priority chemicals account for 92% of spill numbers, and 91% of spill volume. This utility is about the same as the previous priority list and easily satisfies the starting criteria.

Table 4 contains a list of priority substances from various organizations and shows how this new priority list relates to these substances and to previous priority lists.

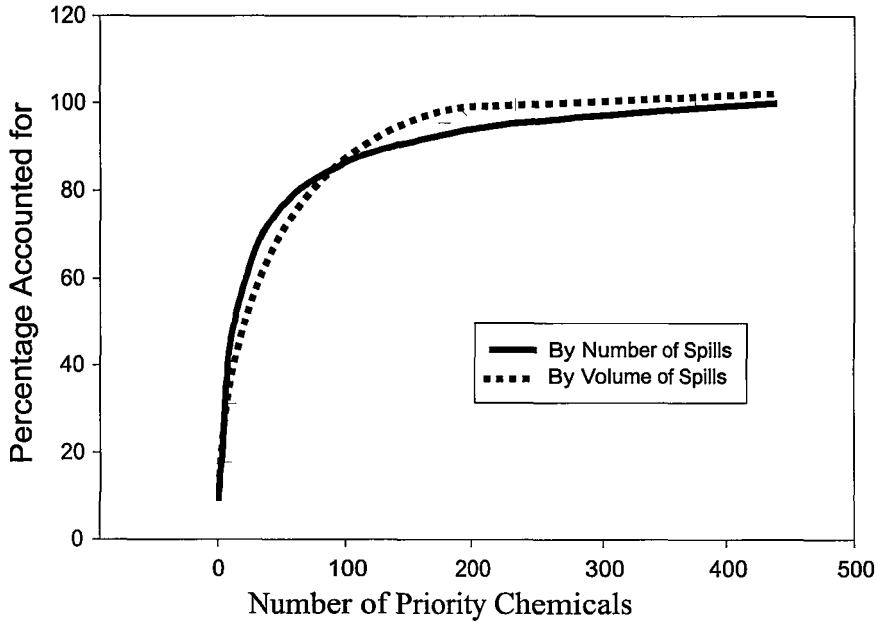


Figure 1 The Priority Chemicals

3.0 References

Fingas, M.F, "The Development of Improved Countermeasures for Chemical Spills in Canada", *Proceedings of the 1984 Hazardous Materials Conference*, Hazardous Material Institutes, Rockville, Maryland, pp. 255-260, 1984.

Fingas, M.F., N. Stone, D. LeBlanc, G. Sergy, B. Mansfield, G. Cloutier and P. Mazerolle, "Development of a New Chemical Spill Priority List", in *Proceedings of the Seventh Technical Seminar on Chemical Spills*, Environment Canada, Ottawa, Ontario, pp. 115-189, 1990.

Fingas, M.F., "The Development of a new Spill Priority List", *Spill Technology Newsletter, Vol. 16, No.3*, pp. 1-8, 1991.

Fingas, M.F., N. Laroche, G. Sergy, B. Mansfield, G. Cloutier and P. Mazerolle, "A New Chemical Spill Priority List", in *Proceedings of the Eighth Technical Seminar on Chemical Spills*, Environment Canada, Ottawa, Ontario, pp. 223-332, 1991.

Table 2 The Spilled Substances and Their Toxicity

			Aquatic Toxicity (in ppm)				Mammalian Toxicity (in ppm)			
NAME	Number of Spills	Spill Amount (tons)	Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Ori-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
1,1-dichloroethane	1	0.00004696				1000	725			13000
1,2-propanediamine	1	0.03			1010		2230			
1,3-butadiene	4	0.22887825					5480			128250
1,4-dioxane	3	0.001			10000		7120		12788	12788
1-decene	1						10000			
1-methyl-2-pyrrolidone	1	0.09766					3914			
2,4-D	51	14.3636885	200	263	130	120	375			
2-chloro-4-hexanone	1	0.0224								
2-ethylhexanoic acid	1	0.00908					3000			
2-ethylhexanol	4	7.68	35		28.2		3730			
2-ethylpyridine	1	0.008918			414					
2-methyl-5-ethylpyridine	1	0.0018368								
2-thioethanol	1	0.000007					244	4070		
3-methoxypropylamine	1									
8-hydroxyquinoline benzoate	1	0								
9,10-anthraquinone	1	0.35					6000			150
acephate	2	0.23	500	600			700			
acetaldehyde	1			53	30.8	10000	661			13300
acetic acid	9	0.15352542	200	11	82		3310	5620		
acetic anhydride	10	29.1043246		75		45	1780			1000
acetone	4	0.19834325	5540	8300	7000	10	5800			18568
acetonitrile	4	39.003148		1850	1300	100	2460			5655
acetylene	3	0	0.4							
acrylamide	5	0.245		12	14		124			
acrylic acid	2	0.276275					33.5		1802	
acrylonitrile	4	6.7		12	16		78			425
adipic acid	1	2.75		330	97		11000			
aldrin	1	0.0000288	0.036	0.013		0.028	39			
aluminum alkyl compounds	2	2.004								
aluminum chloride	8	29.4462016	0.56				3450			
aluminum fluoride	1	3					103			
aluminum oxide	3	100.47146								
aluminum phosphide	1	0								
aluminum sulphate	52	223.2571452					6207			
aminocarb	3	0.41	13.57	3.1	8.5		30			

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Ori-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
amitrole	1	0.2				30	1100			
ammonia	225	178.7559487	1	1.5	4	80				2000
ammonium bisulphate	1									
ammonium bisulphite	1	0.2								
ammonium chloride	4	3.03879704	81	0.9	144	13	1650			
ammonium hydroxide	123	692.0088598	6.25				350			
ammonium nitrate	98	1510.210443		800			2217			
ammonium persulphate	1					120	689			
ammonium phosphate	1									
ammonium sulphate	23	22.40344236	23		20	202	2840			
ammonium thiosulphate	3	6.700322		440	833	530	2890			
ammonium xylenesulphonate	1	0.00574								
antimony trioxide	1	0.2			80		34600			
argon	3	4.006								
arsenic	7	16.242	0.55		9.9	3.8	763			
arsenic trioxide	2	1	12		109		14.6			
asbestos	11	64.1762								
atrazine	16	1.51708692	11	18476	15	31	672			587.6
avenge	5	1.86					206			
azinphos-methyl	2	0.624	0.0062	0.0061	0.093	0.0059	7	5.3		
bacillus thuringiensis	12	7.91304					20000			
barium	3	0.05	42.7			410				
barium carbonate	1	1.188					418			
barium chlorate	1	5.5								
barium sulphate	6	124.2	10464							
bensulide	2	0.6014					271			
bentazon	1	0.000504					1100			510
benzaldehyde	1	0.00169556	6	1.07	10		1300			
benzene	50	88.2	5	63	24	15	930			8000
benzene phosphorus dichloride	1	0.0056			62					
benzenesulphonic acid	2	4.50182			18		0.89			
benzoic acid	1	0.9				1540	1700	5		
benzoyl chloride	3	1.345761			34		1900	325		
boric acid	1	0.028694	100			133	2660			
bromacil	1	0					641	432		

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Ori-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
bromadiolone	1	0.00098					0.49			
bromine	1	0			16500	1	2600	405		
bromoxynil	1	0.2					190			
busan (2-bromo-4'-hydroxyacetophenone)	7	0.04676								
butadiene dimer	1	0.014					3.08	6095		
butyl acetate	4	0.7843475		100	327	4730	10768			390
butyl acrylate	4	0.001157					900			2730
butyl alcohol	8	7.9319975			1910	2802.5	790			8000
butyl cellosolve	2	0.000728					470			450
butyl mercaptan	1			5.5			1500			4020
butyl methacrylate	3	0.005					16000			4910
butylate	4	0.905056					4000		2102	
butylene	2	9.30922								
cadmium oxide	1						72		47	
calcium	3	4.90378								
calcium carbide	5	1.26								
calcium carbonate	27	268.251644								
calcium chloride	52	498.6678977		10650		649	1000			
calcium hydroxide	18	45.219788					7340			
calcium hypochlorite	21	19.04265416	0.07	0.0623			850			
calcium nitrate	2	0.7		2400			3900			
calcium oxide	34	536.086238								
calcium silicon	1									
calcium sulphate	1	0.002368		2980						
caprolactam	4	0.41223					1210		66	
carbamate	2	0.20028								
carbaryl	3	1.1012	4.3	6.8	9	0.005	230			
carbofuran	10	0.477258	0.28	0.24	0.87		5	9		
carbon 14	1									
carbon black	11	21.31074					15400			
carbon dioxide	6	30.247725								
carbon disulphide	8	80.320112				2.1	2780		8025	
carbon monoxide	7	0.02							1807	
carbon tetrachloride	1		1.97	125	4	35	2350			8000
carboxin	4	1.6					430	2044		

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Ori-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
cesium	1	7.048E-07					1700			
cesium chloride	1	0.00126	181				2600			
chlordane	1		0.026	0.06	0.1	0.153	283			
chlorine	124	30.61175392	0.02		0.09	0.12		293		
chlorine dioxide	9	17.11925928					292			
chlorine trifluoride	1	0.2409						299		
chlorobenzene	1	0.02	350	15	28	21.36	1110	2965		
chloroethylphosphonic acid		0.0111475					4000			
chloroform	4	0.00053424	2.09	100	58		695			9779
chlorophenol	2	0	3	6	10	10	200	2		
chlorosulphonic acid	1						50			
chlorothalonil	1	0.00028					10000	28		
chlorpyrifos	14	0.64855842	0.0104	0.015	0.15	0.0004	82			14
chromic acid	45	38.6058304	24			0.01				
copper chloride	2	0.0426636	0.042	1.1		0.1				
copper chromium arsenate	2	0.015925								
copper cyanide	2	0.013432	0.1	0.2	1.2	12.311	1265			
copper sulphate	8	36.2489256	0.45	1.1	0.075	0.05	300			
creosote	18	0.005212					725			
cresol	4	0.44	8.4	10.9	12.8		1454			
cresylic acid	5	0.003540236					1500			
cyanide	10	1.3050336								
cyclohexylamine	5	1.679747					11	1852		
cygon	3	0.00008185					60			
cymenes	1					6.5	2800	1846		
dacthal	2	0.02					3000			413
dalapon	1	0.54		105						
decanol	1	0.00014			2.4		4720		618	
demeton	1	0.01		0.11	3.2		1.7			
diacetone	1	2.3					2520			
diammonium sulphate	1	0.931658	36.7		20	202	2840			
diazinon	17	0.555316635	1.35	0.12	10.3		66			277
dibenzoyl peroxide	1	0.00122728					7710			
dibutyl-p-phenylene	1	0.000014								
dibutyltin compounds	1	0.033								

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Ori-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
dicamba	5	0.2364182	28.4	50			1039			
dichloromethane	2	0.1824075		220	99		1600	14924		
diclofop-methyl	6	0.1					512			585
dicyanodiamide	1						500			
diethanolamine	10	8.7585731		2100	100	1.4	0.62			
diethylamine	3	3.605025	104		855	56	540			4000
diethylene glycol	3	2.37459			100	0.6	12565			
diethylene triamine pentaacetic acid	1	0.0603288								
diisobutyl dithiophosphinate	1	0.0979								
diisobutylene	3	0.8007227								
diisocyanate	3	2.24315464								
diisononyl phthalate	1	0.004312								
diisopropanolamine	1	0.4945					4765			
diisopropyl ether	1	0.000056								
diisopropylamine	1	0.032265					770		1152	
dimethoate	7	4.96025	6.2	28			60			
dimethyl disulphide	1	2384					200			805
dimethyl disulphonate	1	0.01								
dimethyl sulphide	3	0					3300	40250		
dimethyl terephthalate	1	0.416					3200			
dimethylacetamide	1	1.1					4300	2475		
dimethylamine	6	0.16806	68				698		4725	
dimethylcyclohexylamine	2	0.205								
dimethylphosphine	1	0.00000056								
dinitrophenol	1	0.00837	12	20	19.4					
dinitrotoluene	1	540					750			
dinoseb	1				0.36	0.24	25			
dioctyl phthalate	9	6.604734					30000			
dioxin	3	0.02					0.022			
diphenyl	1	0.24					2140			
diphenyl oxide	2	0.87					2450			
diphenylmethane	3	0.4183274					2250			
diquat	1	0.024	11.2	35	14		231			
dithiocarbamate	5	1.8200168								
diundecyl phthalate	1	0.0112								

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Orl-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
dodecylbenzene	1	0.00112								
EPTC	4	0.41148					916			
ethanethiol	1	0.002					682			4420
ethanol	45	352.2149308	13000		14000	1000	7060			20748
ethanolamine	9	4.714200848	150	329.16	2070	140	1720			
ethyl acetate	6	0.1265968	452		260	716.8	5620			19600
ethyl acrylate	9	0.53495792			2.5		800			1414
ethyl hexyl phthalate	2	0.91872								
ethyl mercaptan	1						682			4420
ethyl nitrite	1	0.09								160
ethylamine	7	0.05902582				110	400	5540		
ethylbenzene	58	149.7739	9	60	29		3500			
ethylene	1	7								
ethylene dibromide	2	3.5000868		18			108			
ethylene glycol	349	199.950697					4700			
ethylene glycol monobutyl ether	4	0.30968385		1490			2400			
ethylene oxide	6	0.004193135	19	27	84	2000	72			800
ethylenediamine	6	0.27989			119	0.88	1200	123		
fenitrothion	7	0.2027032	100	2.6	4		250			33
ferric chloride	47	23.32664057	3.4			15	450			
ferric nitrate	4	225.4					3250			
ferric oxide	6	170.9723341								
ferric phosphate	1	2.2								
ferric sulphate	12	7.29677094								
ferrous chloride	7	3.26948393					450			
fluoboric acid	2	0.68472								
fluorescein	6	126.1263184					300			
fluorine	3	0.618775	2.3					185		
formaldehyde	41	47.39029797	50	40	24.1	52	100	164		
formic acid	6	9.046065		175			1100			
fosamine ammonia	2	0.007028					11000	8065		
freon	73	14.41362437								
fumaric acid	2	0.0390882		5000						
furfural	3	0.0541776			32		65			175
glycidol	1	0.00056					420			580

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Orl-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
glyphosate	24	3.2947473	8.3		2.3		4873			1736
guthion	1	0.00154					7	5		
halon	26	0.656748494								
heavy water	1	0								
helium	2	0								
heptene	2	0.022295				50				
hexamethylenediamine	17	1.1973695					750			
hexamethylenetetramine	1	0.0061468			49800		569			
hexanoic acid	1				200		3000			433
hexene	1	0.126								32000
hydrazine	10	24.81776616		1.3	5.98	0.81	60			570
hydrobromic acid	1	o						2858		
hydrochloric acid	377	770.7733863		3.5				3124		
hydrocyanic acid	2	0.0033024	0.057		0.167		3.7			
hydrofluoric acid	10	0.9343108						1276		
hydrofluorosilicic acid	20	101.3329621								
hydrogen	12	8.551								
hydrogen chloride	12	17.608425						3124		
hydrogen fluoride	2	10.07						1276		
hydrogen peroxide	40	96.41022267					2000			1440
hydrogen sulphate	1	9								
hydrogen sulphide	4	0.22295	0.4	0.3	0.6			634		
inorganic chromate	3	3.2								
iron sulphite	2	1.15								
isobutyl alcohol	2	0.180675					2460			
isobutyl isocyanate	1									
isobutyl xanthate	1	0.0504								
isocyanates	7	0.751								
isodecanol	1	0.00381672					6.5			
isophoronediamine	1	0.0001472								
isophthalic acid	19	1175.876189					10400			
isoprene	1	0.000644		42.54	80					63554
isopropane	1	15								
isopropanol	26	11.98710775			11130		5045			16000
isothiazol	1	0.7								

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Ori-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
isovaleric acid	1	0.0005					2			
lead acetate	2	0.4		250						
lead chloride	1		0.200	200	200		1947			
lead chromate	2	0.05					12000			
lead oxide	3	0.035			1000					
lead sulphate	4	48.622032		3800	1300					
linuron	1	0.01911					1146			5
lithium metal	3	0.01821612	9.28							
magnesium	1	0.0056								
magnesium bisulphate	2	2.22264								
magnesium chloride	3	34.4914	1355			888.4	2800			
magnesium hydroxide	1	1.7					8500			
magnesium oxide	3	2.0756								
magnesium sulphate	10	21.4245875		3800		459.3				
malathion	14	0.684090036	0.17	0.11	9		290			3
maleic anhydride	27	6.09313938		138			400			
maneb	2	0.1	3			1	3000			
manganese	2	0.164					9000			
MAPP	1									
MCPA	5	2.41584		100			700			164
MDI	17	5.8416075					9200	17		
mecoprop	1	0.0014					650			
mercuric chloride	1		0.11	0.118	0.16	0.025				
mercuric iodide	1	0.0810264					18			
mercury	65	103.2176028	0.005							
metachlor	1	3.7					930			2086
methane	1									
methanol	80	1290.688963	20000	13500	28400	100	5628			64000
methoxychlor	2	0.1128005	0.0447	.032-.075	0.0075-.039	0.006	1855			
methoxypropylamine	1									
methyl chloride	3	35.24		550			1800			2525
methyl chloroform	1	0.27416025					9600			18000
methyl iodide	1	0.00228					76			220
methyl isobutyl ketone	2	0.00365911					2080			24000
methyl methacrylate	7	13.0100768		240	260	1760	7872			18738

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Ori-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
methyl parathion	1	0.5	2.75	5.72	8.9		6.01			3
methylacrylamide	1	0.14								
methylene bisthiocyanate	1	0.00315								
methylnaphthalene	1	4.631708								
methylphosphoric acid	2	0.2								
metolachlor	11	0.057604	0.00335				2200			148
MMT	2	0.6					8			8
m-nitro-p-toluidine	1						6860			
molybdenum trioxide	1	0.1					2689			976
monomethylamine	3	14.2					100			1858
morpholine	3	0.00429264	380	350		100	1450			8000
MTBE	3	0.02952885					4000			23576
naphtha	47	33.3951287		3	4.9	1.5	5000			
naphthalene	5	0.8	4		6.14	4.6	490			64
naphthalenesulphonic acid	1	0.2	420							
n-butylamine	1	0.148	180		268		366		263	
neopentylglycol	1	0.22								
nickel carbonate	1	3.12								
nickel carbonyl	4	0.28721856						35		
nickel sulphate	5	0.2743808	33.97	188						
nitric acid	134	23.79410482								
nitrilotriacetic acid	1	0.454	98	198	100	950	1100			
nitrobenzene	1	0.00006384	0.002	43	80	27				556
nitrocellulose	6	0.023625					5000			
nitrogen	32	213.8722559								
nitrogen dioxide	2	4.467698								88
nitrohydrochloric acid	1	0.02								
NO_X	4	0.08753452								
oleum	16	99.22728524		24				347		
ortho-dichlorbenzene	3	0.023751	1.58		33		500			
oxygen	7	194.0841								
paraquat	4	5.02	15				100			
pcbs	367	21.46503764	0.054			0.1	1350			
pentachlorophenol	17	40.10874	1	0.13	0.32	0.53	27			32
pentane	1									121325

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Orl-Rat LD_{50} *(mg/kg)*	Ihl-Rat LC_{50} *1 hour*	Ihl-Rat LC_{50} *2 hour*	Ihl-Rat LC_{50} *4 hour*
perchloroethylene	7	0.07360975			18.4		2629			4961
permethrin	1		0.025				383			30
phenol	47	287.7430848	8.3	20	45	4	317			81
phenolsulphonic acid	7	21.20865					1900			
phenyl isocyanate	1	0.00219								
phosgene	1	0								
phosphoric acid	66	64.3174429					1530	209		
phosphorus	11	0.0212			3					
phosphorus pentoxide	2	71.4						206		
phthalic anhydride	3	2.256906	44.2				1530	34		
picloram	8	1.34628052	11.6				8200			
picric acid	2	0					200			
piperonyl butoxide	1	0.000126	5	0.0042		2.83	6150			
potassium acetate	2	0.258265					3250			
potassium amylxanthate	1						99			
potassium carbonate	4	0.49774					1870			
potassium chloride	22	8191.685796		1200		14.5	2600			
potassium chromate	3	0.0010206			45.6	0.18	180			
potassium cyanide	1	0.0001672	0.064	0.14	0.34		5			
potassium hydroxide	25	13.73254924					273			
potassium nitrate	1	0.2		800		10.2	3750			
potassium permanganate	6	0.016504	0.45	1.2			1090			
potassium sulphide	1	0.000168								
propanil	1	0.00042			8.6	4.2	367			
propargyl alcohol	1	0.002			1.53		20		873	
propyl acetate	3	2.3075305			60	511	9370			
propylene	1	0.002								
propylene glycol	17	18.60701244	10000	1700						
propylene oxide	3	3.605524		141			380			4000
pyridine	5	0.015	4.6		105	1320.7	891	8824		
rhodamine B	2	0.000168	217				887			
silane	1									9600
silica	4	9.3119232								
silicic acid	1	4.5								
simazine	1	0.000272					971			1169

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Ori-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
sodium	4	12.00261								
sodium aluminate	2	1.5								
sodium azide	1		0.8	1.6			27			
sodium bisulphite	10	242.9140045				90	2000			
sodium borohydride	2	0.0642								
sodium carbonate	9	1.95612088		320		524	2050			
sodium chlorate	52	134.2943894	2750				1200	6328		
sodium chloride	35	4058.703523		12946	7650	3114	3000	17288		
sodium chlorite	3	265.4494					165			61
sodium chromate	6	0.05156645	600			0.05				
sodium cyanide	11	49.38545	0.06	0.28	0.15	0.09	6.44			
sodium dichromate	21	20.94946024	69	410		4	50			
sodium dithionite	2	12.1								
sodium ethyl sulphate	1	0.4								
sodium ferrocyanide	1	0.0040824				540				
sodium hydrosulphite	19	8.14583559								
sodium hydroxide	339	3964.468778		9.9		100				
sodium hypochlorite	78	50.009554					5800			
sodium hyposulphite	1	0.00674								
sodium isopropylxanthate	2	0.165								
sodium metabisulphite	1	0.056					2000			
sodium nitrite	13	47.74242								
sodium pentachlorophenate	8	3.9328		0.16			126		20	
sodium phosphate	4	0.079912				126				
sodium silicate	9	1.1975834				49.6	1153			
sodium stearate	2	0.052652								
sodium sulphate	17	93.851647		8000		800	5989			
sodium sulphide	10	0.8838013		25	1.38	9				
sodium sulphite	5	209.71452				52	820			
sodium thiocyanate	3	45.5600351					764			
sodium thiosulphate	1	0.64				805				
sorbitol	1	0.1					15900			
stannic chloride	1	0.155								
strychnine	1	0.00544		0.87			2.35			
styrene monomer	36	74.60043097	2.5	25.05	30	40				

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Ori-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
sulphamic acid	2	2.8147032			42		3160			
sulphonic acid	2	0.00294								
sulphur	114	6612.294188		10000						1246
sulphur chloride	1	0.000676								150
sulphur dioxide	24	6.40805512						2520		
sulphuric acid	506	5310.450003		42			2140		125	
sulphurous acid	2	0.10336272								
tannic acid	1	0.0000198					2260			
TCA	2	0.066			2000	3100	0.2			
tebuthiuron	2	0.001					644			389
terbufos	1	0.22					1.6			
terephthalic acid	2	0.062514					6400			
tert-butyl peroxide	2	0.011					25000			4100
tetrabromomethane	1									
tetraethyl lead	3	3.07		0.23			12.3	63		
tetrahydrofuran	3	0.1426956			2160	10000	1650			21000
tetrahydronaphthalene	1	0.1					1.62			275
thioglycolic acid	2	0.1			30		114			
tin fluoborate	1	1								
titanium dioxide	5	3.13744								
titanium tetrachloride	2	0.000016								
toluene	58	100.6274276	0.02		36.2		636			12791
toluene diisocyanate	11	2.4065432			164.5		5800			14
toluene sulphonic acid	1	0.00047775								
treflan	1	0.014					1930	200		
triallate	3	0.07					800			
trichlorfon	2	7.587	4.85	3.8	109		560			121
trichloroethane	27	1.026632284		40	60	40	9600			18000
trichloroethylene	6	1.4468872	42	45	52	58.1	5650			8450
trichlorotrifluoroethane	2	0.014508								
triclopyr	2	0.000056					630			
tricresyl phosphate	2	0.06279448	0.26	1000			3000			
triethanolamine	1	0.4			11800	1390	4.92			
trifluralin	13	0.3736	0.12	0.12	0.105	0.193	1930	200		
trimethyl phosphate	2						840			

Table 2 The Spilled Substances and Their Toxicity *(continued)*

NAME	Number of Spills	Spill Amount (tons)	Aquatic Toxicity (in ppm) Rainbow Trout	Bluegill	Fathead Minnow	Daphnia Magna	Mammalian Toxicity (in ppm) Ori-Rat LD_{50} (mg/kg)	Ihl-Rat LC_{50} 1 hour	Ihl-Rat LC_{50} 2 hour	Ihl-Rat LC_{50} 4 hour
trimethylamine anhydrous	1	0.0006356					500			7729
triphenyl phosphite	1	0.0035					444			
urea	25	138.674167				10000	8471			
urea formaldehyde	6	14.62965144								
urea nitrate	12	1.6451712								
vanadium pentoxide		0.09	62				10			17
vinyl acetate	19	68.78090788		18	29	330	2900			3185
vinyl chloride	42	84.38357011					500			
viscose (cellulose xanthate)	8	60.32								
xanthate	3	0.07182								
xylenes	42	82.10627652	14	19	40	0.233				
zinc chloride	4	0.241186475	4	7		0.06791	350			
zinc oxide	1	0.088614	6				7950			
zinc phosphate	1	0.02726636	0.09				1990			
zinc stearate	1	0.0438					10000			
zinc sulphate	6	2039.34151	2.08	3.3	14		2000			
zirconium	1			7						

Table 3 The Top Priority Chemicals

NAME	Priority Number	NAME	Priority Number
sulphuric acid	1	pentachlorophenol	50
pcbs	2	halon	51
ammonium hydroxide	3	vinyl acetate	52
chlorine	4	diazinon	53
hydrochloric acid	5	isophthalic acid	54
ammonia	6	chlorpyrifos	55
sodium hydroxide	7	atrazine	56
toluene	8	malathion	57
ethylene glycol	9	oleum	58
ammonium nitrate	10	sodium hydrosulphite	59
sulphur	11	calcium hydroxide	60
methanol	12	MDI	61
phosphoric acid	13	sodium sulphate	62
sodium chlorate	14	propylene glycol	63
nitric acid	15	hexamethylenediamine	64
mercury	16	trifluralin	65
phenol	17	sodium cyanide	66
ethylbenzene	18	creosote	67
sodium hypochlorite	19	carbofuran	68
benzene	20	hydrazine	69
2,4-D	21	diethanolamine	70
calcium chloride	22	sodium nitrite	71
carbon disulphide	23	hydrogen chloride	72
formaldehyde	24	metolachlor	73
ferric chloride	25	acetic anhydride	74
freon	26	copper sulphate	75
aluminum sulphate	27	toluene diisocyanate	76
ethanol	28	sodium pentachlorophenate	77
naphtha	29	bacillus thuringiensis	78
vinyl chloride	30	hydrogen	79
chromic acid	31	sodium bisulphite	80
xylenes	32	ferric sulphate	81
hydrogen peroxide	33	asbestos	82
sodium chloride	34	urea nitrate	83
styrene monomer	35	chlorine dioxide	84
maleic anhydride	36	carbon black	85
calcium oxide	37	ethanolamine	86
nitrogen	38	dimethoate	87
potassium hydroxide	39	magnesium sulphate	88
calcium carbonate	40	aluminum chloride	89
trichloroethane	41	arsenic	90
isopropanol	42	ethyl acrylate	91
glyphosate	43	hydrofluoric acid	92
urea	44	acetic acid	93
ammonium sulphate	45	sodium carbonate	94
sodium dichromate	46	butyl alcohol	95
calcium hypochlorite	47	sodium sulphide	96
sulphur dioxide	48	fenitrothion	97
potassium chloride	49	sodium silicate	98

Table 3 The Top Priority Chemicals

NAME	Priority Number	NAME	Priority Number
hydrofluorosilicic acid	99	trichlorfon	148
zinc sulphate	100	hydrogen sulphide	149
phosphorus	101	monomethylamine	150
cyanide	102	cresol	151
picloram	103	propylene oxide	152
dioctyl phthalate	104	aminocarb	153
fluorescein	105	sodium chromate	154
ferrous chloride	106	ferric nitrate	155
viscose (cellulose xanthate)	107	methyl chloride	156
dimethylamine	108	busan (2-bromo-4'-hydroxyacetophenone)	157
ethylamine	109	caprolactam	158
naphthalene	110	nickel sulphate	159
phenolsulphonic acid	111	magnesium chloride	160
methyl methacrylate	112	chloroform	161
cyclohexylamine	113	benzoyl chloride	162
formic acid	114	lead sulphate	163
ethylene oxide	115	arsenic trioxide	164
ethylenediamine	116	fluorine	165
oxygen	117	sodium thiocyanate	166
barium sulphate	118	methyl parathion	167
MCPA	119	titanium dioxide	168
acrylonitrile	120	benzenesulphonic acid	169
paraquat	121	nitrocellulose	170
trichloroethylene	122	butylate	171
tetraethyl lead	123	butyl acetate	172
sodium sulphite	124	furfural	173
potassium permanganate	125	ortho-dichlorbenzene	174
pyridine	126	ethylene dibromide	175
perchloroethylene	127	dithiocarbamate	176
diclofop-methyl	128	calcium carbide	177
acrylamide	129	EPTC	178
azinphos-methyl	130	ethylene glycol monobutyl ether	179
ferric oxide	131	chlorophenol	180
sodium chlorite	132	dimethyl disulphide	181
avenge	133	MMT	182
dicamba	134	nickel carbonyl	183
carboxin	135	acetone	184
carbon dioxide	136	ammonium thiosulphate	185
zinc chloride	137	potassium carbonate	186
phthalic anhydride	138	hydrocyanic acid	187
isocyanates	139	cresylic acid	188
ethyl acetate	140	sodium	189
urea formaldehyde	141	silica	190
carbon monoxide	142	acrylic acid	191
acetonitrile	143	dioxin	192
ammonium chloride	144	vanadium pentoxide	193
diethylamine	145	phosphorus pentoxide	194
carbaryl	146	aluminum oxide	195
2-ethylhexanol	147	butyl acrylate	196

Table 3 The Top Priority Chemicals

NAME	Priority Number	NAME	Priority Number
methoxychlor	197	diisobutylene	246
dichloromethane	198	terbufos	247
n-butylamine	199	calcium nitrate	248
morpholine	200	copper chloride	249
acephate	201	diammonium sulphate	250
1,3-butadiene	202	chlordane	251
TCA	203	acetylene	252
dinitrotoluene	204	barium carbonate	253
hydrogen fluoride	205	*diphenyl oxide*	254
potassium chromate	206	sodium dithionite	255
propyl acetate	207	1,4-dioxane	256
tetrahydrofuran	208	rhodamine B	257
bensulide	209	butylene	258
copper cyanide	210	butyl cellosolve	259
thioglycolic acid	211	dimethyl sulphide	260
diethylene glycol	212	tebuthiuron	261
triallate	213	zinc phosphate	262
diphenylmethane	214	MTBE	263
calcium	215	dimethylacetamide	264
tricresyl phosphate	216	mercuric iodide	265
cygon	217	bromoxynil	266
argon	218	lead oxide	267
permethrin	219	diisopropylamine	268
maneb	220	methyl iodide	269
potassium cyanide	221	lead acetate	270
inorganic chromate	222	xanthate	271
aluminum fluoride	223	magnesium bisulphate	272
tetrahydronaphthalene	224	isobutyl alcohol	273
benzoic acid	225	aluminum alkyl compounds	274
sodium phosphate	226	cadmium oxide	275
barium	227	potassium acetate	276
NO_X	228	picric acid	277
diisocyanate	229	sodium aluminate	278
sulphamic acid	230	dacthal	279
lithium metal	231	2-thioethanol	280
butadiene dimer	232	benzaldehyde	281
magnesium oxide	233	iron sulphite	282
diquat	234	butyl methacrylate	283
triethanolamine	235	diacetone	284
aldrin	236	treflan	285
chlorobenzene	237	isodecanol	286
guthion	238	adipic acid	287
nitrogen dioxide	239	bromadiolone	288
demeton	240	linuron	289
metachlor	241	triclopyr	290
nitrilotriacetic acid	242	fluoboric acid	291
propargyl alcohol	243	bromacil	292
sodium azide	244	zinc oxide	293
strychnine	245	dinoseb	294

Table 3 The Top Priority Chemicals

NAME	Priority Number	NAME	Priority Number
fosamine ammonia	295	tert-butyl peroxide	344
boric acid	296	bentazon	345
isovaleric acid	297	sodium stearate	346
isopropane	298	1,2-propanediamine	347
lead chloride	299	mecoprop	348
carbon tetrachloride	300	cymenes	349
chlorine trifluoride	301	simazine	350
amitrole	302	heptene	351
hydrogen sulphate	303	sodium metabisulphite	352
glycidol	304	dinitrophenol	353
methyl isobutyl ketone	305	decanol	354
nitrobenzene	306	piperonyl butoxide	355
manganese	307	tin fluoborate	356
9,10-anthraquinone	308	ethyl mercaptan	357
acetaldehyde	309	ethyl hexyl phthalate	358
ethylene	310	1,1-dichloroethane	359
trimethyl phosphate	311	copper chromium arsenate	360
fumaric acid	312	ethyl nitrite	361
propanil	313	trichlorotrifluoroethane	362
potassium nitrate	314	isothiazol	363
barium chlorate	315	methyl chloroform	364
hexamethylenetetramine	316	sodium thiosulphate	365
dimethylcyclohexylamine	317	mercuric chloride	366
terephthalic acid	318	dicyanodiamide	367
carbamate	319	1-methyl-2-pyrrolidone	368
molybdenum trioxide	320	chlorothalonil	369
methylphosphoric acid	321	antimony trioxide	370
methylnaphthalene	322	ammonium persulphate	371
silicic acid	323	sodium ethyl sulphate	372
naphthalenesulphonic acid	324	sulphonic acid	373
dalapon	325	hexanoic acid	374
sodium isopropylxanthate	326	neopentylglycol	375
diphenyl	327	ammonium bisulphite	376
butyl mercaptan	328	2-ethylhexanoic acid	377
ethanethiol	329	hexene	378
chlorosulphonic acid	330	stannic chloride	379
magnesium hydroxide	331	sorbitol	380
triphenyl phosphite	332	methylacrylamide	381
nickel carbonate	333	chloroethylphosphonic acid	382
sulphurous acid	334	diisobutyl dithiophosphinate	383
cesium chloride	335	cesium	384
trimethylamine anhydrous	336	titanium tetrachloride	385
dimethyl terephthalate	337	zinc stearate	386
potassium amylxanthate	338	hydrobromic acid	387
sodium borohydride	339	helium	388
bromine	340	isoprene	389
ferric phosphate	341	diethylene triamine pentaacetic acid	390
lead chromate	342	isobutyl xanthate	391
diisopropanolamine	343	calcium sulphate	392

Table 3 The Top Priority Chemicals

NAME	Priority Number	NAME	Priority Number
sulphur chloride	393		
tannic acid	394		
dibutyltin compounds	395		
benzene phosphorus dichloride	396		
2-ethylpyridine	397		
zirconium	398		
2-chloro-4-hexanone	399		
nitrohydrochloric acid	400		
diundecyl phthalate	401		
dimethyl disulphonate	402		
sodium hyposulphite	403		
dibenzoyl peroxide	404		
ammonium xylenesulphoanate	405		
magnesium	406		
sodium ferrocyanide	407		
diisononyl phthalate	408		
methylene bisthiocyanate	409		
phenyl isocyanate	410		
propylene	411		
2-methyl-5-ethylpyridine	412		
dodecylbenzene	413		
m-nitro-p-toluidine	414		
toluene sulphonic acid	415		
silane	416		
potassium sulphide	417		
isophoronediamine	418		
1-decene	419		
diisopropyl ether	420		
dibutyl-p-phenylene	421		
pentane	422		
dimethylphosphine	423		
3-methoxypropylamine	424		
8-hydroxyquinoline benzoate	425		
aluminum phosphide	426		
ammonium bisulphate	427		
ammonium phosphate	428		
calcium silicon	429		
carbon 14	430		
heavy water	431		
isobutyl isocyanate	432		
MAPP	433		
methane	434		
methoxypropylamine	435		
phosgene	436		
tetrabromomethane	437		

Table 4 The Top Priority Materials

The Top Ten Chemicals	
ammonia	hydrochloric acid
ammonium hydroxide	pcbs
ammonium nitrate	sodium hydroxide
chlorine	sulphuric acid
ethylene glycol	toluene

The Top Fifty Chemicals	
2,4-D	mercury
aluminum sulphate	methanol
ammonia	naphtha
ammonium hydroxide	nitric acid
ammonium nitrate	nitrogen
ammonium sulphate	pcbs
benzene	pentachlorophenol
calcium carbonate	phenol
calcium chloride	phosphoric acid
calcium hypochlorite	potassium chloride
calcium oxide	potassium hydroxide
carbon disulphide	sodium chlorate
chlorine	sodium chloride
chromic acid	sodium dichromate
ethanol	sodium hydroxide
ethylbenzene	sodium hypochlorite
ethylene glycol	styrene monomer
ferric chloride	sulphur
formaldehyde	sulphur dioxide
freons	sulphuric acid
glyphosate	toluene
hydrochloric acid	trichloroethane
hydrogen peroxide	urea
isopropanol	vinyl chloride
maleic anhydride	xylenes

The Top 150 Chemicals (next 100 chemicals)	
2-ethylhexanol	hexamethylenediamine
acetic acid	hydrazine
acetic anhydride	hydrofluoric acid
acetonitrile	hydrofluorosilicic acid
acrylamide	hydrogen
acrylonitrile	hydrogen chloride
aluminum chloride	hydrogen sulphide
ammonium chloride	isocyanates
arsenic	isophthalic acid
asbestos	magnesium sulphate
atrazine	malathion
avenge	MCPA
azinphos-methyl	MDI
bacillus thuringiensis	methyl methacrylate
barium sulphate	metolachlor
butyl alcohol	monomethylamine

Table 4 The Top Priority Materials

The Top 150 Chemicals ctd.(next 100 chemicals)

calcium hydroxide
carbaryl
carbofuran
carbon black
carbon dioxide
carbon monoxide
carboxin
chlorine dioxide
chlorpyrifos
copper sulphate
creosote
cyanide
cyclohexylamine
diazinon
dicamba
diclofop-methyl
diethanolamine
diethylamine
dimethoate
dimethylamine
dioctyl phthalate
ethanolamine
ethyl acetate
ethyl acrylate
ethylamine
ethylene oxide
ethylenediamine
fenitrothion
ferric oxide
ferric sulphate
ferrous chloride
fluorescein
formic acid
halons
naphthalene
oleum
oxygen
paraquat
perchloroethylene
phenolsulphonic acid
phosphorus
phthalic anhydride
picloram
potassium permanganate
propylene glycol
pyridine
sodium bisulphite
sodium carbonate
sodium chlorite
sodium cyanide
sodium hydrosulphite
sodium nitrite
sodium pentachlorophenate
sodium silicate
sodium sulphate
sodium sulphide
sodium sulphite
tetraethyl lead
toluene diisocyanate
trichlorfon
trichloroethylene
trifluralin
urea formaldehyde
urea nitrate
vinyl acetate
viscose (cellulose xanthate)
zinc chloride
zinc sulphate

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
(2-C orophenyl) th ourea															x					x	x		x		
(bis(2-chloroethyl)amino)uracil, 5-			Z												x						x				
(p-di(chloroethyl)amino) phenyl-L-alanine, 3-															x						x		x		
(Trifluoromethyl) benzenamine, 3-																	x			x					
Acenaphthene												x	x		x						x			x	
Acenaphthylene												x	x		x						x				
Acetaldehyde		x	Y		x		x	x	x		B3			x	x	x		x	x		x	x	x		
Acetamide											B3				x							x			
Acetic acid	Z		x	x			x	x		x				x	x	x		x	x		x				
Acetic anhydride	Z		x	x				x		x				x	x	x		x	x		x				
Acetone		x	x	x			x	x		x				x	x	x		x	x		x	x	x	x	
Acetone cyanohydrin			Y					x	x						x		x	x		x	x		x		
Acetonitrile	Z	x						x						x	x	x					x	x	x		
Acetophenone			Z												x						x		x		
Acetyl bromide								x							x						x				
Acetyl chloride			Z					x	x						x	x					x		x		
Acetylene			x	x	x			x	x	x															
Acrolein			Y				x	x	x		B3	x	x		x	x	x			x	x	x	x	x	
Acrylamide	Z	x	Y				x	x			B3				x		x			x	x	x	x		
Acrylic acid		x						x						x	x	x		x			x	x			
Acrylonitrile	Z	x	x	x			x	x	x	x	B3	x	x	x	x	x	x	x	x	x	x	x	x		
Adipic acid			Z	x				x							x			x			x				
Adiponitrile			Z					x								x	x			x					
Aldrin			x							x		x	x		x		x			x	x	x	x	x	
Allyl alcohol		x	Y					x							x	x	x			x	x		x		
Allyl chloride		x	Z					x							x						x	x			
Allylamine								x									x			x					
Aluminum		x					x*																		
Aluminum alkyl halides								x	x													x		x	
Aluminum chloride	Z		Y	x				x																	
Aluminum phosphate			Z							x												x			
Aluminum phosphide								x	x						x		x			x	x		x		
Aluminum sulfate	Y		x	x				x		x					x	x		x			x				
Aminobiphenyl, 4-							x				B3				x							x		x	

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1998	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Aminocarb			x	x						x															
Aminopyridine, 4-			N																	x	x		x		
Amiton			N														x			x					
Amitrole															x						x	x	x		
Ammonia	x	x	x	x	x		x	x	x	x				x	x	x	x	x	x	x	x	x	x	x	
Ammonia solutions					x			x	x					x											
Ammonium acetate								x							x						x				
Ammonium benzoate								x							x						x				
Ammonium bicarbonate								x							x						x				
Ammonium bisulfite															x						x				
Ammonium carbamate								x							x						x				
Ammonium carbonate								x							x						x				
Ammonium chlorate								x																	
Ammonium chloride	Z		x	x			x	x		x					x						x				
Ammonium chromate								x							x						x				
Ammonium citrate								x							x						x				
Ammonium dichromate								x							x						x				
Ammonium fluoride								x							x						x				
Ammonium hydrogen fluoride								x							x						x				
Ammonium hydrogen sulphate								x																	
Ammonium hydroxide	x		x							x					x	x					x				
Ammonium nitrate	x		x	x				x	x	x								x	x			x			
Ammonium nitrate fertilizers								x	x																
Ammonium oxalate								x						x	x						x				
Ammonium phosphates			x	x						x															
Ammonium picrate			N					x	x						x						x		x		
Ammonium sulfamate			N					x							x	x					x				
Ammonium sulfate	Y		x	x						x								x				x			
Ammonium sulfide								x						x	x										
Ammonium sulfite								x							x										
Ammonium tartrate								x							x						x				
Amyl acetate								x							x						x				
Aniline		x	x					x		x	B3			x	x	x	x	x	x	x	x	x	x		
Aniline hydrochloride								x																	

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled In Can.	ARET Lists	EPA 1985	EPA 1990	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
[illegible]ne								x			B2				x										
Anthracene		x	Z								B1	x	x		x						x	x		x	
Antimony		x*					x*					x	x*		x						x	x		x	
Antimony pentachloride								x							x						x				
Antimony pentafluoride								x	x								x			x					
Antimony potassium tartrate								x							x						x				
Antimony trichloride								x							x						x				
Antimony trifluoride															x						x				
Antimony trioxide			Y					x							x						x				
Antimycin A																	x			x			x		
Antu																	x			x	x		x		
Arsenic	Z	x*	Z					x				x	x*		x						x	x	x	x	
Arsenic acid			Y					x						x	x						x		x	x	
Arsenic pentoxide			Z					x							x		x			x	x		x		
Arsenic trichloride								x							x					x	x				
Arsenic trioxide			Z					x						x	x	x								x	
Arsenous oxide																	x			x	x		x		
Arsine			Y	x	x			x	x	x							x			x				x	
Asbestos	Z	x	Y			x		x		x	B2	x	x		x						x	x		x	
Atrazine	Z		x							x															
Auramine															x						x	x	x		
Avenge	Z																								
Azaserine															x						x		x		
Azinphosethyl			Y														x			x					
Azinphosmethyl	Z		x					x	x	x							x			x	x				
Bacillus thuringiensis	Z																								
Barban			Z							x					x										
Barium								x														x	x	x	
Barium cyanide								x							x						x		x		
Barium sulfate	Z		Y	x						x															
Benz[c]acridine															x						x		x		
Benzal chloride															x		x			x	x	x	x		
Benzene	Y	x	x	x	x	x		x		x	B3	x	x	x	x	x		x	x		x	x	x	x	
Benzenedicarboxylic acid anhydride, 1,2-																					x	x	x		

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1987NPRI	1990 EPS	1991 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled In Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Benzenedicarboxylic acid, [bis(2-ethylhexyl)]ester, 1,2-																					x	x	x		
Benzenedicarboxylic acid, diethyl ester, 1,2-																					x	x	x		
Benzenesulfonyl chloride								x									x			x	x		x		
Benzidine			Z			x		x			B3	x	x								x	x	x	x	
Benzo[a]anthracene											A1	x	x		x						x		x	x	
Benzo[a]pyrene											A1	x	x		x								x	x	
Benzo[b]fluoranthene											A1				x									x	
Benzo[ghi]perylene											A1	x	x		x						x				
Benzo[k]fluoranthene											A1	x	x		x										
Benzoic acid			x	x				x		x					x						x				
Benzonitrile			Z					x							x						x				
Benzophenone			Z																						
Benzotrichloride								x							x		x			x	x	x	x		
Benzotrifluoride			x					x		x															
Benzoyl chloride		x	Z					x						x	x						x	x			
Benzyl chloride		x	Z				x	x			b2			x	x	x	x			x	x	x	x		
Benzyl butyl phthalate		x	Z				x					x	x		x						x	x		x	
Beryllium			Z					x	x		B2	x	x*		x						x	x	x	x	
Beryllium nitrate								x							x						x				
Biphenyl		x	Y				x			x					x										
bis(2-chloroethoxy)methane												x	x		x										
bis(2-ethylhexyl) phthalate	Z	x				x					B1	x	x		x		x			x	x	x	x	x	
bis(chloromethyl) ether						x					B3	x	x		x										
Boron trichloride								x	x								x			x					
Boron trifluoride								x	x								x			x					
Bromine			Z		x			x	x								x			x					
Bromine solutions					x			x	x																
Bromo-4-phenoxybenzene, 1-												x	x		x										
Bromoacetone								x							x						x		x		
Bromodichloromethane												x	x		x						x	x		x	
Bromoform			x					x		x		x	x		x						x	x	x	x	
Brucine			Y					x							x						x		x		
Butadienes		x	Z	x			x	x	x		B3				x		x	x	x	x		x			
Butane					x			x	x																

Chemical	2000 ESD	1997NFPI	1990 EPS	1991 EPS	MIAC 1998	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1990	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Butyl acetate							x	x						x	x	x					x				
Butyl acrylate		x						x								x		x				x			
Butyl alcohol	Z	x	x	x				x		x					x	x		x	x		x	x	x		
Butyl formate			Y					x		x															
Butyl vinyl ether								x									x			x					
Butyl-2,4,6-trinitro-m-xylene, 5-tert-								x	x																
Butylamine			Z					x							x	x					x				
Butylene			Z	x				x	x									x							
Butylene oxide		x						x							x							x			
Butyl-N-nitroso-1-butanamine, N-															x						x	x	x		
Butyraldehyde		x	Z	x				x								x		x	x			x			
Butyric acid			Z					x							x	x					x				
C.I. acid green 3		x															x					x			
Cacodylic acid								x							x						x		x	x	
Cadmium		x*	Y									x	x*		x						x	x	x	x	
Cadmium chloride															x		x								
Cadmium compounds, respirable & soluble inorganic forms						x					A2														
Calcium arsenate			Y					x		x					x		x			x	x				
Calcium carbide			Y	x				x	x	x				x	x				x		x				
Calcium carbonate	Y		Z	x																					
Calcium chloride	Y		x	x			x			x								x							
Calcium cyanamide		x					x	x																	
Calcium cyanide			x				x	x	x	x					x						x		x		
Calcium hydroxide	Z		x	x						x						x									
Calcium hypochlorite	Y		x	x				x		x					x						x			x	
Calcium manganese silicon								x																	
Calcium nitrate			Y					x		x															
Calcium oxide	Y		x	x				x		x								x							
Calcium phosphate			x	x						x															
Camphechlor																	x			x	x	x	x		
Camphor oil			Z					x																	
Cantharidin			Z														x			x					
Caprolactam			Z	x			x								x			x							
Captan															x						x	x			

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1998	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Carbamic acid, ethyl ester															x						x		x		
Carbamidoselenic acid															x						x		x		
Carbaryl	Z		x	x						x					x						x	x			
Carbendazim															x										
Carbofuran	Z		x	x						x					x		x			x	x				
Carbon black	Z																	x							
Carbon dioxide	Z		Y	x				x		x								x	x						
Carbon disulphide	Z	x	Y	x			x	x	x					x	x		x		x	x	x	x	x	x	
Carbon monoxide								x	x																
Carbon oxyfluoride															x						x		x		
Carbon tetrachloride		x	x	x		x		x		x	B2	x	x		x	x		x			x	x	x	x	
Carbon-14							x*																	x	
Carbonyl fluoride								x	x																
Carbonyl sulfide			Z					x	x						x										
Carboxin	Z																								
Catechol		x													x							x			
Cesium-137			Y				x*			x														x	
Chlorambucil															x						x		x		
Chlordane			x	x				x	x	x		x	x		x	x	x			x	x	x	x	x	
Chlorine	x	x	x	x	x		x	x	x	x				x	x	x	x	x	x		x	x	x	x		
Chlorine dioxide	Z	x	Y				x	x		x	B3														
Chlornaphazine															x						x		x		
Chloro-3-methylphenol, 4-							x	x				x	x		x						x		x		
Chloroacetaldehyde								x							x		x			x	x		x		
Chloroacetic acid		x						x							x	x	x								
Chloroacetophenone								x							x							x			
Chloroacetyl chloride								x												x	x		x		
Chloroaniline			Y					x		x					x										
Chlorobenzene		x	Z					x				x	x		x	x					x	x	x	x	
Chlorodibromomethane											B2	x	x		x						x			x	
Chlorodifluoroethane								x	x																
Chlorodifluoromethane			Z					x		x														x	
Chloroethane		x	x					x		x		x	x		x				x		x	x		x	
Chloroeth_l vin_l ether, 2-			Z									x	x		x						x		x		

Chemical	2000 ESD	1987NPRI	1990 EPS	1991 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1990	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Chloroform		x	Y	x			x	x			B2	x	x		x	x	x			x	x	x	x	x	
Chloromethyl ether															x		x			x	x	x	x		
Chloromethyl methyl ether						x									x		x			x	x	x	x		
Chloromethylbenzenamine hydrochloride																					x		x		
Chloronaphthalene												x	x		x						x		x		
Chlorophacinone			Z							x							x			x					
Chlorophenol			x					x		x		x	x		x						x		x	x	
Chlorophenyl phenyl ether, 4-							x					x	x		x										
Chloroprene								x							x							x			
Chloropropionitrile, 3-															x		x			x	x		x		
Chloropropyl octyl sulfoxide, 3-																	x			x					
Chlorosulfonic acid								x	x						x						x				
Chlorpyrifos	Z		Y												x						x			x	
Choline chloride			Z																						
Chromic acid	Y		x					x		x					x						x			x	
Chromic sulfate			Z					x							x										
Chromium		x*	Z			x*					B2	x	x*		x						x	x	x	x	
Chrysene											A1	x	x		x						x		x	x	
Coal tar							x																	x	
Cobalt		x*					x*										x			x		x		x	
Cobaltous bromide			Z					x							x						x				
Cobaltous formate								x							x						x				
Copper		x*					x*					x	x*		x						x	x		x	
Copper chloride			Y					x							x						x				
Copper cyanide			x					x	x	x					x						x		x		
Copper diacetate			Z					x							x						x				
Copper nitrate			Z												x						x				
Copper oxide										x															
Copper sulfate	Z		x	x				x		x					x	x					x				
Copper tartrate								x							x						x				
Coumaphos			Y					x	x						x		x			x	x				
Creosote	Z					x		x						x	x									x	
Cresols	Z	x*	x	x						x					x	x				x	x	x	x	x	
Cresylic acid								x		x					x		x			x	x	x	x		

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled In Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Crimidine			Z														x			x					
Crotonaldehyde			Z					x							x		x			x	x				
Cumene		x	Y				x								x		x	x							
Cyanides	Z	x					x			x	B2	x	x		x						x	x	x	x	
Cyanogen								x	x						x						x		x		
Cyanogen bromide			Y					x		x					x		x			x	x		x		
Cyanogen chloride								x	x						x						x		x		
Cyclohexane		x	x	x	x			x		x				x	x	x		x	x		x	x	x		
Cyclohexanone			Z				x	x							x						x	x	x		
Cycloheximide			Y														x			x					
Cyclohexylamine	Z		Y					x		x							x			x					
Cyclopentane								x									x			x					
Cyclophosphamide															x						x		x		
Cyclopropane								x	x																
Cyclotrimethylenetrinitramine								x	x															x	
Dalapon			Z													x					x				
Daunomycin															x						x		x		
DDD												x	x		x						x		x	x	
DDE												x	x		x					x				x	
DDT			Y									x	x		x						x		x	x	
Diallate			Y							x					x						x	x	x		
Diaminotoluene		x																			x	x	x		
Diazinon	Z		x							x					x						x			x	
Dibenzo[a,h]anthracene											A1	x	x		x						x		x	x	
Dibenzo[c,g]carbazole, 7,H-											A1														
Dibenzofurans						x		x			A1				x		x					x		x	
Dibenzopyrene, 1,2:7,8-											A1				x						x		x		
Diborane								x	x								x			x					
Dibromo-1-propanol phosphate, 2,3-			Z																		x	x	x		
Dibromo-3-chloropropane, 1,2-											B3				x						x	x	x	x	
Dibromomethane			Z				x	x							x						x	x	x		
Dibutyl ether			Z					x								x									
Dibutyl phthalate		x										x	x		x		x			x	x	x	x	x	
Dicamba	Z		x	x						x					x						x				

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Dichlobenil			Z												x						x				
Dichlone			Y												x						x				
Dichloro methyl ether																				x	x	x	x		
Dichloro(1,1'-biphenyl)-4,4'-diamine, 3,3'-																					x	x	x		
Dichlorobenzene		x		x				x			A2	x	x		x						x	x	x	x	
Dichlorobenzidine						x					B1	x	x		x									x	
Dichlorodifluoromethane			Z					x				x	x		x						x		x		
Dichloroethane, 1,1-								x			B2	x	x		x						x		x	x	
Dichloroethane, 1,2-		x	x	x	x	x		x		x		x	x	x	x			x			x	x	x	x	
Dichloroethyl ether			Z								B2	x	x		x		x			x	x	x	x	x	
Dichloroethylene, 1,1-		x					x	x				x	x	x	x	x			x		x	x	x		
Dichloroethylene, 1,2-							x	x				x	x	x	x						x		x	x	
Dichloroisopropyl ether								x				x	x		x										
Dichlorophenol, 2,4-		x	Z				x				B3	x	x		x						x	x	x	x	
rop ı , 2,6-															x						x				
Dichlorophenoxyacetic acid, 2,4-	Y		x	x						x					x	x					x	x	x	x	
Dichlorophenyl isocyanate, 3,4-								x	x								x								
Dichloropropane, 1,1-			Z												x						x				
Dichloropropane, 1,2-		x					x					x	x		x	x					x	x	x	x	
Dichloropropene, 1,2-												x	x		x										
Dichloropropene, 1,3-							x				B3				x						x	x	x	x	
Dichlorvos			x							x					x		x			x	x	x		x	
Diclofop-methyl	Z																								
Dicrotophos			Y														x			x					
Dieldrin			x							x		x	x		x						x		x	x	
Diepoxybutane, 1,2:3,4-															x		x			x	x	x			
Diethanolamine		x	x							x					x	x						x			
Diethyl phthalate		x	Z									x	x		x						x	x	x	x	
Diethyl sulfate		x						x							x					x					
Diethyl sulfide								x																	
Diethyl-p-nitrophenyl phosphate			Z												x						x		x		
Diethylamine	Z		x					x		x				x	x	x					x				
Diethylhydrazine, N,N'-															x						x		x		
Diethylnitrosoamine															x						x	x	x		

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1998	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Diethylstilbestrol															x						x		x		
Dimefox			Z												x		x			x					
Dimethoate	Z		Z												x		x			x	x		x		
Dimethoxy-(1,1'-biphenyl)-4,4'-diamine, 3,3'-																					x	x	x		
Dimethyl aminobenzene															x						x	x	x		
Dimethyl ether				x				x	x																
Dimethyl ethyl amine			Z							x															
Dimethyl hydrazine																	x			x	x	x	x		
Dimethyl phthalate		x	Z									x	x		x		x			x	x	x	x		
Dimethyl sulfate		x	Z				x	x							x		x			x	x	x	x		
Dimethyl sulfide								x									x			x					
Dimethyl(1,1'-biphenyl)-4,4'-diamine, 3,3'-																					x	x	x		
Dimethyl-1,2-benzanthracene, 7,12-											B1				x						x		x		
Dimethylamine	Z		x				x	x	x	x					x	x					x		x		
Dimethylaniline, N,N-		x	Z					x		x					x										
Dimethylbenzylhydroperoxide, alpha,alpha-															x						x	x	x		
Dimethylcarbamoyl chloride								x							x						x	x	x		
Dimethyldichlorosilane								x	x								x				x				
Dimethylformamide							x	x							x										
Dimethylhydrazine, 1,1-								x	x						x										
Dimethylhydrazine, 1,2-								x	x						x						x		x		
Dimethylphenol, 2,4-												x	x		x									x	
Dinitroaniline			Z					x																	
Dinitrobenzene			Z					x	x						x						x			x	
Dinitrocresols		x	Y				x	x			B2	x	x		x		x			x	x	x	x	x	
Dinitrophenol								x	x						x						x				
Dinitrophenol, 2,4-			Y				x					x	x		x						x	x	x	x	
Dinitrotoluene		x						x					x		x						x			x	
Dinitrotoluene, 2,4-		x	Z								B3	x			x						x	x	x	x	
Dinitrotoluene, 2,6-		x									B3	x			x						x	x	x	x	
Dinoseb			x	x						x					x		x			x	x		x		
Dioxane		x				x	x	x			B2				x						x	x	x	x	
Dioxolane								x									x			x					
Diphacinone			Z														x			x					

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NFPI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Diphenylamine			Z				x			x															
Diphenylhydrazine, 1,2-			Z								B3	x	x		x						x	x	x	x	
Diphenylmethane-4,4'-diisocyanate			Z	x			x								x							x			
Dipropylamine								x							x						x		x		
Dipropylaminobenzenediazonium zinc chloride, 4-								x																	
Diquat			x							x					x						x				
Disulfoton			Y					x	x						x		x			x	x		x	x	
Dithiobiuret			Z												x		x			x	x		x		
Diuron			Z												x						x				
Endosulfan			Y									x	x		x		x			x	x		x	x	
Endosulfan sulfate												x			x									x	
Endothall			Y												x						x		x		
Endrin			x									x	x		x		x			x	x		x	x	
Epichlorohydrin		x	Z				x	x			B3				x	x	x	x		x	x	x	x		
EPN			Z														x			x					
Ethanethioamide															x						x	x	x		
Ethanolamine	Z		Z	x				x										x							
Ethion			Y					x	x						x	x	x			x	x			x	
Ethoprophos																	x			x					
Ethoxyethanol, 2-		x					x	x							x							x			
Ethyl 4,4'-dichlorobenzilate																					x	x	x		
Ethyl acetate	Z		Z				x	x						x	x	x					x		x		
Ethyl acrylate	Z	x	Y				x	x		x				x	x	x			x		x	x	x		
Ethyl alcohol	Y		x	x			x	x		x	B3					x		x							
Ethyl chloroformate		x						x														x			
Ethyl mercaptan			Y				x	x		x															
Ethyl methacrylate								x							x						x		x		
Ethyl methanesulfonate															x						x		x		
Ethylamine	Z		Y					x	x	x					x	x					x				
Ethylbenzene	Y	x	x	x	x		x	x		x		x	x	x	x	x		x			x	x			x
Ethylene		x	x	x	x			x	x	x								x	x			x			
Ethylene cyanohydrin																x				x	x				
Ethylene dibromide			Z	x			x	x			B3				x						x	x	x	x	
Ethylene glycol	x	x	x	x			x			x					x	x		x				x			

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1998	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Ethylene oxide	Z	x	x	x	x		x	x	x		B2			x	x		x	x	x	x	x	x	x		
Ethylene thiourea		x	Z								B3				x										
Ethylenediamine	Z							x							x	x	x								
Ethylenediamine tetraacetic acid								x							x						x				
Ethyleneimine			Z					x	x						x		x			x	x	x	x		
Ethylhexanol	Z		x	x						x								x							
Ethyl-N-nitrosocarbamide, N-																					x	x	x		
Famphur															x						x		x		
Fenitrothion	Z		x	x						x							x			x					
Fensulfothion			Z														x			x					
Ferric ammonium citrate								x							x						x				
Ferric ammonium oxalate								x							x						x				
Ferric chloride	Y		x	x				x		x				x	x	x			x		x				
Ferric hydroxide			Z							x															
Ferric oxide	Z		Y							x															
Ferric sulphate	Z							x		x					x										
Ferrous chloride	Z														x						x				
Ferrous sulfate			Y					x		x					x	x					x				
Fluenetil			Z														x			x					
Fluoranthene			Z								A1	x	x		x									x	
Fluoren-2-yl acetamine, N-9H-																					x	x	x		
Fluorene												x	x		x						x			x	
Fluorine			Z		x			x	x						x		x			x	x		x	x	
Fluoroacetamide			Z												x					x	x		x		
Fluoroacetic acid			Z					x												x					
Fluoroscein	Z																								
Fonophos			Y														x			x					
Formaldehyde	Y	x	x	x			x	x		x	B3			x	x	x	x	x	x	x	x	x	x	x	
Formic acid	Z		x	x			x	x		x					x						x		x		
Formparanate															x		x			x					
Freon (as class)	Y																								
Fumaric acid			Z					x							x						x				
Furfural			Z				x	x							x	x									
Gasolines					x		x	x											x						

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Glycerine			Z																						
Glycidaldehyde								x							x	x		x			x		x		
Glyphosate	Y		Y							x															
Halons	Y					x																			
Heavy water			Y							x															
Heptachlor												x	x		x						x	x	x	x	
Heptachlor epoxide												x			x						x			x	
Hexachlorobenzene			Z			x		x			A1	x	x		x						x	x	x	x	
Hexachlorobutadiene			Y				x	x				x	x		x							x		x	
Hexachlorocyclohexane, alpha-											A1	x	x		x									x	
Hexachlorocyclohexane, gamma-			x							x	A1	x	x		x		x			x	x	x	x	x	
Hexachlorocyclohexane, mixed isomers												x	x		x									x	
Hexachlorocyclopentadiene		x	Z				x	x			B1	x	x		x		x			x	x	x	x	x	
Hexachloroethane		x	Z					x				x	x		x						x	x	x	x	
Hexachloronaphthalene							x										x			x		x			
Hexachlorophene			Y					x							x						x		x		
Hexaethyl tetraphosphate			Z					x							x						x		x		
Hexahydrobenzene																					x	x	x		
Hexamethylenediamine	Z							x										x	x						
Hexane			x	x				x		x					x	x		x						x	
Hexanoic acid								x	x																
Hydrazine	Z	x	x	x				x	x	x	B3				x		x			x	x	x	x	x	
Hydrochloric acid	x	x	x	x	x		x	x	x	x				x	x	x	x	x	x	x	x	x	x	x	
Hydrocyanic acid		x	Y					x	x						x	x	x	x	x	x	x	x	x		
Hydrofluoric acid	Z	x	x	x	x			x	x	x				x	x	x	x		x	x	x	x	x		
Hydrofluorosilicic acid	Z																								
Hydrogen	Z		Z	x				x	x																
Hydrogen chloride, anhydrous	Z				x			x	x										x						
Hydrogen fluoride, anhydrous					x			x	x																
Hydrogen peroxide	Y		x	x			x	x	x	x				x		x	x		x	x					
Hydrogen selenide								x	x								x			x					
Hydrogen sulfide			Y	x	x		x	x	x		B3				x		x			x	x		x	x	

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1987NPRI	1990 EPS	1981 EPS	MIAC 1998	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1990	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Hydroquinone		x	Y					x							x		x			x		x			
Indeno(1,2,3-cd)pyrene											A1	x	x		x									x	
Isobutyl acetate								x						x							x				
Isobutyl alcohol			Z				x	x							x						x		x		
Isobutylamine								x						x							x				
Isobutylene								x	x									x							
Isobutyraldehyde		x						x														x			
Isobutyric acid								x							x						x				
Isobutyronitrile								x									x			x					
Isodrin			Y												x		x								
Isofluorophate																	x			x	x		x		
Isophorone			Z				x					x	x		x						x				
Isophorone diisocyanate								x									x			x					
Isophthalic acid	Z																								
Isoprene								x							x						x				
Isopropyl alcohol	Y	x	x	x				x		x							x	x	x			x			
Isopropylmethylpyrazoyl dimethylcarbamate			Z																	x					
Isosafrole		x													x						x		x		
Kelthane															x						x	x		x	
Kepone			Y												x						x		x	x	
Lactonitrile			Z														x			x					
Lasiocarpine															x						x		x		
Lead		x*				x	x*					x	x*		x						x	x	x	x	
Lead acetate								x							x						x				
Lead arsenate			Z					x							x						x		x		
Lead azide, wetted								x	x																
Lead chloride			Z					x							x						x				
Lead iodide								x							x						x				
Lead oxide			x	x						x															
Lead phosphate															x						x		x		
Lead stearate								x							x						x				
Leptophos							x*										x			x					

Chemical	2000 ESD	1997NPRI	1990 EPS	1991 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled In Can.	ARET Lists	EPA 1985	EPA 1990	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Lithium hydride								x									x			x					
Magnesium hydroxide			Y	x						x															
Magnesium oxide			Z							x															
M[illegible]t[illegible]h[illegible]t[illegible]	Z																								
Malathion	Z		x	x						x					x	x					x			x	
Maleic acid			Z					x							x	x					x				
Maleic anhydride	Y	x	x	x				x		x					x	x		x			x	x	x		
Maleic hydrazide															x						x		x		
Malononitrile			Z					x							x		x			x	x		x		
Maneb			x					x		x															
Manganese		x					x*								x									x	
MCPA	Z		x	x						x															
Mechloroethamine																	x			x		x			
Mercuric acetate			Y					x									x			x					
Mercuric arsenate								x																	
Mercuric chloride			Y					x									x			x				x	
Mercuric cyanide								x	x						x						x				
Mercuric sulfate								x							x						x				
Mercuric sulfide			Z							x															
Mercuric thiocyanate			Y					x							x										
Mercurous nitrate			Y					x							x						x				
Mercury	Y	x*	x	x	x	x	x*	x		x		x	x*		x						x	x	x	x	
Mercury fulminate								x	x						x						x		x		
Methacrylonitrile								x							x		x			x	x		x		
Methane					x		x	x	x	x										x	x			x	
Methapyrilene															x						x		x		
Methiocarb			Y														x			x	x				
Methomyl										x					x		x			x	x				
Methoxychlor			x							x					x						x	x	x	x	
Methoxyethanol, 2-		x					x															x			
Methoxyethylmercuric acetate			Y														x			x					
Methyl acrylate		x					x	x								x						x			

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Methyl alcohol	Y	x	x	x			x	x		x				x	x	x	x	x	x		x	x	x		
Methyl bromide		x	Z			x		x	x			x	x		x	x	x			x	x	x	x		
Methyl butyl ether		x						x														x			
Methyl tert-butyl ether								x							x									x	
Methyl chloride		x	x				x	x	x	x		x	x	x	x	x		x	x		x	x	x	x	
Methyl chloroformate								x							x		x			x	x		x		
Methyl ethyl ketone		x	x	x						x				x	x	x		x	x		x	x	x	x	
Methyl ethyl ketone peroxide			Z						x	x					x						x		x		
Methyl hydrazine								x							x		x			x	x	x	x		
Methyl iodide		x	Z					x							x					x	x	x	x		
Methyl isobutyl ketone		x	Z	x				x			B3				x	x					x	x	x	x	
Methyl isocyanate								x							x		x			x	x	x	x		
Methyl isothiocyanate								x									x			x					
Methyl mercaptan								x	x						x		x			x	x		x		
Methyl methacrylate	Z	x	x	x		x		x		x				x	x	x		x	x		x	x	x	x	
Methyl parathion			Y												x	x				x	x			x	
Methyl phenkapton			Z													x				x					
Methyl phosphoric dichloride								x	x								x			x					
Methylamine	Z		x	x			x	x	x	x				x	x						x				
Methylbenzenamine hydrochloride															x						x	x	x		
Methylbenzene																					x	x	x		
Methyldinitrobenzene																					x	x	x		
Methylene chloride		x	x	x		x		x		x	B2	x	x		x	x		x			x	x	x	x	
Methylenebis(2-chloro)benzenamine, 4,4'-																					x	x	x		
Methylenebis(2-chloroaniline), 4,4'-		x									A1				x									x	
Methylene*bis*(phenyl isocyanate)	Z	x																				x			
Methylenedianiline, 4,4'-		x													x										
Methylenedioxy-4-propylbenzene, 1,2-															x						x		x		
Methylethylbenzene																					x	x	x		
Metolcarb															x		x			x					
Mevinphos			Y					x	x						x		x			x	x		x		
Mexacarbate			Z												x		x			x	x		x		

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1990	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Mitomycin C															x		x			x	x		x		
Mo-o-roto-hos			Z														x			x					
Morpholine			Z	x				x																	
Motor fuel anti-knock com ounds								x	x										x						
Muscimol															x		x			x	x		x		
Mustard gas																	x			x		x			
N-l-d			Y												x	x					x			x	
Naphtha	Y		Z	x	x			x						x											
Na hthalene	Z	x	x				x	x		x		x	x		x	x		x			x	x	x	x	
Naphthalenedione, 1,4-															x						x		x		
Naphthenic acids								x							x						x				
Naphthylamine							x	x			B2				x						x	x	x		
Naphthylthiourea								x							x										
Nickel		x*										x	x*		x		x			x	x	x		x	
Nickel carbonyl			Y					x	x	x					x		x								
Nickel chloride			Z					x							x						x				
Nickel cyanide								x													x		x		
Nicotine								x							x		x			x	x		x		
Nicotine sulfate			Z					x									x			x					
Nitrating acids								x	x					x											
Nitric acid	Y	x	x	x	x			x	x	x				x	x	x	x	x		x	x	x			
Nitric oxide								x	x						x		x								
Nitrilotriacetic acid		x	Z	x			x															x			
Nitroanilines			x					x		x					x										
Nitrobenzene		x	Z					x				x	x		x	x	x	x		x	x	x	x		
Nitrogen	Y		x					x		x								x							
Nitrogen dioxide			Y				x	x	x	x					x	x	x							x	
Nitroglycerin		x	Z	x			x	x	x						x						x	x	x		
Nitrophenols		x	Z					x				x	x		x						x			x	
Nitropropane		x	Z					x			B2				x						x	x	x		
Nitrosodimethylamine, N-			Z				x				B3	x	x		x		x				x	x		x	
Nitrosodi hen lamine, N-		x	Z								B3	x	x		x						x	x		x	

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Nitrosodipropylamine, N-											B3	x	x		x						x	x	x	x	
Nitrosomorpholine, N-											B3				x							x			
Nitrosopiperidine, N-															x						x	x	x		
Nitrosopyrrolidine, N-															x						x		x		
Nitrotoluenes			Z					x							x						x				
Nitrous oxide			Y					x		x															
Nitroxylenes								x																	
Nonane			Z					x		x															
Nonylphenol			x	x			x			x															
Octamethylpyrophosphoramide															x					x	x		x		
Oleic acid			Z				x																		
Oleum	Z		Z	x																					
Osmium tetroxide								x							x		x			x	x	x	x		
Oxamyl															x		x			x					
Oxathiolane-2,2-dioxide, 1,2-																					x	x	x		
Oxygen	Z		x					x	x	x								x							
Ozone							x										x			x					
Paraldehyde								x							x						x				
Paraquat	Z		x							x							x			x					
Parathion			x					x	x	x					x	x	x			x	x	x	x	x	
Parathion methyl																	x			x	x				
PCBs	x		x	x		x		x		x	A1	x	x		x	x				x	x	x		x	
Pentachlorobenzene			Z												x						x		x	x	
Pentachloroethane								x							x		x			x	x		x		
Pentachloronitrobenzene															x						x	x	x		
Pentachlorophenol	Y		x	x			x	x		x	A1	x	x		x	x	x			x	x	x	x	x	
Peracetic acid		x															x			x		x			
Perchloromethyl mercaptan								x									x			x	x		x		
Phenanthrene			Z								A1	x	x		x						x			x	
Phenol	Y	x	x	x			x	x	x	x	B3	x	x	x	x	x	x	x	x	x	x	x	x	x	
Phenolsulfonic acid	Z		Y					x		x															
																	x			x	x		x		

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NFPI	1990 EPS	1981 EPS	MIAC 1998	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Phenylenediamine, p-		x	Z					x		x					x							x			
Phenylmercuric acetate			Y					x		x					x		x			x	x		x		
Phenylphenol, 2-		x	Z																			x			
Phenylsilatrane																	x			x					
Phenylthiourea			Z												x		x			x	x		x		
Phorate			Z												x		x			x	x		x	x	
Phosgene		x	Z				x	x	x	x				x	x		x	x		x	x	x	x		
Phosmet			Z														x			x					
Phosphamidon			x							x							x								
Phosphine			Z					x	x	x					x		x			x	x		x		
Phosphoric acid	Y	x	x	x				x		x				x	x	x		x	x		x	x			
Phosphorus	Z	x	x	x			x	x		x				x	x	x	x	x		x	x	x		x	
Phosphorus oxychloride								x						x	x	x	x								
Phosphorus pentasulfide								x							x						x		x		
Phosphorus pentoxide			Y					x		x							x			x	x	x			
Phosphorus trichloride								x						x	x		x			x	x				
Phosphorus, white		x						x	x										x						
Phthalic anhydride	Z	x	x	x				x		x								x			x	x	x		
Picloram	Z		x							x															
Picoline, 2-								x							x						x		x		
Piperidine								x							x		x			x					
Potassium arsenate								x							x	x									
Potassium arsenite								x							x		x								
Potassium chloride	Y		x	x						x															
Potassium chromate								x							x	x					x				
Potassium cyanide			x					x	x						x	x	x			x	x		x		
Potassium dichromate			Z												x						x				
Potassium hydroxide	Y		x	x				x		x				x	x	x		x	x		x				
Potassium nitrate								x						x					x						
Potassium permanganate	Z		x					x		x				x	x	x					x				
Potassium silver cyanide															x		x			x	x		x		
Promecarb															x		x			x					

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1987NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Propane					x			x	x																
Propargyl alcohol			Y												x						x		x		
Propiolactone															x		x			x		x			
Propionaldehyde		x	Z					x							x							x			
Propionic acid			x					x		x					x	x					x				
Propionic anhydride			Z					x							x						x				
Propionitrile								x							x		x			x	x		x		
Propyl alcohol							x	x								x									
Propyl benzene, n-							x	x																	
Propyl chloroformate								x									x			x					
Propylamine			Z					x							x										
Propylene		x	x	x				x	x	x								x				x			
Propylene chlorohydrin			Z					x		x															
Propylene glycol	Z		x	x						x								x							
Propylene oxide	Z	x	x	x	x		x	x	x	x				x	x	x	x	x	x	x	x	x				
Propyleneimine								x									x			x	x	x	x			
Pyrene											A1	x	x		x		x			x	x				x	
Pyridine	Z	x	x					x		x				x	x										x	
Quinoline		x	Z					x			B3				x						x	x				
Quinone		x	Z				x	x							x						x	x	x			
Reserpine															x						x		x		
Resorcinol			Z					x							x	x					x		x		
Selenious acid															x		x			x	x		x		
Selenium		x*					x*	x				x	x*		x									x	
Selenium dioxide															x						x		x		
Selenium disulfide								x													x		x		
Selenium oxychloride								x									x			x					
Silver		x*					x*					x	x*		x						x	x	x	x	
Silver cyanide								x						x	x						x		x		
Silver nitrate			Z					x							x						x				
Sodium			Z					x		x					x	x			x		x				
Sodium aluminate			Y	x				x		x															

Chemical	2000 ESD	1997NFPI	1980 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Sodium anthraquinone sulfonate			Z														x			x					
Sodium arsenate			Z					x							x		x			x	x				
Sodium arsenite			Y	x				x		x					x	x	x			x	x			x	
Sodium azide			Y					x							x		x								
Sodium bisulfite	Z		Z	x			x							x	x						x				
Sodium borohydride			Y	x				x		x															
Sodium cacodylate								x									x			x					
Sodium carbonate	Z		x	x						x								x							
Sodium chlorate	Y		x	x	x		x	x		x								x	x						
Sodium chloride	Y		x	x						x															
Sodium chlorite	Z						x	x																	
Sodium chromate			Y					x		x					x						x				
Sodium cyanide	Z		x	x			x	x	x	x				x	x	x	x			x	x		x		
Sodium dichloroisocyanurate				x											x										
Sodium dichromate	Y		Y	x											x	x					x				
Sodium fluoride			x					x		x					x						x				
Sodium fluoroacetate			Z					x									x				x		x		
Sodium fluorosilicate			Z					x																	
Sodium hydrosulfide			Z					x	x	x					x	x									
Sodium hydrosulfite	Z		x											x											
Sodium hydroxide	x		x	x				x		x				x	x	x		x	x		x	x			
Sodium hypochlorite	Y		x	x						x					x						x				
Sodium methylate								x							x						x				
Sodium nitrate			Y					x		x				x		x			x						
Sodium nitrite	Z							x							x						x				
Sodium pentachlorophenate	Z							x									x			x					
Sodium phosphate, tribasic			Z					x							x						x				
Sodium phosphates			Y	x				x							x	x					x				
Sodium selenite			Z												x		x				x				
Sodium silicate	Z		x	x						x								x							
Sodium sulphate	Z		Z	x														x				x			
Sodium sulphide	Z							x								x									

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NPRI	1990 EPS	1991 EPS	MIAC 1986	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled In Can.	ARET Lists	EPA 1985	EPA 1990	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Sodium sulphite	Z		x	x						x															
Stannic chloride			Z					x		x															
Strychnine			Y					x							x	x	x			x	x		x		
Strychnine sulfate			Z														x			x					
Styrene	Y	x	x	x				x		x				x	x	x		x	x		x	x		x	
Styrene oxide		x													x							x			
Sulfotepp			Z														x			x	x		x		
Sulphur	Y		x	x				x		x						x									
Sulphur chloride			Z					x		x				x	x	x					x				
Sulphur dioxide	Y		x	x	x			x	x	x							x		x	x					
Sulphur tetrafluoride									x								x			x					
Sulphur trioxide								x	x								x			x					
Sulphuric acid	x	x	x	x	x		x	x	x	x				x	x	x	x	x	x	x	x	x			
Sulphuryl chloride			Z	x				x		x															
Terephthalic acid			x	x						x								x				x			
Terphenyls			Z	x		x				x															
Tetrachlorobenzene, 1,2,4,5-			Z												x						x		x		
Tetrachlorodibenzo-p-dioxin, 2,3,7,8-						x					A1	x	x		x						x				x
Tetrachloroethane		x					x	x				x	x		x						x	x	x		x
Tetrachloroethylene	Z	x	x	x		x		x		x		x	x		x	x		x							x
Tetrachlorophenol, 2,3,4,6-			Y								B2				x						x		x		x
Tetraethyl lead	Z		x	x	x					x	B2			x	x	x	x			x	x		x		
Tetraethyl pyrophosphate			Y												x					x	x		x		
Tetrahydrofuran								x						x							x		x		
Tetramethyl lead			Z														x			x					
Tetranitromethane								x	x						x					x	x		x		
Thallic oxide															x		x			x	x		x		
Thallium			Z				x*					x	x*		x						x	x			
Thallium acetate			Z												x						x		x		
Thallium carbonate															x		x			x	x		x		
Thallium chloride															x					x	x		x		
Thallium nitrate								x							x										

Chemical	2000 ESD	1997NFPI	1990 EPS	1991 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Thallium peroxide																				x	x		x		
Thallium sulfate			x							x					x		x								
Thioazin																	x			x	x		x		
Thiobis-(4,6-dichlorophenol), 2,2'-			Z																	x					
Thiofanox															x		x			x	x		x		
Thioglycolic acid			x					x		x							x								
Thionyl chloride			Z					x		x															
Thiophenol															x		x			x	x		x		
Thiosemicarbazide			Z												x		x			x	x		x		
Thiourea		x	Z				x				B2				x										
Thiram			Y							x														x	
Titanium dioxide			x	x						x								x							
Titanium tetrachloride		x						x							x					x		x			
Toluene	x	x	x	x	x			x		x		x	x	x	x	x		x	x		x	x	x	x	
Toluene-2,4-diamine			x							x					x						x	x	x		
Toluene-2,4-diisocyanate	Z	x	x	x			x	x		x	B3			x	x		x	x	x	x	x	x			
Toluene-2,6-diisocyanate		x									B3						x			x	x	x			
Toluidine			Z				x	x							x										
Toxaphene			Y				x					x	x		x	x								x	
TP acid esters, 2,4,5-															x								x		
TP acid, 2,4,5-			Z												x						x		x	x	
Tri-(1-aziridinyl) phosphine oxide								x																	
Trichlorfon	Z		x	x						x					x		x			x	x	x			
Trichloro-2,2-bis(p-methoxyphenyl)ethane, 1,1,1-																					x	x	x		
Trichloroacetyl chloride								x									x			x					
Trichlorobenzene		x	Z					x				x	x		x						x	x		x	
Trichloroethane, 1,1,1-	Y		x	x		x		x		x		x	x		x	x		x			x	x	x	x	
Trichloroethane, 1,1,2-		x										x	x		x						x	x	x	x	
Trichloroethylene, 1,1,1-																					x	x	x		
Trichloroethylene, 1,1,2-	Z	x	x			x		x		x	B3	x	x		x	x								x	
Trichloroethylsilane								x							x		x			x					
Trichlorofluoromethane				x								x	x		x						x		x		

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1987NPRI	1990 EPS	1991 EPS	MIAC 1998	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Trichlorophenol			Z												x						x				
Trichlorophenol, 2,4,5-							x								x						x	x	x	x	
Trichlorophenol, 2,4,6-											B1	x	x		x									x	
Trichlorophenoxyacetic acid, 2,4,5-			x							x					x						x		x		
Trichlorophon																				x	x	x			
Triethanolamine			Y							x					x										
Triethanolamine dodecylbenzenesulphonate								x							x						x				
Triethylamine			Z					x						x	x						x				
Trifluralin	Z		x	x						x					x							x		x	
Trimethylamine			Z					x	x	x					x						x				
Trimethylchlorosilane								x									x			x					
Trinitrobenzene								x	x						x						x		x	x	
Trinitrophenol								x	x													x			
Trinitrotoluene			x	x			x	x	x	x														x	
Trypan blue															x						x		x		
Turpentine			Z	x				x								x									
Uranium							x*	x																x	
Uranium (233, 234, 235)																								x	
Uranium dioxide			Z	x						x															
Uranyl acetate								x							x						x				
Uranyl nitrate			x							x					x										
Urea	Y		Y	x														x							
Urea formaldehyde	Z																								
Urea nitrate	Z							x	x																
Vanadium		x					x*															x*			
Vanadium pentoxide			Y					x							x		x			x	x		x		
Vinyl acetate	Z	x	x	x				x		x				x	x	x	x	x	x	x	x	x			
Vinyl bromide								x	x		B3										x				
Vinyl chloride	Y	x	x	x	x	x		x	x	x		x	x	x	x			x	x		x	x	x	x	
Warfarin			Z												x		x			x	x		x		
Xylene	Y	x	x	x	x			x		x				x	x	x		x	x					x	
Xylenol			Z					x							x	x					x			x	

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.	SARA ex. Dang.	CERCLA Haz.	SARA Ex. Toxic	RCRA Haz.	Tox & Dis Reg	OSHA 29CFR
Zinc		x*					x*	x				x	x*		x						x	x		x	
Zinc acetate			Z					x							x						x				
Zinc borate								x							x						x				
Zinc bromide			Z					x		x					x						x				
Zinc carbonate								x							x						x				
Zinc chloride	Z		x	x				x		x					x	x					x			x	
Zinc cyanide			x					x		x					x						x		x		
Zinc fluoride								x							x						x				
Zinc nitrate								x							x						x				
Zinc oxide			x	x						x											x				
Zinc phenolsulfonate								x							x						x				
Zinc phosphide								x	x						x		x			x	x	x			
Zinc sulphate	Z		x	x				x		x					x										

Appendix -- List of Lists - abbreviated

Chemical	2000 ESD	1997NPRI	1990 EPS	1981 EPS	MIAC 1996	CEPA 2000	CEPA List II	TDG Sch. 2	TDG SCh. 12	Spilled in Can.	ARET Lists	EPA 1985	EPA 1980	US Railroad	US Reportable	USCG Spill	EPA Ex Danger	US top 100	AAR Hazard.

Legend: Code / List [* = and its compounds]

2000 Priority List: Top 10 (x), 11-50 (Y), 51-150 (Z) (Environment Canada - Emergencies Science Divison [ESD])
1997 National Pollutants Release Inventory (NPRI) (Environment Canada)
1990 Priority List: Top 150 (x), 151-250 (Y), 251-500 (Z) (Environment Canada)
1981 Priority List (Environment Canada)
MIAC 1996 Priority List
Canadian Environmental Protection Act (CEPA) Priority Substance List (2000)
CEPA Priority Substance List PSLII (1995) (Environment Canada)
TDG Schedule 2 (1996)
TDG Schedule 12 (1994)
Spill History in Canada (1974-84)
ARET Substance List (A1etc) denotes list (1995)
U.S. Coast Guard CHRIS List (1992)
EPA 129
EPA 65
U.S. Railroad Spill List
EPA Reportable Quantities List, 40 CFR parts 117 & 302 (1997)
U.S. Coast Guard Spill List
EPA Acutely Toxic or Potentially Dangerous Chemicals List (1986)
U.S. Top 100
AAR Hazardous Materials Data Base (1981)
SARA Section 302 Extremely Hazardous Substances (1987)
CERCLA Hazardous Substances (1987)
SARA Section 313 Toxic Chemicals (1987)
RCRA Hazardous Wastes (1987)
Agency for Toxic Substances and Disease Registry Priority List (1995)
OSHA 29 CFR 1910 List of Highly Hazardous Chemicals, Toxics and Reactives

Isla de Cabras Explosives Site Emergency Response Removal Action

Gregory B. DeAngelis
On-Scene Coordinator (OSC)
United States Environmental Protection Agency (EPA)
Edison, New Jersey, USA
deangelis.gregory@epa.gov

Abstract

This case study presents multi-agency planning, coordination and execution for the detonation and destruction of approximately 44 tons of shock sensitive deteriorating explosive and pyrotechnic material located at the entrance to San Juan Harbor, Puerto Rico. The paper discusses the following:

- A site history of how the situation evolved;
- Mitigating factors considered;
- The use of air modeling as both a planning tool and an effective method for dealing with a wary public environmental organization;
- The coordinated activities of both planning and operations at different levels of government;
- The rationale for the Pre and Post Sampling operations;
- Real-time air monitoring performed during detonation operation;
- Safety protocols and protective measures for detonation;
- Different methods used in the destruction of explosives and pyrotechnics;
- Resultant methods for disposal of the residual explosive and pyrotechnic material based on laboratory analytical results.

1.0 Site History

1.1 Physical Location

The site is located on the northeastern side of Isla de Cabras, Toa Baja, Puerto Rico and is near the Catano and Palo Seco areas of San Juan. The site occupies about 5 acres on the end of the Isla de Cabras peninsula which is the western side of the entrance to the San Juan harbor. Directly across the harbor entrance is the historic fort area of El Morro (Old San Juan). All ship and boat traffic including cruise ships must pass within a few hundred yards of the site to enter the harbor. Due to the trade winds, the site is directly in the path of the landing approach for Isla Grande Airport which is located across the harbor. There are adjacent beaches about 100 yards to the south which are used by hundreds of people every weekend. The site is only partially fenced and offers easy access to the public. Public entry to the area was evidenced by fishing tackle debris, cigarettes and alcohol containers strewn about the trailers which contained the pyrotechnic materials. The site was operated by the Puerto Rico Police Department (PRPD) for weapons qualifications, explosive demolition training and explosive storage.

1.2 Background

Prior to 1992, the PRPD would normally get rid of confiscated explosives and pyrotechnics by giving them to the Department of Defense (DOD) located in Puerto

Rico for destruction. In 1992, the EPA promulgated the "Military Munitions Rule" (40 CFR 266.203-205) which identified the non-emergency destruction of explosive materials as a Resource Conservation and Recovery Act (RCRA) waste that required storage, treatment and disposal at an approved facility. As such, this restricted the DOD from destroying munitions unless continued storage of the munitions created an imminent safety hazard, ie, an emergency situation. In addition, if the DOD accepted a "waste", they would be responsible for associated waste disposal costs. This initially prevented the PRPD from turning over confiscated explosives and pyrotechnics to the DOD to detonate or destroy. Because of strict air regulations, a shortage of funds and the lack of a Puerto Rican government disposal facility suitable for explosives, the PRPD "temporarily" stored the explosive materials at the Isla de Cabras site. The site had two 40-foot trailers, two 20-foot truck trailers and a concrete bunker that were used as "temporary" storage facilities. These storage locations were packed from floor to ceiling with fireworks, pyrotechnics and explosives that had been confiscated by the PRPD. These materials were stored at uncontrolled temperature and humidity conditions since 1992. Due to their probable deterioration, they were considered potentially shock sensitive and would be exempt from the "Military Munitions Rule" because of the imminent emergency situation. Some of the explosive materials were previously stored in cinder block bunkers and were placed into the trailers in October 1997. The trailers were located about 50 feet from the bay and salt water intrusion severely deteriorated the trailers rendering them incapable of being moved. In addition, the high humidity and possible water damage accelerated the deterioration of the explosive materials. The explosive materials continued to deteriorate until their destruction during June-August 1999.

1.3 Emergency Response Situation/Actions

Based on inspections conducted by Alcohol, Tobacco and Firearms (ATF) personnel, the EPA was requested to assess the site situation by an US Department of Justice (DOJ) Attorney to help rectify the explosives deterioration problem. On August 11, 1997, the EPA performed an expedited removal assessment (ERA) which included documenting site conditions and gathering information to determine site eligibility for a Comprehensive Environmental Response, Compensation and Liability Act (CERCLA) removal action. The ERA confirmed the presence of reactive and toxic, explosive and pyrotechnic materials in a deteriorating state. Initial removal resulted on the explosive materials being moved from the bunkers, repackaged and placed "temporarily" into truck trailers until the materials received proper disposal. Discussions between the Governor's Office of Public Safety & Security, the Puerto Rico National Guard (PRNG), the PRPD, the EPA and the ATF proceeded for about 18 months to determine the best way to transport the materials to Camp Santiago at the south side of the island for destruction. Initial removal plans had the explosive and pyrotechnic materials being repackaged, loaded on DOT-approved trucks, transported through heavily populated areas of San Juan (Palo Seco and Catano) and Caguas, unloaded into ammunition bunkers at Camp Santiago, put into a trench, soaked in kerosene and then burned. The resultant contaminated soil/ash was to be collected and sent to an appropriate disposal facility. Hurricane George struck the island in September 1998 thereby delaying the discussions and the decision to proceed. This planning process identified many concerns about public safety during

movement of the explosive materials.

In November 1998, EPA recommended that the explosive and pyrotechnic materials be destroyed at the Police Firing Range at Isla de Cabras rather than be transported across the island. This decision alleviated public safety concerns about the movement of the materials across the island. In addition, by using the prevailing sea breezes at Isla de Cabras, the smoke plumes generated during explosives destruction could be kept over the ocean. This protected both the public and the environment. Using a five year history of winds (direction and speed), an air dispersion model was developed for the impact of a smoke plume resulting from detonation of four different types of pyrotechnics/explosives in 2,000 lbs batches. The model covered three-hour (24-hour period) and one-hour (morning only) time increments. Once the air dispersion model was developed by EPA Environmental Response Team (ERT) and Response Engineering and Analytical Contract (REAC) personnel, the model was used to support the plan to destroy the explosive and pyrotechnic materials at the Police Firing Range. The air dispersion model for the destruction of explosive/pyrotechnic materials on Isla de Cabras was evaluated and accepted by representatives of the Comunidades Unidas Contra la Contaminacion (CUCCO) *(Translation: Communities United Against Pollution)*, ATF, PRPD and EPA.

On June 22-23, 1999, background air and soil samples were collected to establish site conditions before explosive and pyrotechnic materials were destroyed. The site removal action was carried out by PRPD explosives experts; EPA personnel provided on site safety review, soil sampling and air sampling/monitoring support. ATF agents were also at the site to observe explosive/pyrotechnic destruction activities. The PRPD prepared a work plan for site detonation activities; the work plan incorporated EPA comments. The explosive/pyrotechnic destruction operation began on June 24, 1999, with functional commercial grade fireworks being ignited by a licensed fireworks company with local television news crews filming the detonation. The PRPD segregated the commercial fireworks prior to the EPA representatives' arrival. The Antilles Fireworks Company donated their time to set up and ignite the functional fireworks. On the morning of June 24, 1999, the PRPD installed a bomb basket on site in preparation for the detonation of the explosive materials. On June 25, 1999, the PRPD conducted test detonations of different sizes of explosives to ensure that noise levels were not disruptive and the bomb basket could effectively accommodate the detonation size. After testing, explosives consisting mainly of bundled groups of 600 M-80, 500 M-100, and 250 M-200 firecrackers wrapped in seven feet of 50 grain detonation cord were electronically detonated in a bomb basket buried in sand.

Pyrotechnics burning operations began on July 1, 1999, and were delayed by a late delivery of kerosene. The "GO" decisions for all burns were based on the meteorological conditions at the site. In addition, based on historical wind directions and speeds, it was determined that the burns would take place only between the morning hours of 6:00am to 12:00 noon. However, as long as the winds did not change, burns and detonations were carried out throughout the afternoon hours as well. Initially, ERT and REAC personnel had set up a meteorological station to record weather conditions. Later, the range flag was used to determine the wind direction. The pyrotechnics were burned in an old block bunker that was modified by

removing the concrete roof (replaced with multiple layers of chain-link fence) and replacing the wooden door with a metal door. The bunker modifications were completed on June 23, 1999. On July 1, 1999, pyrotechnics materials were placed on wooden pallets in the modified bunker, soaked with kerosene and ignited using an electrical device. The resultant ash was so hot that later burns were accomplished by tossing whole cases of pyrotechnics onto the hot coals. In this manner, many burns could be completed in a day. The non-functional commercial grade fireworks were cut apart and the fireworks material was burned with the pyrotechnics. Data-rams and Gillian Pumps were placed at five locations within the site to verify air dispersion model predictions with actual burn data. In total, approximately 44 tons of pyrotechnics and explosives were destroyed. Sample analysis results for the resultant ash indicated that the ash could be disposed of as non-hazardous waste.

2.0 Planning

2.1 Use of Air Dispersion Modeling for Decision Making

The air dispersion model was used to confirm the EPA's recommendation to the Puerto Rican Government to change the removal plan and destroy the explosive and pyrotechnic material on site at Isla de Cabras rather than transport the material to Camp Santiago for destruction. It was determined that there were too many risks associated with handling the potentially shock sensitive explosive materials at least 5-6 times and moving the materials 50 miles over rough roads through some heavily populated areas of Puerto Rico. If an accident occurred en route to Camp Santiago, significant time sensitive and labor intensive emergency response measures would be necessary to protect the public from the explosion and resultant smoke plume. The Puerto Rican Government was very receptive to destroying the explosive materials at the Isla de Cabras site. However, prior to conducting destruction operations at Isla de Cabras, EPA wanted to ensure that CUCCO was supportive of the location change for explosives destruction operations to Isla de Cabras. To demonstrate the impact of the destruction of explosive/pyrotechnic materials at Isla de Cabras, an air dispersion model was developed. The air dispersion model looked at the:

- Historical wind directions and speeds for the preceding five years;
- Elevation and location of the burn site;
- Known contaminants concentrations for four different types of explosives and pyrotechnics based on similar US Army pyrotechnic destruction testing;
- Burn durations and solar index/temperature gradients.

The air dispersion model showed the predicted smoke plume and its impacts on a map of the area through contour lines which demonstrated the percentages of impact of areas as 100, 25, 10, 1, and 0.1 based on a table of known explosive and pyrotechnic contaminant concentrations (ppm) from destructive burns (see Figure 1). The map was further broken down into time frames. The model showed the contour lines for three-hour increments and also for one-hour increments from 6am to 12 noon to predict the best time of the day to conduct the burn based on historical winds (see Figure 2). When shown to CUCCO leaders, the air dispersion model also demonstrated the potential impact an accident would have on their communities if there was an explosives detonation while the material was being transported to Camp Santiago. After a site visit, a briefing about the Isla de Cabras burn plan and the

presentation of the air dispersion model, the leaders of CUCCO concurred with the EPA's decision to change the location for the destruction of the explosives and pyrotechnics materials. Generally, the air dispersion model showed that the majority of the time the areas of greatest impact were over the ocean at Isla de Cabras (burns were only to take place when the wind directions were favorable). Without the use of the air dispersion model as a decision-making tool, the cooperation and approval of CUCCO may not have been obtained.

2.2 Mitigating Factors Considered

There were a number of different concerns that had to be carefully considered before conducting explosives and pyrotechnics materials destruction at the Isla de Cabras location. Decisions had to be made to determine the best ways to minimize health impacts. Additionally, there was no provision in the PRPD budget for disposal costs for the explosives and pyrotechnics. As such, the PRPD had very little money to carry out this operation and was constantly concerned about any expenditure of funds and associated personnel costs.

2.2.1 Historical Sites

Many historical sites and treasured buildings are located within a half mile of the Isla de Cabras site. These sites are also some of the biggest tourist attractions in the San Juan area and are extremely visible. Some of the prominent areas include the forts protecting the harbor entrance and the Old San Juan area.

2.2.2 Catano Initiative

The strained relationship between the CUCCO and the Government of Puerto Rico resulted from government-run power plants in the Catano area. The EPA had been litigating air emissions concerns for the Catano/Palo Seco area based on a complaint from the CUCCO. The CUCCO felt that the Government of Puerto Rico was not properly regulating air emissions from companies and power plants in the area. The CUCCO believed that air emissions were the cause of many illnesses in the area. The EPA investigated the situation and brought complaints against two power plants and five other companies for EPCRA 313 violations. This litigation was referred to as the "Catano Initiative". The EPA had a legitimate need to involve the CUCCO in the decision-making process for the burning pyrotechnics at Isla de Cabras. While the relationship between the CUCCO and the Government of Puerto Rico was one of mistrust, previous EPA actions in support of the CUCCO were viewed positively by the CUCCO. This positive relationship allowed the EPA to approach the CUCCO and gain their support for an alternative approach to destroy explosive/pyrotechnic materials at the Isla de Cabras site.

2.2.3 Ecological Protected Areas/Environmentally Sensitive Areas

The entire San Juan Bay and estuary is considered a protected environmentally sensitive area. This area is one of the few manatee habitats in Puerto Rico and is also a highly visible spot in the center of a tourist area. Because the estuary was highly polluted at one time, the remarkable progress made in the past decade in cleaning up the estuary is a source of great pride to the local residents.

2.2.4 Public Beaches

There are public beaches on both sides of the Isla de Cabras peninsula. Most of the peninsula, with the exception of the northern tip, has a park-like setting. The beaches and park are heavily used for swimming, picnics and fishing. On weekends and evenings, there are hundreds of people using the beaches.

2.2.5 Explosive Handling

Initially, there was some concern about the explosive handling capability of the PRPD because of rumored incidents of explosive mishaps and the apparent lack of concern about the proper storage of explosive materials. However, meeting with PRPD explosive experts and discussions with an ATF inspector about PRPD capabilities alleviated the concerns.

2.2.6 Port Operations

Because the explosives destruction site was located at the entrance of the San Juan harbor, it was critical that the destruction operation not impact port operations. The San Juan harbor is the main port for all of Puerto Rico. There is a constant stream of cargo, fishing and cruise ships entering and exiting the port during all hours of the day.

2.2.7 Isla Grande Airport Approach

Aircraft landing and taking off from the Isla Grande Airport fly directly over the location where explosives detonation and pyrotechnic burning took place. The Federal Aviation Administration (FAA) was consulted and issued a warning to pilots to alter their approaches/take offs during the period of the planned burn and detonation operations. Even so, during the burn/detonation operations, there was a constant watch for small planes that either ignored or were unaware of the FAA warning.

2.2.8 Residential Area Impacts

The impact of burn/detonation operations on residential areas was assessed using air modeling results. The air model contamination contour lines (.1 percent) indicated that there would be minimal residential impact of burning/detonation at Isla de Cabras. In addition, during the initial detonations, personnel were stationed at the entrance to Isla de Cabras to ensure that the noise level from detonations was within acceptable levels.

3.0 Site Air and Soil Monitoring and/or Sampling

3.1 Pre- and Post-Rational

Because the Isla de Cabras operations included open air burning and detonations, there was a need to identify potential impacts upon the surrounding area. The air model had identified locations where potential impacts might occur. This allowed a comparison of the Pre-operations sampling results to the real-time air monitoring results during detonations and pyrotechnic burns and soil sampling results at the conclusion of the burn/detonation operations.

3.2 Pre-Operations Sampling

Prior to the destruction of the explosives and pyrotechnic materials at the site, air and soil samples were collected. These pre-operations samples were used to determine the background levels of projected contaminants at the site.

3.2.1 Air Monitoring/Sampling

Real-time Ram air monitoring was conducted to determine background particulate levels. The highest background particulate level was 65.4 μ/m^3. Air sampling was performed for particulates and 21 metals. There were two sampling periods consisting of six sampling stations (see Figure 3). The locations of the sampling stations varied with the prevailing meteorological conditions of the day. Background air samples had non-detectable levels of particulate (Nuisance Dust) and only iron, lead and zinc were detected above the method detection limit (MDL):

- Iron: 1.1 $\mu g/m^3$ at two stations
- Lead: 0.63 $\mu g/m^3$ at one station
- Zinc: 0.58 $\mu g/m^3$ at one station

3.2.2 Soil Sampling

Soil samples were collected at 14 locations for Total Analyte List (TAL) metals analyses. Two sample locations were located upwind, four sample locations were located downwind and all six sample locations were within 50 yards of the burn bunker. Two additional soil samples were collected off site at the nearby east and west public beach areas. The soil samples contained a large number of metals with concentrations above the MDL. Aluminum, calcium, iron and magnesium had the highest concentrations in the majority of the samples.

3.3 Operations Air Sampling and Monitoring

Real-time air monitoring and air sampling were conducted during the first few days of detonation and burn activities to confirm the projected results from the air model and to compare the air monitoring and sampling data with the pre-operations sampling results. Real-time Ram air monitoring was done at six stations for a period of four hours. As expected, the highest real-time sample reading was obtained at the station closest to the disposal activity; a particulate reading of 8,108.1 $\mu g/m^3$ was obtained. The two highest metal concentrations obtained during the operations phase came from two different downwind stations on different days. The concentrations for potassium (160 $\mu g/m^3$, 440 $\mu g/m^3$) and aluminum (49 $\mu g/m^3$, 110 $\mu g/m^3$) were the highest readings recorded during the sampling periods. Volatile organic compound (VOC) sampling and analysis were also done to validate the air model data. VOC analysis was performed for 46 target analytes based on previously identified contaminants from pyrotechnic and explosive destruction. The highest VOC concentration (27 ppb benzene) was obtained at closest station closest to the burn and detonation operations.

3.4 Post-Operations Sampling

At the conclusion of the burn/detonation operations, samples were collected for the resultant ash from the pyrotechnic burning; soil samples were collected at locations adjacent to the burn/detonation site. The ash was analyzed for metals to

determine acceptable disposal methods. The soil sample results were compared to the background soil results to determine if there was any significant soil metal contamination on the site resulting from the explosives detonation and/or pyrotechnic burning. The post-operations soil sampling data did not indicate a significant difference between before and after analyte levels. A large number of metals were detected in the ash samples at concentrations above the MDL. Aluminum, calcium, iron and magnesium had the highest concentrations, however, but the concentrations of the four metals were still within the background soil metals concentration range. Toxicity Characteristic Leaching Procedure (TCLP) analyses were conducted to determine the metals mobility. Only arsenic (33 µg/L) and barium (590 µg/L) were detected in the TCLP leachate and their concentrations were well below the maximum acceptable TCLP concentrations (mg/L).

4.0 Coordination and Agencies Roles

Coordination for both the planning and the actual detonation and burn operations involved many different individuals and groups. The following offices/groups (listed alphabetically) were involved in either the planning or actual detonation and burn operations at the Isla de Cabras site.

- Advisors to the Governor for Public Safety and Security and for the Environment and Natural Resources. Coordinated the overall project and the purchase and installation of an incinerator to destroy future confiscated explosive materials;
- ATF. Conducted inspections of bunkers and was supportive of EPA efforts to destroy the explosives and pyrotechnic materials;
- Antilles Fireworks Company. Donated its personnel's time and expertise in displaying functional commercial fireworks at an evening presentation;
- CUCCO. Leaders of the organization were invited to the Isla de Cabras destruction site and were briefed on the destruction plan. The plan was accepted and approved by CUCCO leaders. CUCCO approval was critical to the success of detonation/burn operations;
- DOD (Aberdeen Proving Grounds, MD). Provided data and expertise for the pyrotechnic burns;
- DOJ. Initially brought the situation to the attention of EPA;
- FAA. Posted notice to local pilots concerning the detonations within air space around the Isla de Cabras site;
- Federal Bureau of Investigation (FBI). A representative of the FBI explosives team was on site during the explosives detonations to gain additional experience;
- Isla de Cabras PR Dept. of Recreation, Isla de Cabras Public Park. Provided no-cost access to the park and allowed air sampling to occur in the park;
- Puerto Rico Environmental Quality Board (EQB). Referred the site to EPA and had minimal involvement in the coordination of the project;
- Puerto Rico Fire Department (PRFD). Supported the operation by having a pumper and ambulance on site during burns;

- PRNG. Under initial removal plans, the PR National Guard was to provide a location at Camp Santiago to conduct the burn and a bunker to temporarily store material awaiting destruction;
- PRPD. Responsible for the explosive and pyrotechnic materials and conducted the removal action using its explosive experts;
- United States Coast Guard (USCG) Marine Safety Office (MSO). The USCG Marine Safety Office was notified of ongoing operations. The USCG notified Port Authorities and Harbor Masters of detonation and burn operations;
- US EPA. The EPA On-Scene Coordinator provided overall safety oversite and technical support for air and soil sampling and air monitoring;
- US EPA Environmental Response Team (ERT). Provided air monitoring/sampling and soil sampling direction to REAC contractors and assisted the OSC perform safety oversite;
- REAC. Developed the air dispersion model and performed air monitoring and air and soil collection;
- USEPA SUPERFUND Technical Assistance Response Team (START). Provided support to the OSC by keeping a site log and visitor log, provided video and digital camera support and general overall site support;

5.0 Health and Safety Plan and Work Plan

The "plan" was a combined Work Plan and Health and Safety Plan. It was written by the PRPD and was reviewed by the EPA and START explosive experts. Plan approval required almost a year and 3-4 revisions were required before the plan was accepted. The initial plan lacked adequate detail and numerous comments and suggestions were received for the original and subsequent plan revisions. Health and safety plan preparation, revision and acceptance were hindered by language translation issues during correspondence between the PRPD and the EPA.

6.0 Operations

6.1 Commercial Fireworks

The Antilles Fireworks Company donated equipment and personnel to put on a fireworks display using approximately 300-400 lbs of commercial grade fireworks at the Isla de Cabras site. Upon mobilization to the site, personnel from the PRPD and the fireworks company separated functional fireworks from and non-functional fireworks in the boxes of confiscated commercial fireworks. The fireworks were loaded into "mortar tubes" and an electrical detonation box was used to ignite the fireworks. The inspection and loading process took approximately six hours. The fireworks display began at 7:30pm and lasted for about 15 minutes. Coincidentally, the fireworks display occurred on Juan Batista (John the Baptist) Day which is a traditional day of celebration with fireworks for the patron saint and namesake of San Juan. The fireworks display was advertised to the public and the press was invited to attend the display. The fireworks display provided a good opportunity to publicize and influence the story on the upcoming disposal of the explosives and pyrotechnics at the site.

6.2 Explosives

Over the weeks following the fireworks display, explosives detonations were performed at the Isla de Cabras site. The detonated explosives included more than 160,000 individual M-80, M-100, M-200, and M-500 firecrackers. The M-200 firecrackers are equivalent to 1/4 stick of dynamite. The "firecrackers" were placed in various size and shape bundles, wrapped in 50 grain detonation cord with an electric blasting cap, set in a bomb basket (set into the ground and surrounded with sandbags) and were remotely detonated from behind a concrete wall at a distance of about 75 yards. During the initial detonations of the M-80, M-100, or M-200 firecrackers, an observer was placed at the peninsula entrance to monitor the noise level produced by the detonation. Ultimately, about 600 M-80 firecrackers were wrapped with masking tape into the shape of a cheese wheel with 7 feet of detonation cord. About 400 M-100 firecrackers were wrapped in the same manner as the M-80s. The M-200 firecrackers were wrapped in groups of 250 and the M-500 firecrackers were wrapped in groups of 20. Once the package configuration was determined for each type of "firecracker", packages were prepared for all of the firecrackers. Meteorological conditions allowed more detonations per day than originally planned. A total of 283 detonations were completed over a seven-day period. Detonations were completed during down periods when the ash from the pyrotechnic burns was cooling.

6.3 Pyrotechnics

There was an old cider block bunker (4m x 2m x 3m) with a concrete floor, concrete roof and wooden door at the detonation/burn site. The old bunker was modified to create a makeshift incinerator to burn the pyrotechnic material. The bunker was modified by removing the concrete roof, installing a metal door and cutting small windows in the sides to allow ventilation. Chain-link fencing was placed over the roof opening and screen was placed on the windows. Corrugated metal was placed on the inside walls to redirect the heat away from the cider blocks. The block bunker was not expected to survive the pyrotechnic burning and the bunker had to be reinforced with banding after four weeks of pyrotechnic burning. The chain-link fencing on the top of the bunker melted and had to be replaced after two weeks of burns.

The pyrotechnic materials had been stored in three tractor trailers on site. There were approximately 44 tons of materials to be burned. Only the amount of pyrotechnics to be burned was removed from the trailers and taken to the burn area. Originally, the pyrotechnic materials were taken out of their boxes and placed on pallets. Layers of pyrotechnics and cardboard were stacked to a height of about four feet. Diesel fuel was sprayed on the pyrotechnic pile and the pile was lit. A large amount of ash was created the very hot ash tended to extinguish the fire. During the first burn, additional diesel fuel had to be poured on the fire to keep it burning. Later burns were more successful when cases of pyrotechnic materials were tossed on the hot coals left from previous burns. Additional diesel fuel was not required to sustain the fire. After the residual ash reached a depth of 3-4 feet, burn operations were ceased for three days to allow the ash to become cool enough to be removed and stored in an empty bunker. Even after three days, the ash remained very hot. The ash was moved about 50 yards to an empty bunker using wheel barrels to further cool.

During the burn down time, the PRPD crew wrapped bundles of explosives for later detonations.

7.0 Residual Disposal

Approximately 650 cubic feet of ash was generated. The ash was analyzed for TAL and TCLP metals. Potential methods for disposal of the explosive and pyrotechnic residual ash was dependent upon on ash analytical results. The ash was expected to have high metals levels but the analytical results showed no significant elevated levels of metals that would the ash from being disposed of as normal solid waste.

8.0 Lessons Learned

With any operation, hindsight is always better than foresight. As the detonation and burn operation progressed, certain operation aspects were identified that could have made the removal action proceed more smoothly. Some lessons learned during this operation are:

- Use a noise meter for explosive test runs;
- Use full unpacked cases of pyrotechnics during burns thereby reducing the amount of cardboard used and the resultant ash generated;
- Increase the layers of fencing covering the burn chamber to reduce the number of "flyers"; and most importantly
- Get a funding commitment prior to starting the operation to allow the purchase of small equipment/supplies, the use of overtime for burn personnel and pay for residual ash disposal.

Isla De Cabras Pyrotechnic Incineration
Percentage of Maximum Modeled 3-Hour Concentration

12:00 PM - 3:00 PM Burn

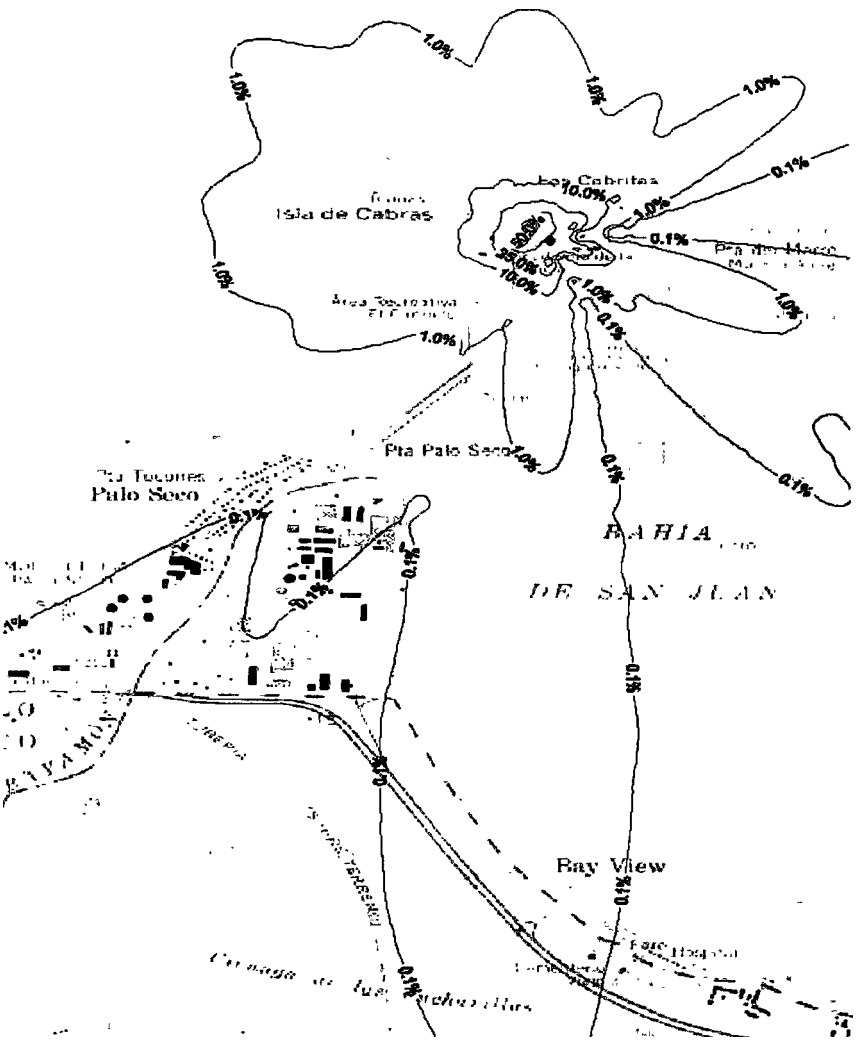
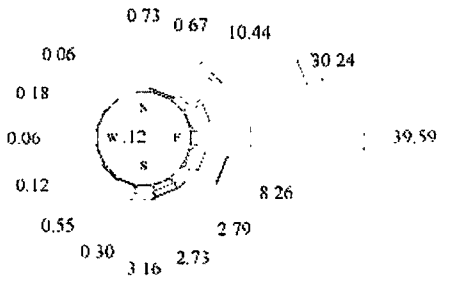
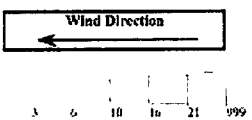


Figure 1: Sample Air Model with Percent Concentrations

Windrose for San Juan, Puerto Rico - June/July
12:00 P.M. - 3:00 P.M.
Based on 1986-1995 National Weather Service Data





WIND SPEED (KNOTS) PERCENT OCCURRENCE						
	1-3	4-6	6-10	10-16	16-21	21
N	0.00	0.24	0.49	0.00	0.00	0.00
NNE	0.00	0.12	0.00	0.24	0.00	0.00
NE	0.00	0.43	1.46	7.29	1.21	0.00
ENE	0.06	0.24	4.13	22.34	3.16	0.00
E	0.06	1.40	12.48	24.23	2.43	0.00
ESE	0.06	0.43	2.91	3.61	0.24	0.00
SE	0.00	0.43	1.33	1.03	0.00	0.00
SSE	0.00	0.00	1.03	1.21	0.18	0.00

WIND SPEED (KNOTS) PERCENT OCCURRENCE						
	1-3	4-6	6-10	10-16	16-21	21
S	0.06	0.30	1.52	1.28	0.00	0.00
SSW	0.00	0.12	0.06	0.12	0.00	0.00
SW	0.06	0.24	0.12	0.12	0.00	0.00
WSW	0.00	0.12	0.00	0.00	0.00	0.00
W	0.00	0.00	0.06	0.00	0.00	0.00
WNW	0.00	0.12	0.06	0.00	0.00	0.00
NW	0.00	0.00	0.06	0.00	0.00	0.00
NNW	0.00	0.00	0.00	0.00	0.00	0.00

Figure 2: Sample Wind Rose (Based on 5 year history)

Isla de Cabras Pyrotechnic Incineration

Air Sampling/Monitoring Locations During Burns

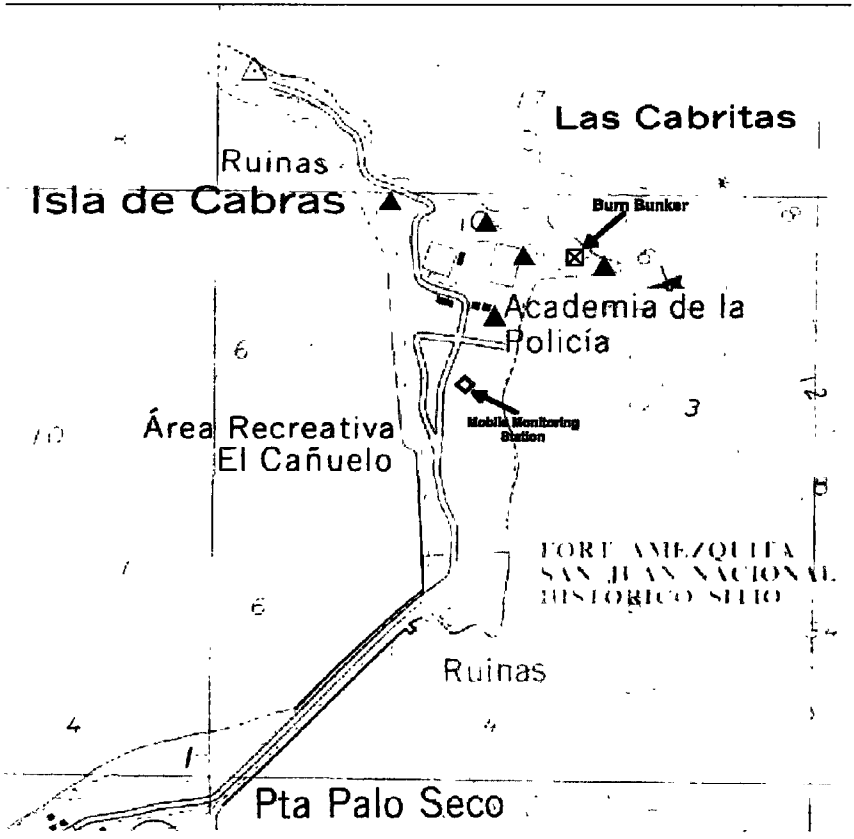


Figure 3: Sample Air Sampling Station Locations

PROCEEDINGS

Second Phytoremediation
Technical Seminar

June 13, 2000
Coast Plaza Suite Hotel
Vancouver, British Columbia
Canada

Seminar sponsored by

Environmental Protection
Service
Environmental Technology
Advancement Directorate
Environment Canada

COMPTE RENDU

Deuxième colloque technique
de phytorémédiation

le 13 juin 2000
Hôtel Coast Plaza Suite
Vancouver, Colombie-Britannique
Canada

Colloque commandité par le

Service de la protection de
l'environnement
Direction générale pour
l'avancement des technologies
environnementales
Environnement Canada

NOTICE

The papers in these Proceedings are published as submitted by the authors. Any statements or views presented here are those of the authors. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Inquiries related to the technical content of papers in this seminar should be directed to the author(s).

Inquiries related to the **Phytoremediation Technical Seminar**, in general, should be directed to:

Emergencies Science Division
Environment Canada
3439 River Road
Ottawa, Ontario, Canada
K1A 0H3
Phone: (613) 998-9622
Fax: (613) 991-9485
www.etcentre.org/conferences/index.html

Cover Photograph
Oil application during the Ste. Croix (Quebec) Phytoremediation experiment in a freshwater wetland along the St. Lawrence River.

Photo courtesy of: Fisheries and Oceans Canada

AVIS

Les textes contenus dans le présent document sont publiés tels qu'ils sont présentés par les auteurs. Les déclarations et opinions apparaissant dans ce document sont celles des auteurs. La mention de marques de commerce ou de produits commercialisés ne constitue ni une approbation ni une recommandation d'emploi.

Toute demande d'information relative au contenu technique des textes devrait être faite directement auprès des auteurs concernés.

Les demandes relatives au **Colloque technique de phytorémédiation** devraient être adressées à:

Division des urgences - science
Environnement Canada
3439, chemin River
Ottawa, Ontario, Canada
K1A 0H3
Tél: (613) 998-9622
Fax: (613) 991-9485
www.etcentre.org/conferences/index.html

Photographie de la couverture
Application d'hydrocarbure lors de l'expérience en phytorémédiation à Ste. Croix (Québec) dans des marécages d'eau douce le long du Fleuve Saint-Laurent.

Courtoise de: Pêches et Océans Canada

TABLE OF CONTENTS
TABLE DES MATIÈRES

PAGE

PAGE

Constructed Wetlands for Treatment of Condensate Hydrocarbons in Cold Climates

B. J. Moore[1], S. D. Ross[1], M.J. Brown[1], D.B. Gibson[2]
[1]Komex International Ltd.
[2]University of Calgary, Alberta
Calgary, Alberta, Canada
bmoore@calgary.komex.com

Abstract

A pilot scale subsurface flow constructed wetland is being tested as an innovative remedial solution for ex-situ treatment of condensate-contaminated groundwater. The wetland was implemented in 1997 to assess its potential as a lower cost alternative to mechanical-based treatment. This paper presents results on hydrocarbon removal mechanisms and hydrocarbon removal efficiency.

Inflow water to the wetland contains between 15 to 20 mg/L of C_5-C_{10} hydrocarbons, including approximately 50% BTEX compounds. The wetland subsurface is aerated during winter to prevent freeze-up. The use of subsurface aeration enables 100% hydrocarbon removal during winter. During the spring, summer, and fall, the hydorcarbon removal efficiency varies between 30% to 100%. Hydrocarbon removal efficiency appears to be temperature related. Hydrocarbons not removed in the wetland are subsequently removed along the outflow channel.

The main hydrocarbon removal mechanism appears to be volatilization, and to a lesser extent, biodegradation and dilution. Plant uptake is not a factor at present. Winter operation has been successful for three winters, through the use of subsurface aeration coupled with surface straw insulation.

1.0 Introduction

A constructed wetland was implemented at the Gulf Strachan Gas Plant in 1997 to evaluate its feasibility for ex-situ treatment of extracted groundwater contaminated with natural gas condensate, as an alternative to mechanical treatment. Constructed wetlands have been used more frequently of late for treatment of wastewater and stormwater (Hammer, 1989; Reed *et al.*, 1995). However, the use of constructed wetlands for treatment of dissolved phase hydrocarbons is relatively new. Wetlands have been evaluated for tertiary treatment (*i.e.*, polishing) of low levels of dissolved hydrocarbons (Litchfield, 1993; Nix and Bishay, 1996). However, this application may be the first constructed wetland used in the world used for treating relatively high levels of dissolved phase hydrocarbons.

The site is located near Rocky Mountain House, approximately 200 km northwest of Calgary, Alberta. A pump and treat system has been operating since 1992 to prevent off-site migration of dissolved and free phase hydrocarbons. The extracted groundwater is being treated by a mechanical system with primary treatment provided by a shallow tray air stripper. Life-cycle remediation costs indicate that long-term pump and treat system operation costs can be substantial. In many cases operation and maintenance costs are much higher than the initial capital expenditure.

A pilot scale constructed wetland was implemented in 1997 to assess its potential as a lower cost, reduced maintenance alternative to conventional treatment

using a shallow tray air stripper (CAPP, 1998; 1999). Should the wetland prove economically viable, the wetland capacity will be expanded to enable full scale treatment of groundwater at the site.

This paper presents results on the following: (a) hydrocarbon removal efficiency; (b) hydrocarbon removal mechanisms; and, (c) effect of increased flow rates on treatment efficiency.

2.0 Design, Operation and Monitoring

2.1 Conceptual Design

Given that the temperature in Rocky Mountain House drops as low as –40°C during winter, special design considerations are required to maintain a wetland for year round remediation. The constructed wetland system is comprised of four stages, described below:

- groundwater extraction;
- pre-wetland treatment;
- constructed wetland; and
- outflow channel.

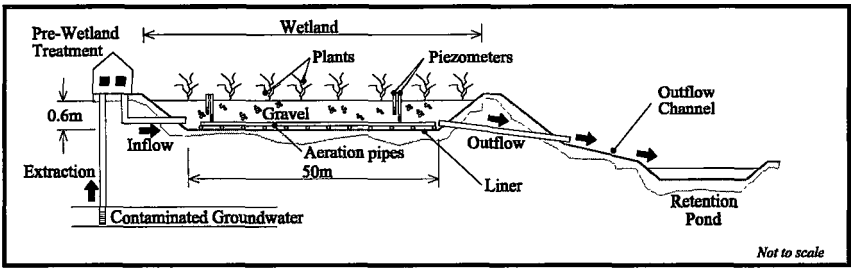


Figure 1 Constructed Wetland Cross Section Schematic

2.1.1 Groundwater Extraction

Groundwater containing dissolved phase hydrocarbons is pumped from recovery wells, located downgradient of the wetland. The water generally contains between 15 and 20 mg/L of total purgeable hydrocarbons (TPH, C_5 to C_{10}), containing approximately 50% BTEX compounds (benzene, toluene, ethylbenzene, and xylenes). Occasional blebs of free phase hydrocarbons are also extracted.

Groundwater extraction rates typically vary seasonally between 20 to 60 L/min. During 1997-1999, approximately, 25% of the extracted groundwater was directed to the pilot scale wetland, with the remainder treated by the air stripper system. In 2000, the inflow rate was increased to 50% of the total flow.

2.1.2 Pre treatment

Pre-treatment initially consisted of a 20,000 L aerated holding tank, and nutrient addition. The purpose of the holding tank was free phase hydrocarbon removal, and aeration to promote precipitation of dissolved iron and manganese and stimulate aerobic biodegradation. The aeration tank resulted in an average 20% reduction in hydrocarbon concentrations, and an increase in dissolved oxygen (DO) levels from 0.1 to 3.4 mg/L. Only a 10% reduction in dissolved iron and manganese levels was observed.

In 1999 the aeration tank was replaced by an oleophilic filter. The oleophilic filter was implemented so that the constructed wetland flow system could be operated independent of the air stripper treatment system, and shutdowns associated with the air stripper would not affect flow to the constructed wetland. The filter also represents a reduction in size and cost of pre-treatment relative to the holding tank. The filter effectively removed free product, but did not affect dissolved phase concentrations. The DO concentrations entering the wetland with the oleophilic filter were 0.1 mg/L.

2.1.3 Constructed Wetland

The wetland consists of a gravel-filled cell with dimensions of 50 m long x 17 m wide x 0.6 m deep. To protect groundwater quality beneath the wetland, the cell is bermed and double lined. To protect the plants from livestock intrusion, an electric fence lines the perimeter.

The water surface is maintained at approximately 0.1 m below surface to reduce potential impact on wildlife, and allow a buffer against potential ice or frost buildup. The approximate volume of water in the wetland is 155,000 L, based on a gravel porosity of 36%.

A network of 13 piezometers was installed for water monitoring (Figure 2). Four double piezometers were installed (CW-2A/B, 5A/B, 8A/B, and 11A/B) along the flow centreline to evaluate potential differences between near surface and subsurface water. The "A" series are screened at approximately 0.0 to 0.3 metres below ground surface (mbgs), and the "B" series piezometers are screened at approximately 0.3 to 0.6 mbgs. Nine piezometers with screen intervals between 0.0 to 0.6 mbgs were also installed (CW-1, 3, 4, 6, 7, 9, 10, 12, 13). After establishing that uniform flow distribution is occurring in the wetland, monitoring is conducted primarily along the centreline of flow in the wetland.

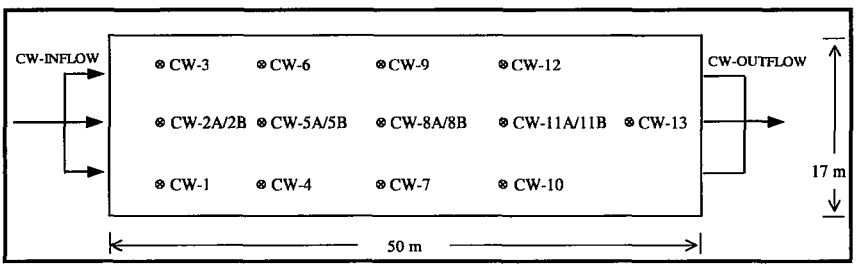


Figure 2 Piezometer Locations in Constructed Wetland

Planted vegetation consists primarily of *Phragmites australis* (phragmites), a reed grass indigenous to Alberta, chosen for its deep root penetration, high oxygen transfer to its roots, and robust growth. The phragmites were 0.3 m high, and in good health when planted. Approximately 400 mature cattails, *Typha latifolia,* were also planted during July 1997. The cattails were randomly distributed among the phragmites. The vegetation was planted at approximately 0.6 m spacing. The plants are healthy, with no signs of stress. This result is consistent with 1997 laboratory testing conducted to simulate field conditions, which showed no impact by hydrocarbons on plant health (Komex, 1997; Moore *et al.*, 1999a).

The plants have grown to a 1 m height, and cover approximately 50% of the wetland. In 1999, the root penetration of the phragmites and cattails reached a depth of 30 cm, a 100% increase over 1998. No adverse effects of competition between the cattails and phragmites were observed. Since the original planting, 21 new species of plants have invaded the wetland from the surrounding area.

2.1.4 Outflow Channel

Wetland discharge flows into a heated sump and is discharged into a 15 m long surface outflow channel. This channel is gravel-filled, and drains to an adjacent pre-existing surface water retention pond. Should hydrocarbons reach the retention pond, infiltrating water flows downgradient for re-capture by recovery wells.

2.2 Operation

The main operating requirements with the wetland involve (a) water flow rates, (b) nutrient addition, and (c) aeration and heating during winter operation

(a) Water flow rates

During 1998, the average inflow rate to the wetland was approximately 12 L/min (17 m^3/d). The residence time of water in the wetland at this rate is approximately 14 days. Commencing in December 1999, the inflow rates were increased to 24 L/min (34 m^3/d).

(b) Nutrient addition

To stimulate plant growth, nutrients are added at regular intervals during May to October. An added benefit of the nutrient addition is an expected increase in microbial activity. Nutrients are added using a dual Dositron in-line feeder system. Three different nutrient regimes were used. During May/June, a 10-52-10 mixture (% Nitrogen-Phosphorous-Potassium) was used to stimulate root growth. During July to September a 50:50 mixture of calcium nitrate and 20-10-20 was used to stimulate plant growth. During October, monopotassium phosphate (0-51-34) was used in the fall for reproduction/budding. The plants are dormant during winter.

(c) Winter operation

To reduce the potential for freeze-up during winter operation, and enhance mass removal rates, air was injected into the base of the wetland from November to May during 1997 to 1999. Air is injected into sixteen aeration lines oriented perpendicular to flow along the base of the wetland at a constant pressure of 33.5 kPa

with an air compressor. Outflow points on the north side of the wetland were periodically checked to confirm that air flow was occurring across the entire width of the wetland. As an additional precaution, the wetland surface was insulated at surface with 0.15 m of straw.

To provide an additional heat source during the winter, if necessary, four loops of 16 mm diameter Kitec heat tubing were installed at the base of the wetland during wetland construction. Connected to a surface boiler, the tubing can provide heat to the wetland by circulating a heated, non-toxic glycol solution. During the first two winters, the additional heating was not required. However, when the pretreatment tank was discontinued, the temperature of the inflow water was reduced by approximately 4°C. Consequently, during the winter of 1999/2000, additional heating through glycol circulation in subsurface tubing was necessary to prevent the wetland from freezing. The boiler system maintained the wetland water temperature near 5°C.

2.3 Monitoring Methods

Water depth, pH, electrical conductivity, and dissolved oxygen were monitored regularly in the wetland using handheld instruments. Water and air temperature were monitored continuously using on-site monitors equipped with data loggers. Flow rates were measured with an in-line electromagnetic flowmeter.

Water samples were collected every month to two months during 1997 to 1998, and monthly during 1999/2000. Samples were collected using standard protocol and submitted for laboratory analysis of main ions and dissolved iron and manganese and BTEX and total purgeable hydrocarbon (TPH, C_5-C_{10}) analyses.

Vapours at surface were monitored using six vapour collection vessels (VCVs), inserted into the surface of the wetland along the flow centreline. The VCVs consist of 45 gallon steel drums, with the top end sealed and fitted with a swagelock valve for sampling. The bottom end is open, and inserted below the water surface of the wetland, leaving a 0.18 m headspace above surface. Hydrocarbon vapour concentrations were measured using a GasTech Organic Vapour Analyzer (OVA) calibrated to hexane gas. The O_2 and CO_2 concentrations were measured with a GasTech 4 Gas Analyzer.

To evaluate plant health in the wetland, 10 test plots, each 2 m^2, were selected at random. Plant measurements were made during July, 1997, 1998 and 1999. The number of shoots per plant, height of tallest tiller, and number of leaves on the tallest tiller were individually compared for the ten test plots. Root penetration was determined for phragmites and cattails.

3.0 Hydrocarbon Removal in Wetland

3.1 Hydrocarbon Removal During Spring to Fall

At temperatures above freezing, water is treated without subsurface aeration. At lower temperatures during May and November, hydrocarbon removal efficiency varied from 30 to 60%, respectively. During warmer temperatures, (*e.g.*, September 1998) 100% removal efficiency was observed. Analytical results indicate that removal of BTEX and TPH ($C_5 - C_{10}$) were similar (Table 1). Relevant wetland data are also shown in Table 1. Shown in Figure 3 are representative results for BTEX removal during different water temperature conditions in the wetland.

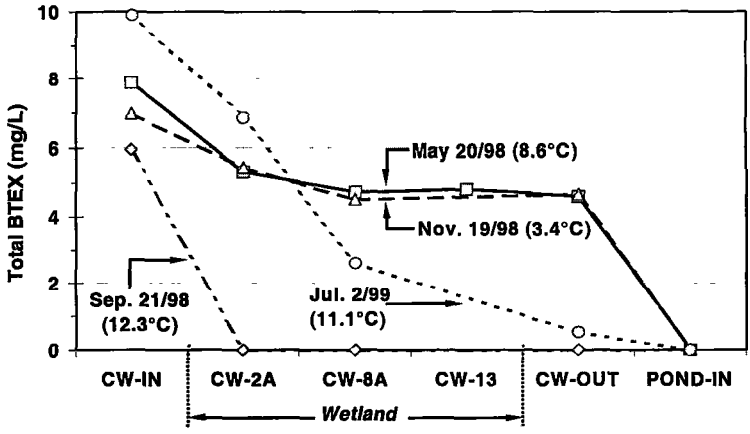


Figure 3 BTEX Removal With No Aeration (May to November)

During 1999, a decrease in removal efficiency was observed relative to previous years. As shown in Figure 3, the removal efficiency in July 1999 was significantly reduced relative to September 1998. This drop in efficiency is likely due to a compression of the surface straw layer over time due to moisture retention, thus limiting wetland interaction with the atmosphere. The straw has been removed.

3.2 Hydrocarbon Removal During Winter Operation

Complete hydrocarbon removal, including BTEX, was observed with aeration during winter months (Figure 4). The removal was observed despite water temperatures as low as 0.3°C, and air temperatures as low as –40°C.

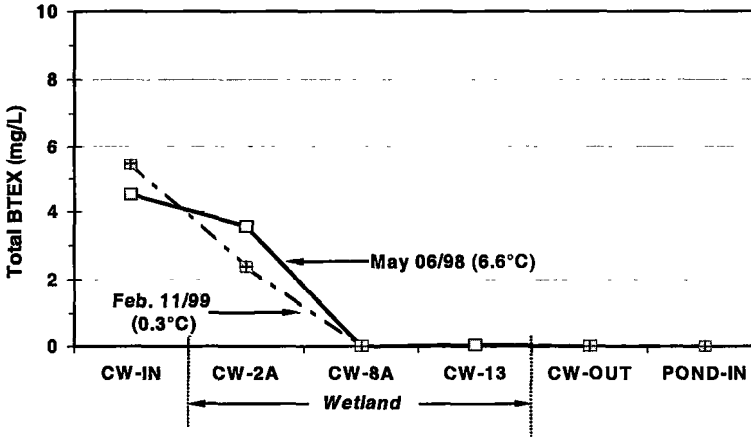


Figure 4 BTEX Removal Using Aeration (December to May)

3.3 Effect of Temperature on Hydrocarbon removal

As suggested in Figure 3, a correlation between mass removal and temperature is apparent. Results from 1997-1998 indicate that without aeration of the wetland subsurface, hydrocarbon removal efficiency in the wetland was generally 100% at water temperatures above 12°C. As temperatures decrease to 5°C , the hydrocarbon removal efficiency declined to between 30 to 40%. With aeration, hydrocarbon removal efficiency at nominal flow rates of 12 L/min is typically 100%, irrespective of temperature (See Figure 5).

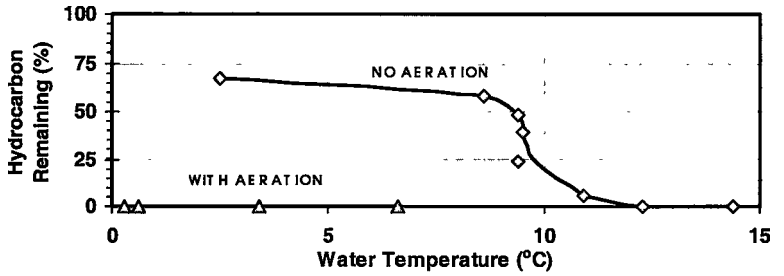


Figure 5 Hydrocarbon remaining at outflow versus temperature

3.4 Effect of Flow Rate on Hydrocarbon Removal

Results indicate that a nominal flow rate of 12 L/min, 100% hydrocarbon removal efficiency was obtainable. Commencing in December 1999, flow rates were doubled to approximately 24 L/min. At this flow rate, hydrocarbon removal was typically 100%. However, breakthrough of hydrocarbons was observed at the outflow during one sampling event. This result suggests that the maximum flow rate in the wetland during winter is less than 24 L/min. An observed significant decrease in efficiency observed during February, 2000 was attributed to a drainage of the wetland occurring prior to the sampling, resulting in a reduced residence time of water in the wetland.

3.5 Outflow Channel

As shown in Figure 3, approximately 40 to 60% of the hydrocarbon influx reached the wetland outflow on May 20, 1998 and November 19, 1998. Sampling at the outflow channel discharge indicates these remaining hydrocarbons were completely removed within the outflow channel, prior to discharge to the retention pond. The residence time of water in the outflow channel is approximately 1 minute.

The removal efficiency of the outflow channel therefore exceeds the wetland at temperatures below 12°C. During winter, when the outflow channel is ice-covered, data indicate removal efficiency in the outflow channel is limited.

4.0 Hydrocarbon Removal Mechanisms

4.1 Overview

As discussed below, there are at five mechanisms potentially attenuating dissolved phase hydrocarbon concentrations in the wetland: volatilization,

biodegradation (aerobic and anaerobic), dilution, sorption, and plant-related processes. At present, the main mechanism appears to be volatilization, and to a lesser extent, aerobic biodegradation.

4.1.1 Volatilization

Volatilization describes the partitioning of hydrocarbons from the soil phase, dissolved phase, and/or liquid phase into the vapour phase. The C_5-C_{10} condensate hydrocarbons have a high vapour pressure and are therefore highly volatile.

Based on surface vapour monitoring, volatilization is presently identified as the main removal mechanism, accounting for approximately 50 to 75% of the observed reduction in dissolved phase concentrations. Hydrocarbon vapour concentrations were typically highest within the first 10 m of the wetland.

Mass removal due to volatilization was calculated by assuming that hydrocarbon vapour concentrations in the VCVs were representative of conditions across the wetland subsurface. Approximately 50% of the volatilization occurred in the first 10 m of the wetland. This is based on significantly higher vapour concentrations in the VCV at CW-2A (450 ppm), relative to VCVs further along the flow path (100 ppm dropping to 50 ppm by CW-13). Reduced volatilization toward the latter half of the wetland was likely due to a lack of mixing between deeper water and near surface water (*i.e.*, laminar flow).

4.2 Biodegradation

Biodegradation of hydrocarbons is facilitated by naturally-occurring microbes in the wetland. Condensate hydrocarbons are biodegradable under both aerobic (with oxygen) and anaerobic (no oxygen) conditions. Aerobic biodegradation is a significantly faster process, during which O_2 is consumed, and CO_2 is produced (Atlas, 1997).

During 1997 to 1998, aerobic biodegradation was occurring through utilization of DO present in the inflow water, due to pre-wetland aeration. Following pre-wetland aeration, the DO levels in the inflow water reached a maximum of 3.4 mg/L. The DO levels then dropped to 0.1 mg/L by piezometer CW-2A, and remained at 0.1 mg/L throughout the remainder of the wetland. For every 3.5 mg/L of DO consumed, 1 mg/L of hydrocarbon is degraded (Hinchee *et al.*, 1992). Assuming all the DO uptake is due to microbial consumption, approximately 0.9 mg/L of hydrocarbon were aerobically biodegraded due to the presence of DO in the influent water. The DO consumption in the inflow water would therefore account for only 5 to 10 % of the hydrocarbon removal. During 1999, pre-treatment aeration was discontinued (Section 2.1.2) , so that consumption of the DO in the influent was no longer occurring.

Additional oxygen is supplied to the wetland through diffusion from atmosphere. VCV monitoring indicate aerobic biodegradation near the wetland surface, is occurring, based on the occurrence of O_2 consumption and CO_2 production.

As noted above anaerobic conditions are present throughout the wetland. Geochemical indicators of anaerobic biodegradation (*i.e.*, increased iron and manganese, and reduced nitrate and sulphate concentrations) are not apparent in the wetland water relative to the inflow. Anaerobic biodegradation is not expected to be

a significant factor, as anaerobic biodegradation rates of hydrocarbons are slow relative to the 14 day residence time of water in the wetland (Morgan *et al.*, 1993).

4.3 Dilution

Dilution refers to reduction in concentrations due to mixing and/or dispersion. Based on rainfall data, dilution does not appear to be a major factor at the Strachan wetland. A typical 10 mm rainfall event equates to approximately 10,000 L of water (assuming 1,000 m^2 catchment in the wetland). Assuming a volume of water of 155,000 L in the wetland, a typical rainfall event would result in a water dilution of 6%. Rainfall at the site is sporadic, with an average total rainfall of 95 mm/year.

4.4 Sorption

Sorption refers to the partitioning of hydrocarbons to a substrate, such as soils, biofilm, or plant biomass. The lack of soils in the wetland minimizes sorption potential at present. However, as biofilm builds up on the gravel surface, and plants become more established, hydrocarbon sorption to organic matter is expected to be a factor.

4.5.1 Plant-Based Attenuation Processes

Various attenuation processes may occur with respect to plants. Two processes of potential relevance include aerobic biodegradation around the plant root rhizosphere, and uptake of hydrocarbons into the plant (Cunningham *et al.*, 1996). Aerobic biodegradation is expected to occur due to oxygen supply through leakage around the plant root rhizosphere. Both aerobic biodegradation and plant uptake appear to be negligible factors at present based on no significant increase in hydrocarbon removal rates despite a 40% increase in plant coverage. The maximum depth of plant root penetration is currently 0.3 m bgs. It is anticipated that as the roots reach the projected maximum depth of 0.6 m bgs, and plant density increases, the potential for oxygen transfer to the subsurface will be increased.

4.6 Removal Mechanisms in the Outflow Channel

Monitoring of removal mechanisms in the outflow channel was not conducted. However, based on the low residence time in the channel (< 1 min), and observed splashing and turbulent flow, volatilization is expected to the main removal mechanism.

5.0 Summary

Inflow water to the wetland contains between 15 to 20 mg/L of C_5-C_{10} hydrocarbons, including 50% BTEX compounds. Hydrocarbon removal efficiency in the wetland is typically 100% with aeration. Without aeration, 100% removal was typically observed at temperatures exceeding 12°C. At lower temperatures, treatment efficiency in the wetland decreases to as low as 30%. Temperature appears to be a significant factor in the variable removal rates. Hydrocarbons not removed in the wetland are subsequently removed along the outflow channel due to volatilization.

A reduction in treatment efficiency was observed in September 1999. This reduction may be related to the matting of an insulating layer of straw at surface. The straw has now been removed.

Winter operation has been successful for three winters. Overall, the wetland displays promising results for year-round treatment of condensate contaminated groundwater. At present, the main hydrocarbon removal mechanism appears to be volatilization, and to a lesser extent, biodegradation and dilution. Plant related hydrocarbon removal is not a factor at present, pending full establishment of the plant community.

6.0 Acknowledgements

The authors are grateful for funding provided by Gulf Canada Resources Ltd, the Canadian Association of Petroleum Producers, and Environment Canada through the Federal Panel for Energy Research and Development (PERD). In-kind contributions have been provided by Komex International Ltd. The authors wish to thank Dr. Mohyuddin Mirza of Alberta Agriculture for his assistance with plant growth, and Dr. Sherwood Reed of Environmental Engineering Consultants in Vermont for technical review. The authors also wish to thank project manager Lin Callow of Gulf Canada for his insight and support.

7.0 References

Atlas, R.M., *Principles of Microbiology, 2nd Edition,* WCB/McGraw-Hill, 1298 p., 1997.

CAPP (Canadian Association of Petroleum Producers), *Constructed Wetland Pilot Project – 1997 Summary Report and Proposed 1998 Workplan,* Unpublished Report prepared by Komex International Ltd., Calgary, AB, 1998.

CAPP (Canadian Association of Petroleum Producers), *Constructed Wetland Pilot Project – 1998 Summary Report and Proposed 1999 Workplan,* Unpublished Report prepared by Komex International Ltd., Calgary, AB, 1999.

Cunningham, S.D., T. Anderson, A. Schwab, and F. Hsu, "Phytoremediation of Soils Contaminated with Organic Pollutants", in *Advances In Agronomy, Vol. 56.*, ed. D. L. Sparks, Academic Press, New York, NY, pp. 55-114, 1996.

Hammer, D.H., *Constructed Wetlands for Wastewater Treatment: Municipal, Industrial, and Agricultural,* Lewis Publishers Inc., Chelsea, Michigan, USA, 1989.

Hinchee, R.E., S.K. Ong, R.N. Miller, D.C. Downey and R. Frandt, *Test Plan and Technical Protocol for a Field Treatability Test for Bioventing,* U.S. Air Force Center for Environmental Excellence, Brooks Air Force Base, Texas, 1992.

Komex International Ltd., *The Effect of Dissolved Hydrocarbons on the Survival and Production of Phragmites Australis: A Laboratory Evaluation,* Unpublished Report Prepared for Environment Canada Science Horizons Program, 1997.

Litchfield, D.K., "Constructed Wetlands for Wastewater Treatment at Amoco Oil Company's Mandan, North Dakota Refinery", In *Constructed Wetlands For Water Quality Improvement,* ed. G. Moshiri, Lewis Publishers, 1993.

Montgomery, J.H., and L.M. Welkom, *Groundwater Chemicals Desk Reference,* Lewis Publishers, Chelsea, MI., 1991.

Moore, B.J., S.D. Ross, D. Gibson, and P.E. Hardisty, "Constructed Wetlands for Treatment of Dissolved Phase Hydrocarbons". Proceedings of the Environment Canada Phytoremediation Symposium. Calgary, Alberta. June 1999.

Moore, B.J., L. Callow, S.D. Ross, and D. Gibson, 1999b. "Constructed Wetlands for Treatment of Condensate Hydrocarbons in Cold Climates". Proceedings of the Battelle Wetlands and Remediation Conference, Salt Lake City, Utah. November 1999.

Morgan P., S.Lewis, and R.Watkinson, "Biodegradation of Benzene, Toluene, Ethylbenzene, and Xylenes in Gas-condensate Contaminated Water", *Environmental Pollution*, Vol. 82., pp. 181-190, 1993.

Nix, P.G., and F.S. Bishay, "Application of Constructed Wetlands for Treatment of Oil Sands Wastewater: A Research Overview", Presented at the Twenty-third Annual Toxicity Workshop, Calgary, AB, 1996.

Reed, S., R. Crites, and J. Middlebrooks, *Natural Systems for Waste Management and Treatment (2 Ed).* R.R. Donnelley and Sons, U.S.A. pp. 179-180, 1995.

Table 1 Flow Rate, Temperature, TPH and BTEX Concentration vs. Time

Date Sampled	Wetland Aeration	Average Flow Rate	Average Temperature			Total Purgeable Hydrocarbons (C_5-C_{12})			Total BTEX		
			Water		Air						
			CW-2A	CW-13	Outside	CW-IN	CW-OUT	TPH Removal	CW-IN	CW-OUT	BTEX Removal
		(L/min)	(°C)	(°C)	(°C)	(mg/L)	(mg/L)		(mg/L)	(mg/L)	
Sept. 11/97	No	33	-	14.4	13.4	13.7	0.02	99.9%	9.63	<0.0045	100%
Oct. 9/97	No	14	-	9.4	7.1	22.6	6.6	71%	12.1	2.85	76%
Nov. 20/97	Yes	24	6.5	3.4	-5.1	19.8	<0.04	100%	9.54	<0.002	100%
Jan. 14/98	Yes	24	5.7	0.5	-22.0	22.2	11.6	48%	8.60	3.42	60%
Feb. 4/98	Yes	19	7.1	0.6	-2.7	8.6	<0.04	100%	5.1	<0.002	100%
Feb. 18/98	Yes	15	6.6	0.6	-3.6	27.7	0.9	97%	10.9	<0.002	100%
May 6/98	Yes	7	8.4	6.6	13.0	8.4	0.2	98%	4.5	0.002	99.9%
May 20/98	No	11	9.1	8.6	10.4	9.6	6.1	36%	7.9	4.6	42%
Jun. 4/98	No	10	8.6	9.4	12.2	15.0	6.2	59%	11.0	5.3	52%
Jun. 17/98	No	7	9.8	9.5	11.0	15.9	6.5	59%	7.4	2.9	61%
Sept. 21/98	No	15	9.0	12.3	10.7	12.7	<0.1	100%	6.0	<0.002	100%
Nov. 19/98	No	17	5.8	2.5	-6.2	13.8	8.8	36%	7.0	4.7	33%
Feb. 11/99	Yes	10	4.6	0.3	-2.9	9.1	<0.1	100%	5.4	<0.002	100%
Apr. 29/99	Yes	11	5.9	0.3	15.6	13.2	<0.1	100%	8.0	<0.002	100%
Jul. 2/99	No	9	8.1	10.9	14.6	21.3	2.6	88%	8.0	0.5	94%
Aug. 18/99	No	7	10.4	12.5	7.9	11.6	2.1	82%	7.2	1.3	82%
Sept. 24/99	No	10	7.9	10.6	10.5	16	9.2	42%	8.5	6.0	29%
Oct. 6/99	No	15	6.1	6.1	2.8	-	12	-	-	6.5	-
Nov 11/99	Yes	16	5.2	-	-0.3	13	<0.1	100%	6.0	<0.002	100%
Nov. 24/99	Yes	15	5.0	1.9	-2.0	19	0.6	97%	9.0	0.3	97%
Dec.16/99	Yes	24	3.9	1.9	-4.4	9.0	<0.1	100%	8.2	<0.0024	100%
Jan. 31/00	Yes	22	4.2	4.2	-9.5	13.5	<0.1	100%	7.9	<0.0024	100%
Feb. 29/00	Yes	22	3.5	3.2	-4.3	20.3	5.2	74%	10.5	3.0	71%

Anaerobic/Aerobic System For Removal Of High Levels Of Heavy Metals From Water – Report From A Full Summer Of Operation.

A.G. Mattes, Nature Works Remediation Corporation*
W. F. Duncan, Cominco Limited
*Winfield, British Columbia, Canada
mattes@cablelan.net

Abstract

A combined anaerobic/aerobic system was designed to remove high levels of heavy metal from landfill leachate. The system, designed to treat leachate originating from a closed and capped landfill site was built and planted in 1997 and has been in operation since mid-summer of 1998. A previous report on the initial 8 weeks of operation in 1998 showed the system was able to remove high levels of zinc (Zn), cadmium (Cd) and arsenic (As) from water.

During the summer of 1999 the system was operated for 18 weeks. The results for this period of operation supported the initial successful results. Significantly higher metal loadings were experienced during this period (increase of >100%) but the system proved to be robust and effective. Over 1.6 million L of water were treated. Average metal removals were as follows: Zn reduced from 288 mg/L to 73 mg/L; Cd from 4.56 mg/L to 0.02 mg/L and As from 76.4 mg/L to 0.29 mg/L

1.0 Introduction

In Trail, British Columbia, smelting operations have been in operation since 1896 and initially included open smelting operations. With a century of such activity, there are sources where water is affected by contact with high levels of metals (e.g. landfill leachate). Cominco Limited, who operate a large integrated lead/zinc smelter in Trail, have embarked on a major remediation program and treat the landfill leachate with current treatment technology. The company has also supported research in the development of new technologies using biologically based treatment systems capable of removing metals sufficient to meet current and future regulatory guidelines.

This pilot-scale system was constructed by Northern Water, Environment & Training Services. The system was designed to remove high levels of zinc (Zn), cadmium (Cd) and arsenic (As) from leachate originating from a closed, capped historic landfill site. Design parameters of the original system, construction of an anaerobic digester (added during the second year) and initial results for 1998 have been reported (Duncan et al, 1999).

Following the successful operations during the 8 week trial period (1998), the system was prepared for a full summer (18 weeks) of operations during the summer of 1999. The current paper reports on the changes instituted for the full season's operations, and the effectiveness of the system in removing metals from water. It also presents some preliminary indications of the capability of some of the plants used to serve as accumulating species.

2.0 Changes and Developments During 1999

2.1 Re-Planting

Due to difficulties experienced with plugging that occurred in the outflow pipes of the cells, the system had been shut down during the summer of 1998 during a time when water supply was critical for the plants. Temperatures were very high at this time (30-35°C) and the loss of water resulted in some trees in the first cell suffering dieback. As a result, it was necessary to re-plant these trees. Hybrid poplar trees (*Populus deltoides)* and *Salix exigua* (Coyote willow) were acquired from the Kalamalka Forest Research Station and planted in the first cell prior to leafing out.

2.2 Physical Repairs

Plywood bulkheads constructed during emergency repair work in August 1998 were removed and replaced with stone filled gabions constructed using heavy hardware cloth. At the same time repairs were made to the outflow pipes and valves installed in the outflow pipes in each cell to ensure easier winterizing in subsequent years.

2.3 Additional Equipment Installation

Prior to this year there was no accurate way to monitor the cumulative volume of water input to the system nor to monitor the final outflow. A battery powered, accumulating, flow meter capable of measuring low flow rates of water containing large amounts of suspended sediment was installed at the system input. A similar meter was found not to be capable of measuring the low flow rates at the output and we used a manual spot measurement method for daily flow estimates.

During 1998 a solar powered aeration system was installed to ensure that sufficient dissolved oxygen was present in the water for plant life. In 1999, two additional solar panels were purchased and pumps that operated at lower amperage were installed to ensure 24-hour aeration.

An irrigation system that could pump water from the holding pond either directly the anaerobic cell or to irrigate the area surrounding the anaerobic cell.

2.4 Increased Monitoring

An extensive monitoring system was designed for the summer of 1999. Daily measurements (using a stopwatch and a measured container) were made of water flow rates from the anaerobic cell into the first plant-based treatment cell and from the final plant-based treatment cell to the holding pond. Daily measurements of pH and dissolved oxygen were made at four points; aeration cell between anaerobic cell and tree/grass cell, aeration cell between tree/grass cell and grass cell, aeration cell between grass cell and *Typha* cell and at the input to the holding pond. Weather conditions were also noted.

Weekly grab samples were taken at the four sample points and at the primary input to the system. Water samples were assayed by Cominco's analytical laboratory for metal assays.

2.5 Changes in Metal Levels and Flow Rates

Metal input to the anaerobic cell were more than 2 times higher this year than the mean levels found during last year's 8 week trial operations. Average concentrations increased to 140% higher for As, 76% higher for Cd, and 109% higher for Zn compared to 1998.

We also increased the flow rates to levels above designed rates by 50% higher than last years levels and for a period during July and August we were operating at levels of close to 20,000 L a day (excluding rain events when rates were measured at better than 40,000 L a day from time to time). These high levels were part of tests to test system operational capabilities.

2.6 Sampling

Plants had been growing in the system for two years but this was the first summer that metal-containing water was added to the system beginning in early spring. To assess the rate of metal accumulation in plants samples of each of the plants in the system were taken at two periods during the summer. In August, an initial sample of leaves was taken from the hybrid poplar trees, willows and grass stems from the *Tripsicum dactyloides* in the first cell, grass stems of *Agrostis stolonifera* and *Calamagrostis canadensis* taken from the second cell and leaves from *Typha* sampled from the third cell. In late October a second set of plant samples was taken. In both instances, samples were bagged, labeled then oven dried for 24 hours at 80°C. Samples were then assayed for metals using ICP AES.

2.7 Operational Difficulties & Temporary Shutdown

Visits during the summer months showed no noticeable changes in the system's appearance in terms of plant response. All cells seemed to be growing normally although this summer was atypical for the Trail region with many days of cool rainy weather instead of the normal hot and dry summer months typical of the region. We expect the system to transpire the theoretical capacity (12,000 to 15,000 L a day). The cool rainy summer meant that this expectation was not fully met.

Lack of activity in the anaerobic cell (lack of bubbles and no noticeable odour of H_2S) resulted in problems with metal removal and difficulty in this cell. This failure resulted in Zn concentrations that in the system reached levels that were too high for plants to sustain and some toxicity and subsequent death was observed. Zinc concentrations had stabilized at high levels, (10 times higher than in the previous year) and as plants were dying back we switched to cleaner water as input to the system for a brief period to flush it out.

When the system was drained for repairs it was apparent that the anaerobic matrix had settled and there was much less volume available for removal of metals than the design specifications (estimated loss of 25-33% of the specified biological matrix volume).

When the system was stabilized the water in the holding pond was pumped back into the anaerobic cell. Addition of rhodamine dye added during re-filling examined the plug flow design of the system and whether leaks had developed. While re-filling, 150 kg of liquid invert sugar was added to the system. The water that returned from the holding pond was then allowed to remain in the cell for a period before the entire system was returned to normal operating procedures. Total downtime for repairs, re-

charging and flushing was 10 days.

Addition of liquid invert sugar re-started rapid bacterial growth and, as a result, the system appeared to operate better. The surface of the anaerobic cell showed extensive bubbling and the smell of H_2S gas was noticeable. Plants previously showing indications of high metal loads looked better and since, at the same time, flow levels were reduced to levels that were closer to design optimums, we expected a return to better efficiency levels.

2.8 Anaerobic Cell Sampling

Sampling of the matrix material took place when the cell was emptied of water. Small bore plastic pipe was hammered into the biological matrix, the open end then capped to provide a sealed tube. The pipe was subsequently withdrawn with the core sample intact. Sections were cut according to the depth of the sample, labelled and stored until shipment. The samples were sent on ice to the University of Idaho where they were assayed under the direction of Dr. Frank Rosenzweig. Samples were subjected to a series of dilutions then incubated in darkness in an anaerobic chamber. Sample dishes are subsequently scored for blackening that is indicative of sulphidiogenesis. A second assay performed was a measurement of Acid Volatile Sulphides (AVS) that measures the amount of sulphides that are actually present in the core samples .

3.0 Results

Levels of metal removal efficiencies were comparable to last year's initial trial operations. Removal of Cd and As easily met last year's efficiencies while Zn removal was lower than system design expectations. In part, these changes are due to a much higher level of metals present in the leachate that were, in all cases, nearly double last years levels with spike events that were considerably higher than these already marked increases.

The problem experienced due to a lack of anaerobic activity in the initial treatment cell is most likely due to the fact that our start-up procedure did not allow for sufficient incubation time for a large colony of bacteria to develop. This was complicated by a partial breakdown in the plug flow design of the anaerobic bioreactor and the compaction in the bio-substrate because of the weight of the standing water that remains on top of the anaerobic cell. When these factors are coupled with our decision to push the system to its limits in terms of flow rates to determine the operational capacity there was a marked reduction in metal removal. Following the shutdown and flushing period and the effect of re-charging the bioreactor by providing liquid invert sugar as a rapidly metabolisable food, the anaerobic cell returned to full operating capacity and metal removal returned to the expected high levels.

3.1. Re-planting, Physical Repairs and Installation of New Equipment

All transplanted trees leafed out at the same time as those remaining from previous year's planting. Throughout the summer months these grew as expected however, high Zn levels killed the front line trees - coyote willows (*Salix exigua*) planted 2 years ago - suffered and two of these died. Of the new transplants, some were more affected than others and this appeared to be cultivar dependent.

Construction of the stone filled gabions was an important addition to the operation of the system. The change offers an additional point for visual inspection, an increased opportunity for sampling and a way to better winterize the system when it is drained and shut down for the winter. It also allows us to separate each component cell for repairs and maintenance without draining the entire system.

Information provided from the digital accumulating flowmeter is an essential measurement of the effectiveness of the system. Low flow rates prohibit use of this device at other points in the system during the summer months when evapotranspiration is high and we relied on a manual method.

3.2. Monitoring Operating Conditions

Two important parameters were measured daily throughout the summer – pH and dissolved oxygen (D.O.). Both are of vital importance to plant and bacterial growth and therefore, both were measured daily. Most plants prefer an environment in which the pH is in the neutral range. If the pH is too low a plant will suffer and could die as iron, an essential component of the chlorophyll molecule is replaced by aluminum, a metal that is soluble at low pH. If the pH is too high, many essential mineral nutrients are not soluble and the plant suffers because it lacks these essential factors. As plants require oxygen for their metabolic processes it too is an essential condition that must be monitored. Over the entire summer we found that the pH of the system was generally slightly less than 7 and ranged from a low of 5.47 and a high of 6.99. There were minor differences between cells and the initial pH of the water increased after flowing through the anaerobic cell but the range was consistent and acceptable. D.O. was acceptable for plants (Table 1). This level may possibly be decreased without detriment to plants and this lower D.O. would be beneficial for the anaerobic portions of the wetlands.

Table 1 Mean dissolved oxygen present at each measure point over the course of the summer months.

Cell	Mean Dissolved Oxygen
Input Anaerobic	6.93
Input Tree Cell	5.15
Input 1st Aeration	3.66
Input 2nd aeration	3.81
Holding Pond	4.41

3.3. Metal Levels in Plants Assayed in Plants

The metal of most concern and interest to this situation is Zn. Plants utilize small amounts of this element in their enzyme systems and it is considered a required micronutrient. According to Stout (1961) as modified by Salisbury and Ross (1992), Zn levels considered adequate in dry plant tissue is 20 ppm. Plants can survive with higher levels but there are adverse and often phytotoxic effects as levels increase. Levels in soil water vary but are generally not sufficiently high to affect a plant's survivability. Levels in the water in our system range as high as 748 mg/L at the anaerobic input and 273 mg/L as the highest level obtained at the input to the first plant-based treatment cell. This presents a considerable loading to the plant system. Arsenic, cadmium and lead have no known physiological function for plants and are

considered to be phytotoxic elements. Data available on accumulation levels for these metals is usually expressed in terms of the plant's abilities to accumulate or even hyperaccumulate these elements without suffering irreparable cell dysfunction. Some plants can accumulate large amounts of one or more metals without suffering damage and they are described as hyperaccumulators. No plants that we used obtained the hyperaccumulator levels but on average they all greatly exceeded the essential requirement concentrations by a large factor (Table 2). In another study (data not reported) *Agrostis stolonifera* demonstrated a robust ability to grow in high metal soil but does not demonstrate any appreciable metal uptake. It was included in our planting scheme as it is grows widely in the Trail area. A single sample of *Epilobium grandifolia* (a volunteer that at one time dominated the cells shortly after they were built) was sampled but the results, although high in comparison to many other plants in the study were not included due to the small sample.

Table 2 Assay results from plants harvested (initially at the end of August when high zinc levels had caused some plants in cell one to die back, and secondly at the end of the summer growing season) showing levels of four metals of concern in the area. Data is from plant leaf tissue expressed as dry weight.

Plant	Cell & Position	Zinc ppm	Cadmium ppm	Arsenic ppm	Lead ppm
Salix exigua	First – Front	2980	32	11	173
Salix exigua	First – Front	3570	13	8	59
Salix exigua	First – Middle	3690	10	9	65
Hybrid Poplar	First – Front	2880	15	7	49
Hybrid Poplar	First – Back	4280	16	6	44
Tripsicum dactyloides	First – Front	1980	19	9	79
Tripsicum dactyloides	First – Front	1470	7	11	50
Tripsicum dactyloides	First – Middle	1690	22	10	114
Calamagrostis canadensis	Second – Middle	1750	13	9	79
Typha latifolia	Third – Front	467	3	3	15
Typha latifolia	Third – Middle	638	3	4	24
Second Harvest					
Hybrid Poplar	First- Front	4020	26	9	91
Tripsicum dactyloides	First – Middle	1190	10	6	65
Tripsicum dactyloides	First – Back	890	6	7	54
Calamagrostis canadensis	Second – Front	1430	4	6	30
Calamagrostis canadensis.	Second – Middle	1750	9	8	65
Calamagrostis canadensis.	Second – Back	2330	12	9	109
Typha latifolia	Third – Front	871	5	8	34
Typha latifolia	Third – Middle	1020	7	6	53
Typha latifolia	Third – Back	629	6	8	43
Poplar (control)	adjacent area	1670	52	7	73

To be considered a Zn hyperaccumulator a plant would need to be able to safely store 10,000 ppm or 1% dry weight in its tissues. Levels that define a hyperaccumulator for each of the other three metals (As, Cd, Pb) are metal specific. For lead the level has been set at 10,000 ppm or >1%, and for Cd the level is 100 ppm or >0.01% (Brooks and Baker, 1989). Arsenic levels in plants are generally around 12

ppm (Porter and Peterson, 1975 as cited by McIntyre, 1999). Since this is the same range as cu and Pb in plants and the hyperaccumulator status threshold for these has been set at 10,000 ppm a similar standard has been set for As by Environment Canada's plant database defining plants with metal accumulating abilities (McIntyre 1999).

3.4 Other Metals Found in Plant Tissues

Plant assays also showed that other metals were present in plants and were sometimes elevated. As leachate assays concentrated on the three metals of primary concern, the values given in plant assays are merely indicators of the plants accumulation abilities.

Total metal load of non-essential metal species is the primary concern in this type of remediation practice. For the most part, elements such as Cu, Ni, and Cr, all present at high levels in our plant assays, are either non-essential or only essential as micronutrients. Plant metal levels are given, together with levels that are thought to be adequate (Salisbury and Ross 1992) for normal plant growth (Table 3). In the instance of Cr, a metal with no known physiological use in plants, normal plant level accumulations of <1mg/kg (1 ppm) are used (Baker and Brooks, 1989).

Plants are also accumulating significantly higher levels of essential nutrients and micronutrients such as Cu (5.28 times required amount) and Mn (32.77 times required amount). Higher than necessary levels of the essential nutrients iron, potassium, calcium, magnesium and molybdenum (Fe, K, Ca, Mg, Mo respectively) are also evident at up to twice required levels. The only essential macronutrient that is low is phosphorus (P).

Table 3 Assay levels of selected metals as found in plant leaf tissue taken from all cells in wetlands treatment system. All data presented are mean results from 20 separate plant assays except for Mo (n = 12) & Fe (n= 17)

Measurement	Cu (ppm)	Mo (ppm)	Cr (ppm)	Mn (ppm)	Ca %	Fe %	Mg %	P %	K %
Mean	31.71	1.42	41.40	1638.5	0.74	0.02	0.37	0.12	1.64
Adequate Levels	6	0.1	<1.0	50	0.5	0.01	0.2	0.2	1.0
Control	30.4	2	36	1150	1.85	0.01	0.46	0.18	1.13

Notes: The control plant is a native poplar that was growing in the area bordering the treatment site. As such it has likely adapted to the high metal load found in soils in this area.

3.5 Flow Rates

Flow through was measured at the input to the plant-based treatment cells and the output into the final holding pond (Table 4). Differences between these two measurements are taken to show the daily volume of water transpired, evaporated or utilized for plant growth. This water is taken as 100% clean of contaminating metals.

The past summer was not typical summer in the Trail region where the 3-year average for rain free days is 52 during months of most rapid plant growth. In 1999, there were only 41, a difference of 21%. Rain free days in this calculation include cloudy days when available sunlight is less. September, when plants were not growing

as rapidly had many fewer rainy days than average (30 days rain free as opposed to a 3-year average of 19). Despite the weather the system still showed its ability to clean a substantial amount of water.

In total, more than 3,000,000 litres of water were pumped into the anaerobic cell, all of which received some treatment over the summer. Some evaporated, some remains as a cell charge, however, more than 1.6 million litres were passed into the plant-based treatment system and nearly 25% of that amount was utilized by plants or evapotranspirated. It is important to note here that we used a digital flowmeter to measure input to the anaerobic cell and a manual system to measure the other volume flow rates. The manual system is possibly less accurate and some of the discrepancies might be due to measurement errors. Higher than normal rainfall added to the volume of water in the system and therefore evapotranspiration levels are likely greater than the measured 25%.

Table 4 Water flowing through system as measured at input to plant-based treatment cells and at output to final holding pond. Volumes were calculated by filling a 10-litre container and recording the time. Input and Output were measured 5 days a week and results extrapolated from means derived from these measurements to include weekend volumes. Measurements include data recorded during rain events for input but not output.

Month	Days With No Rain	Days Operating	Input to Plant Cells Days X Mean Measured (Total Litres)	Output to Holding Pond Days X Mean Measured (Total Litres)	Amt. Transpired Difference In -Out (Total Litres)
June	12	23	207552	183149	24403
July	30	31	593836	474982	118854
August	13*	23	367724	195017	172707
Sept.	26*	26	256334	223730	32604
October	21	21	180831	160986	19845
Total	102	124	1606279	1237874	368405
Monthly Mean		25	321255	247574	73681
Daily Mean			12954	9982	2971

* System was shut down for 6 days in August and 4 days in September

3.6 Metal Removal

Metal concentrations from four collection points in the system, the originating leachate, and the holding pond were determined on a weekly basis. Metal levels this year were much higher than during the previous year. These assays show arsenic and cadmium removal rates remain outstandingly high (better than 99%) as was the case during the first year of operation (Table 5).

Levels for zinc removal were of concern late in the summer leading to a brief shut down and recharging of the anaerobic cell. Despite this, levels of zinc in the originating leachate and water volume treated mean that the total zinc (and other metals) removed far exceeded last year's excellent first season's operational results (Table 5). Once re-started the system returned to much better operating efficiencies and, in fact, was able to handle a once only spike input of 748 mg/L (coupled with similar high readings for arsenic (288 mg/L) and cadmium (12 mg/L) – 224% higher than the summer mean for Zn, 277% higher for As and 163% higher for Cd.

The residency time for water in the system was calculated as between 7 – 10 days, depending on flow rates. Calculations were based on observations of spikes

observed in water charged into the system and the subsequent appearances of these spikes in following cells. When these extremely large spikes were experienced the system was able to handle the input and levels after two weeks were measured at the final discharge point of: Zn – 117 mg/L (84.4% reduction); As – 0.25 mg/L (99.91% reduction); and Cd – 0.014 mg/L (99.88% reduction).

Each cell in the system has an anaerobic component and this, together with plant accumulation, rhizosphere sequestration or organic substrate adhesion results in metal removal. Figures 1-3 illustrate the level of Zn, As and Cd removed from the leachate water, both for the system as a whole and for each cell as it removes a percentage of the metal remaining.

Table 5 Mean values for each stage of four-stage biological treatment system showing initial levels of metals as input into anaerobic cell and levels found at each stage of process. Results are based on ICP-AES assays as carried out by Cominco Analytical Laboratory. Samples were taken at fixed points on a weekly basis.

Assay Point	Arsenic mg/L	Cadmium mg/L	Zinc mg/L	Total Percent Metal Removed In Each Cell as % of Cell Input
System Input	76	4.56	288	43.0%
Anaerobic output	14	1.69	194	20.0%
Tree Cell Output	2.80	0.89	163	29.0%
Grass Cell Output	1.28	0.11	116	38.0%
Typha Cell Output	0.29	0.02	72	
% Removed	99.62	99.56	73	

3.7 Post Shutdown Zn Removal Efficiency

The reductions for Zn differed greatly before and after the shutdown period. Reductions in zinc levels as a result of bacterial activity in the anaerobic cell gradually declined over the course of the summer (mean reduction for 12 assays was 10.26%). Post-shutdown, the rate increased to 49% (with a two-week high following the spike (748 mg/L) of nearly 76%.

The increased efficiency following the shutdown is seen in Figure 4. Levels of Zn in the leachate water were considerably higher at the input point yet they were reduced below the average levels for the year.

3.8. Comparison to Last Year's Results

It is not simple to directly compare the results of the initial summer's operations and those reported for the current year because of considerable differences in operations including:

- In 1998 the system operated for a total of 55 days, 1999 – 124 days;
- In 1998 contaminated water was introduced late in the season when the plants were at maximum development and capable of storing large amounts of metals in already mature tissues;
- During 1999 metal containing water was introduced as plants were just moving into their rapid growth phase and therefore young and developing plant tissues were experiencing what could be phytotoxic levels of contamination;
- In 1998, there were fewer assays (4 in 1998, 17 in 1999) and fewer detailed measurements made of volume flow through;

- In 1998 the summer was much hotter and drier than during 1999.

A comparison between the two years is instructive, however, particularly in light of the fact that metal levels were so much higher during the current year (Table 6). Based on treatment days operating in 1998 and 1999 we should expect to remove slightly more than twice the number of moles of metal in 1999 when compared to 1998 removal rates. However, data shows that almost 4 times the number of moles of Zn were removed in 1999 as opposed to 1998, 5.7 times as many moles of As and 4.2 times as many moles of Cd. During 1999, as calculated from the volume of water treated, more than 5700 moles of zinc, 1600 moles of arsenic and nearly 65 moles of Cd were removed from the input water by the plant based treatment system. However, the volume used in this calculation is what was measured as flowing into the plant based treatment cells. In total the measured input into the anaerobic cell was 3,000,000 L and of this about 400,000 L can be considered as the system charge – water that will remain in the cell. Calculating the metal removed in the remaining 1,000,000 L gives removal and sequestration totals of approximately 9260 moles of Zn, 2653 moles of As, and 105 moles of Cd in 1999.

Table 6 Comparison of number of moles of As, Cd and Zn removed during 55 days of operations during summer 1998 and 124 days of operations during summer 1999. Number of moles present, remaining and removed were calculated from mean assay values (mg/L) at anaerobic cell, from total measured volume input into plant-based segment of treatment system and volume sent to holding pond. Absolute reduction in mg/L is also shown. This is derived by subtracting mean levels of metal at output from mean level at input.

Year	Metal	Concentration (mg/L)	Volume (L)	Moles In	Moles Out	Moles Removed
1998	Zn	137.50	687355	1445.53	10.05	1435.58
1999	Zn	288.53	1606279	7088.71	1378.74	5709.97
1998	As	31.75	687355	291.28	3.18	288.10
1999	As	76.40	1606279	1638.01	4.79	1633.22
1998	Cd	2.58	687355	15.78	0.19	15.59
1999	Cd	4.56	1606279	65.17	0.22	64.95

Absolute Metal Levels Removed (difference between mean level at input to system and mean level at output) between 1998 and 1999.

Metal	Removed 1998 (mg/L)	Removed 1999 (mg/L)	Difference Removed 1999-1998 (mg/L)	% Increase Removed
Cd	2.54	4.54	2.00	78.7
As	31.30	76.11	44.81	58.9
Zn	136.26	215.71	79.95	58.7

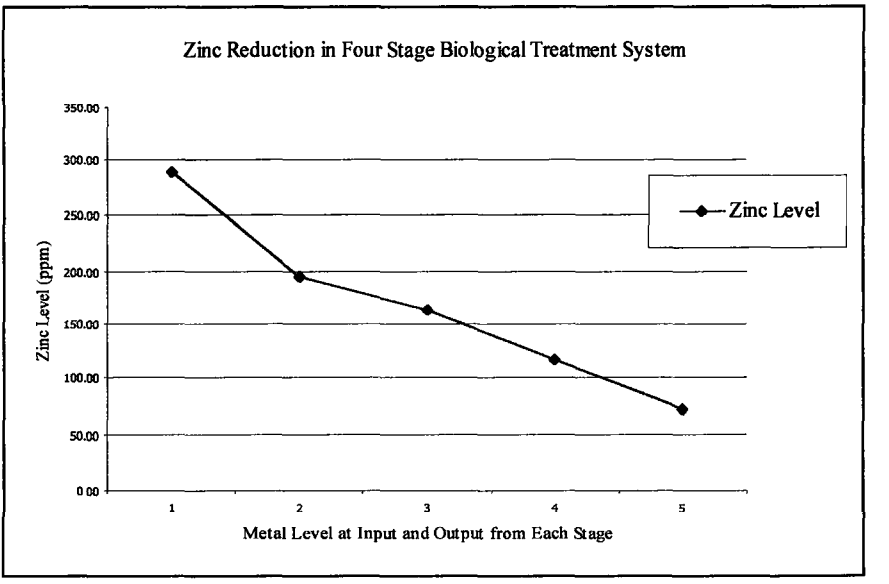


Figure 1 Mean zinc levels as measured by ICP-AES assay as water is treated in system. Initial value (1) shows input levels at anaerobic cell input. Point 2 is output of anaerobic cell; 3 – output of tree cell; 4 – output of grass cell; 5 – output of *Typha* cell.

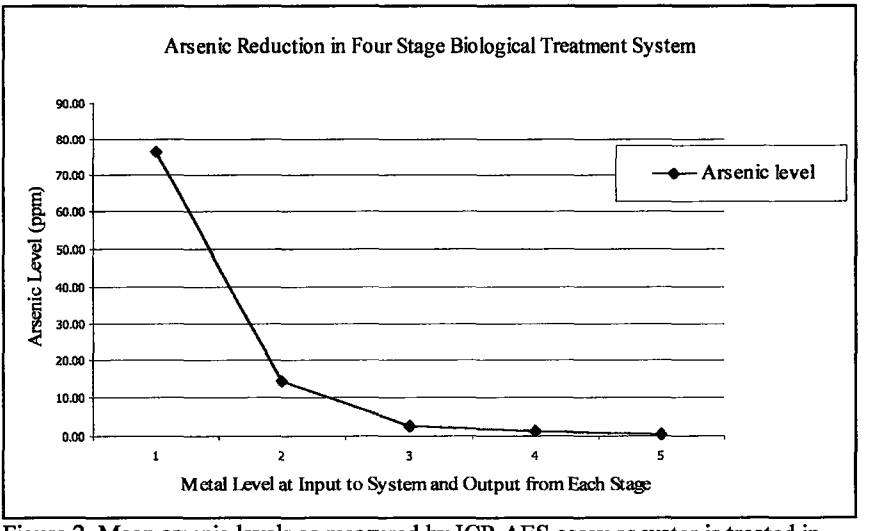


Figure 2 Mean arsenic levels as measured by ICP-AES assay as water is treated in system. Initial value (1) shows input levels at anaerobic cell input. Point 2 is output of anaerobic cell; 3 – output of tree cell; 4 – output of grass cell; 5 – output of *Typha* cell.

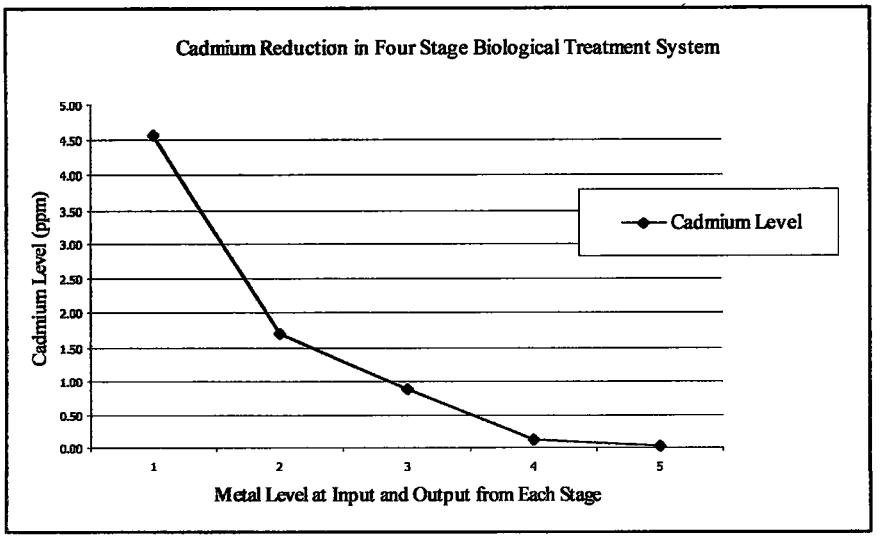


Figure 3 Mean cadmium levels as measured by ICP-AES assay as water is treated in system. Initial value (1) shows input levels at anaerobic cell input. Point 2 is output of anaerobic cell; 3 – output of tree cell; 4 – output of grass cell; 5 – output of *Typha* cell.

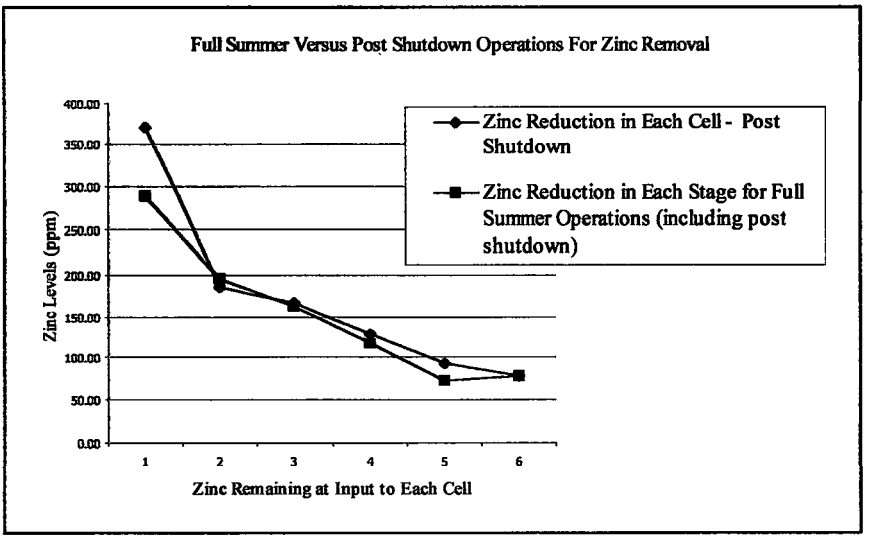


Figure 4 Zinc level reductions in each cell shown as the mean reduction from 17 assays in the case of full summer's operations and as a the mean of four assays following post-shutdown startup. Initial slope between points one and two represent reduction in anaerobic cell. The drop in level and line slope indicate cell efficiency.

3.9 Anaerobic Cell Assay

Six samples of biological matrix taken from the anaerobic cell were assayed for Most Probable Number Analysis (MPN) that gives an estimate of the abundance of cultivable sulphur reducers belonging to physiologically defined taxa. Laboatory assays showed that there was sulphidiogenesis occurring at a level than compares to the range generally found in fresh water sediment. The second assay provided a measurement of Acid Volatile Sulphides (AVS) that measures the amount of sulphides that are actually present in the core samples. The highest value found was for the core sample taken at the output end of the system from the upper segment of the core sample. However, when compared to the concentration of sulphide in freshwater sediment in Lake Coeur d'Alene, our values were 10 times lower.

Low AVS values were not surprising as we had observed over the course of the summer that there was a marked reduction in the level of gas bubbles breaking the surface of the anaerobic cell water layer and that, in fact, as the summer progressed the level appeared to be diminishing. Once the system was re-started with the liquid invert sugar added, bacterial colony activity in the cell as measured by gas bubbles increased and the level of metal reduction in the anaerobic cell, particularly for Zn increased (Figure 4).

4.0 Discussion

The tasks for this summer's operations were to gain a better understanding of the chemistry of the system and to operate it for an entire growing season to be better able to ascertain plant response. Both these goals were accomplished. Increased monitoring lead to a complete and full summer's data on D.O. and pH. Both these factors are important to the system's operations and both are within the operating parameters that we desire.

D. O. levels are suitable for vigorous plant growth. It would be better, however, if they could be driven down very quickly when the water first enters the anaerobic cell. The easiest and most effective way to achieve this goal would be to add a quickly metabolized form of carbon to the water as it is input into the cell. A possible carbon source is liquid invert sugar or acetate. Accordingly, a system will be designed and constructed to ensure that either liquid sugar or acetate is fed into the anaerobic cell each time that it is charged with water.

One important change that is required will be to re-fill the anaerobic cell to its former level. The compaction in the biological matrix is not unexpected, but the severity of the compaction is more than calculated. It is possible that this compaction has resulted in a volume reduction of up to 33%. Since anaerobic digestion is a volume and area based process, such a reduction in volume is a serious matter. A 1 meter thick layer of biological material will be added to the existing anaerobic cell surface and this layer will then be covered with an impermeable layer such as RPE. A layer of sand will then be placed on the top of this to hold it in place. This would re-install the plug flow design and if the RPE was sufficiently large to extend beyond the existing edges, water could not flow out along the edge short-circuiting the plug flow design. This would ensure maximum residency time in the system although it would not correct the small breakthroughs in the plug flow design that were evident when Rhodamine was added to the system.

There might be a system based reason for some of the observed reduction other than the lack of bacterial activities and the increased metal levels observed. A partial reason for the observed differences in reduction might be related to sorption differences in terms of metal attractions to the biological matrix. Some of the high levels of metal removal that were observed last year might have been due to metals binding to sorption sites in the biological matrix that is part of all cells. Once these sites are filled, then one removal component of the system is no longer functioning and the rest of the metal removal factors have an increased load to handle above and beyond the observed increases in metal loadings in the water. Once saturation levels have been reached then any metal reduction is due to bacterial and plant based activity and this level of reduction is what can be maintained indefinitely.

A primary question remains - why did the system not start properly this past summer and lose much of the Zn removal efficiency exhibited last year? One possible reason is that the system was allowed to become dormant over winter. Since there was no additional metal and sulphate containing water added to the system, bacteria were not able to function even though there was sufficient carbon present to metabolize. We will examine this next spring by initiating a new start-up procedure that will charge the system with a large measure of liquid invert sugar and a complete charge of metal containing water. The system will be allowed to rest for a period before beginning further treatment by the plant-based treatment cells.

This is, however, a stopgap measure useful if the system operates only in the summer months. The system must be winterized if it is to be useful on an industrial scale. We require winter operational data to successfully design this for industrial use. Winterizing would mean that the pipeline into the system be replaced and buried to protect it from freezing. It would also require that all other pipelines presently on the surface or close to it be buried as well. New valves would have to be installed and expensive items such as flow meters would have to be protected from weather damage. Furthermore, the level of operations would have to be adjusted to ensure that flooding did not take place and that water was treated to levels achieved during summer operations.

Funding to complete the necessary changes has been secured (Environment Canada and Cominco) and the system will now be renovated in 2000 to be able to be operated year-round. With results similar to present levels of metal removal, it can be proven as an industrial scale technology. Also, as part of the winterizing, the final holding pond will be enlarged. At the same time that this cell is enlarged the system will be improved by utilizing this final stage as a further anaerobic digestion cell. Winterizing, addition of a secondary anaerobic treatment cell, and the addition of liquid sugar to reduce oxygen levels more quickly, could make it possible that even higher levels of metal removal can be attained and maintained through an entire year.

5.0 Conclusions:

The system operated very well in its first full summer of operations. Plants were subjected to very high metal levels and continued to grow and flower. While some suffered – most thrived. Metal levels were much higher than last year but the system operated at very high removal rates as measured by total number of moles of metal removed. There were no physical problems similar to those experienced last season due to outlet pipes becoming plugged. Some adjustments in cell operations (eg flow

rates, addition of sugar) were required but once changes were made the system returned to much higher efficiencies and it appears that we have learned an important aspect relating to the system's operations and how best to ensure anaerobic activity in the cell.

An important aspect of combining an anaerobic digestion system with a subsequent wetlands based treatment methodology is that the metal levels handled are very much higher than those found in single biological treatment systems reported in the literature. Whereas many other reports discuss treating Zn loadings of less than 50 mg/L this prototype system has successfully treated water containing more than 700 mg/L. When the levels for Zn are combined with the high levels of other metals present, the results reported appear here even better.

It is also important to remember that following the re-charging of the system it proved very capable of handling an extraordinary spike event that included metal levels that were 150% greater than the summer mean for Zn alone. This robust performance is important when considering the usefulness of a biological system in industrial applications. Unlike a chemical treatment plant where additional counteracting material can be added, a biological system must include in its design and operating methodology the ability to withstand sudden unexpected spikes. This one did.

Our plants responded extremely well to the metal levels they were subjected to throughout the summer. There was some dieback and even possibly some individual plant death. However, knowledge gained from the assays means that we can address the question of re-planting and plant placement with a much better understanding of what works where. Certainly the coyote willows in the very front of cell one will need to be replaced if they do not come back in the spring. A better design might be to plant a species with a much more pervasive root system rather than a shrub to extend the rhizosphere coverage more thoroughly. Transplanting some of the grasses from the back of cell one and two is a serious consideration as is adding more hybrid willows. Since one cultivar of the hybrid poplars grew so well and seemed relatively unaffected, additional plants of this species will be transplanted from the reserve gardens. Finally, it seems that since the *Agrostis stolonifera* although metal tolerant, appears not to be an accumulator, it should be replaced with *Tripsicum dactyloides* and *Calamagrostis canadensis*.

Of interest to the overall operation is that although *Typha* (originally planted as a final metal removal polishing cell and as a nutrient sink) has shown that it is not a heavy accumulator of metals, however, it can survive and thrive in the system, even in the anaerobic cell where surface water have a very high concentration of metals. Volunteers of this species have established themselves in the corner of the anaerobic cell and consideration will be given to adding additional rhizomes during start-up next spring. Additional plant assays of both plants in the system and plants growing outside the system need to be undertaken. Further work should be done using *Epilobium grandifolia* to confirm the result obtained from the single sample this year.

The results of the bacterial assays are not surprising and reflect the visual observations made during the summer with a marked reduction in marsh gas smell and a lack of vigorous gas bubbling activity on the surface of the anaerobic cell. However, once the system was re-charged these two visual observations were much more similar to those observed last year and it is likely that a second similar core sampling and subsequent testing could result in substantially different MPN and AVS results.

6.0 Acknowledgments

Dr. W Rauser, and Dr. B Husband, University of Guelph for assistance with Greenhouse research and system modeling. Dr. Frank Rosenzweig, University of Idaho at Moscow, for assistance with bacterial assays. National Research Council through the IRAP program with assistance with funding for development of the anaerobic digester and funding for measurement, operations and assays. Dr. Terry McIntyre, Environment Canada for funding assistance for water assays and funding for on-going winterization. Dr. Mark Edwards, Cominco Environment who developed the anaerobic matrix and modeled this cell.

7.0 References

Baker A.J.M. and R.R. Brooks; Terrestrial Plants which Hyperaccumulate Metallic Elements – A Review of Their Distribution, *Biorecovery* Vol. 1 pp: 81-126, 1989

Baker A.J.M., Reeves, R.D., and S.P. McGrath, In Situ Decontamination of Heavy Metal Polluted Soils Using Crops of Metal-Accumulating Plants – A Feasibility Study" in *In Situ Bioreclamation* eds. R.E. Hinchee and R.F. Olfenbuttel Butterworth-Heinemann, Boston, Ma., pp: 600 – 605, 1991

Duncan, B. and A. Mattes, Field Scale Prototype Anaerobic/Wetlands Cells for Removing Heavy Metals from Water, in *Proceedings of the Phytoremediation Technical Seminar,* Calgary Alberta, May 31 – June 1 1999, pp: 149 - 157, 1999

McIntyre T., Development of a Worldwide Data Base on Metal Tolerant and Metal Accumulating Plants for Contaminated Site Remediation, in *Proceedings of the Phytoremediation Technical Seminar,* Calgary Alberta, May 31 – June 1, 1999, pp: 33-59, 1999

Salisbury F.B. and C.W. Ross *Plant Physiology*, fourth edition, Wadsworth Inc., Belmont, California, pp: 117-214, 1992

PhytoPet© – A Database of Plants that Play a Role in the Phytoremediation of Petroleum Hydrocarbons

R.E. Farrell*, C.M. Frick, and J.J. Germida
Department of Soil Science, University of Saskatchewan
Saskatoon, Saskatchewan, Canada
farrell@sask.usask.ca

Abstract

Phytoremediation (i.e., plant–assisted bioremediation) of hydrocarbon contaminated soils is a steadily evolving technology that shows promise as an effective and low-cost alternative to most engineering techniques and traditional bioremediation methods. Recently, however, Frick et al. (1999a, 1999b) identified several significant "research gaps" in the published literature, including the fact that very few studies have been conducted on the phytoremediation of petroleum hydrocarbons under cold climate conditions. The cold climate and short growing season characteristic of the major oil and gas producing regions of western Canada make it particularly important to conduct phytoremediation research on plants adapted to local conditions. These findings underscore the need for new research initiatives to assess the potential of phytoremediation as a method of remediating petrochemical contaminated sites in western Canada.

As a result of the general lack of knowledge regarding the selection and availability of plants suitable for phytoremediation under Canadian climatic and ecological conditions, we surveyed the available literature and developed a database (*PhytoPet*©) containing information on plants with a demonstrated potential to phytoremediate or tolerate petroleum hydrocarbons. The *PhytoPet*© database was then used in conjunction with site surveys to develop a catalogue of plants with the potential to phytoremediate hydrocarbon contaminated soils in the Prairie and Boreal Plain Ecozones of western Canada. Here we provide a demonstration of the *PhytoPet*© database.

1.0 Introduction

Phytoremediation, the use of plants for the *in situ* treatment of contaminated soils, is essentially *ecological engineering* which capitalizes on the naturally occurring synergistic relationships among plants, microorganisms, and the environment that have evolved over millions of years. Phytoremediation takes advantage of the fact that plants have extensive rooting systems which explore large volumes of soil, support larger bacterial populations in the rhizosphere (the region immediately surrounding the root) than in the surrounding bulk soil, and produce exudates which can directly affect the activity of the rhizobacterial populations (Anderson et al., 1993; Shimp et al., 1993; Erickson, 1997; Sylvia et al., 1998). Though generally considered a long-term remediation process limited to soils where the contamination is shallow and occurs at low to medium concentrations, phytoremediation holds significant promise for the cost-effective cleanup of certain types of hazardous wastes including gasoline, diesel fuel, and petroleum hydrocarbons (Cunningham et al. 1995; USEPA, 1998; Siciliano & Germida, 1998).

Development of a Multi-component Phytoremediation System to Remove Persistent Organic Contaminants from Soil

X.-D. Huang, B. R. Glick and B. M. Greenberg
Department of Biology, University of Waterloo,
Waterloo, Ontario, Canada
xdhuang@sciborg. uwaterloo.ca

Abstract:

A number of techniques, both mechanical and biological, have been investigated for the remediation of persistent organic contaminants from soils. However, most of these techniques have been applied independently. As a consequence of using only one process, remediation usually is slow for persistent organic contaminants. To improve remediation, a few techniques that complement different aspects of contaminant removal have been applied to soils in combination resulting in an enhanced multi-process phytoremediation system. This multi-process system has greatly improved and accelerated the overall remediation process resulting in removal of 95% of total PAHs. The remediation system includes: physical (volatilization), photochemical (photooxidation), microbial degradation and plant growth (phytoremediation) processes. The techniques applied to realize these processes are land farming (aeration and light exposure), microbial remediation (introduction of contaminant degrading bacteria) and phytoremediation (plant growth with plant growth promoting rhizobacteria). This system was very effective at removal of persistent soil bound contaminants from soil. It appears that the combination of these components may be a viable solution for remediating persistent organic contaminants from soils.

1.0 Introduction

Large amounts of hazardous waste have been released into aquatic and terrestrial environments due to industrial activities and energy consumption [Neff. 1979; Cook and Dennis, 1983; Safe, 1984]. Many organic contaminants are toxic, mutagenic and carcinogenic, and they are persistent in the environment posing a significant hazard to ecosystems and human health [Safe, 1984; Neff, 1979; Piver& Lindstrom, 1985]. Because of their hazardous nature and persistence in the environment, it is expensive to remediate contaminated tracts of land for new usage. In many cases, it would take decades to clean up these sites. Therefore, research and development of remediation technologies for these types of contamination are needed.

Many techniques have been advanced to remediate persistent organic contaminants from soil [Alexander, 1999; Cookson, 1997; Mcnicoll & Baweja, 1995; Rock, 1997]. However, many are costly and/or inefficient. Physical removal and washing of contaminated soil with solvents is expensive and has met with mixed results. Land farming has been used for *in situ* remediation. However, the practice is primarily effective for removal of small, volatile chemicals. To improve the effectiveness of land farming, nutrient supplements, such as nitrogen and phosphorus, have been applied to enhance natural microbial degradation of contaminants. However, this is generally still limited to relatively small chemicals. Microbial bioremediation with organisms that are capable of degrading contaminants has been

also can be accessed from the main menu. Moreover, regardless of which search filter is used to explore the database, the user can obtain a printout of all information displayed on-screen.

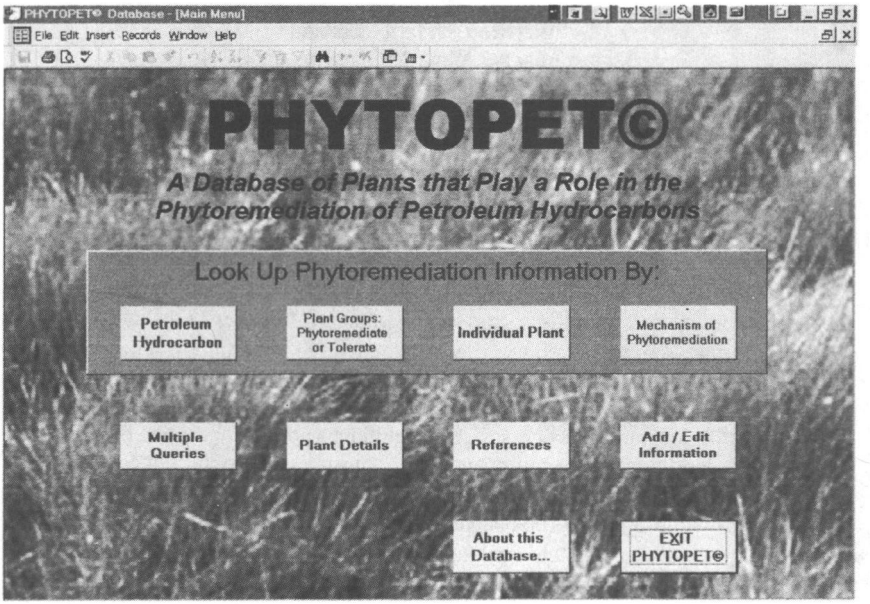


Figure 1 ***PhytoPet*© database window (Microsoft Access 97) showing the main menu**

An additional feature of the database involves the *multiple queries* option (Figure 2). This option allows the user to generate a list of plants that have several characteristics in common, such as habitat, salinity tolerance, the ability to either tolerate or phytoremediate specific petrochemicals, phytoremediation mechanism, and the occurrence of the plant in Western Canada. Once a plant list has been generated, a printout of the list can be obtained and the user can then return to the main menu to obtain the relevant botanical information for each plant species and examine specific information relating to the experimental conditions under which the plant's phytoremediation potential was demonstrated (e.g., type and concentration of contaminant, phytoremediation mechanism, special requirements, etc.).

2.1 An Example of a Multiple Queries Search of the *PhytoPet*© Database

The major oil and gas producing regions of western Canada occur in the Prairie Ecozone (characterized by a climate that ranges from semiarid to humid continental and typically involves long, cold winters and short, very warm summers) and the Boreal Plain Ecozone (characterized by a climate that involves long, cold, snowy winters and short, warm, moist summers) (Acton *et al.*, 1998). Not surprisingly, therefore, the identification of plants that (i) have a demonstrated phytoremediation potential and (ii) can tolerate the relatively harsh climatic

conditions characteristic of the region is one of the major challenges facing the adoption of phytoremediation strategies for the reclamation of petroleum contaminated sites in western Canada.

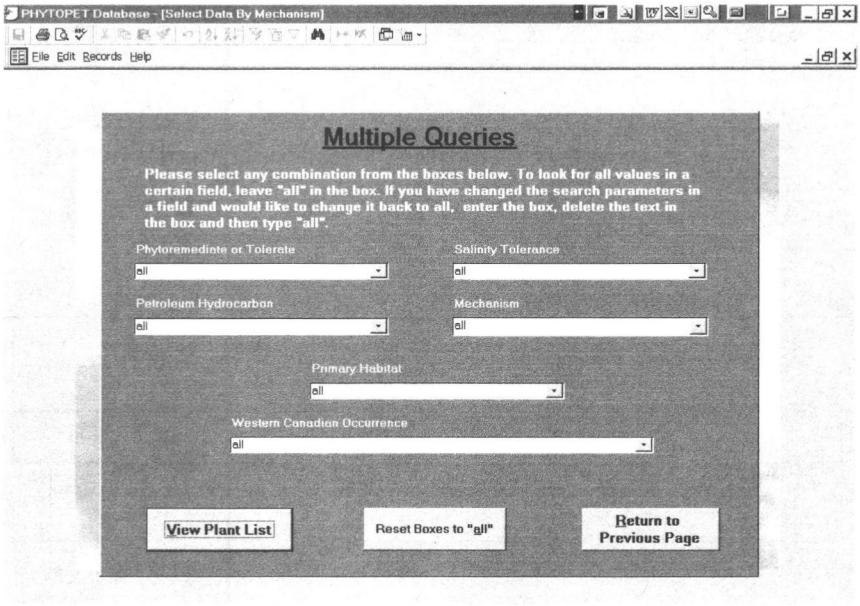


Figure 2 ***PhytoPet*© database window (Microsoft Access 97) showing the *multiple queries* menu**

A multiple queries search of the *PhytoPet*© database was conducted for "*terrestrial plants* with a demonstrated ability to *phytoremediate* petrochemical contaminated soils and which are *native to western Canada*". This search generated a list of 11 plant species capable of degrading (or assisting in the degradation of) a variety of petroleum hydrocarbons (Table 2), and which may have potential for phytoremediation efforts in the Prairie and Boreal Plain Ecozones.

3.0 Use of the *PhytoPet*© Database in Conjunction with On-Site Botanical Surveys

It is generally acknowledged that there is little published information regarding the selection and availability of plants suitable for phytoremediation under western Canadian climatic and ecological conditions (Frick et al., 1999). Therefore, botanical surveys of several sites where the soils had been contaminated by oil or gas production wastes or spills were undertaken during the fall of 1999 (Godwin et al., 2000). Plant species catalogued during the botanical surveys were then cross referenced against those in the *PhytoPet*© database to develop a list of plants to be screened for their phytoremediation potential under local soil and environmental conditions.

4.3 Tree Tissue Sampling

Appropriate preparation and analysis methods for tree tissue sampling is difficult to determine. Summer results for one year only indicated TCAA in three of seven leaf samples at levels of 37- 150 ug/g wet weight. Leaf bud data from March, 1999 indicated TCE at levels of 0.14 to 0.17 ug/g and 1,1,2,2,-TCA at 1.18 and 0.95 ug/g wet weights. VOCs are consistantly found in some tree tissue although not in all samples.

4.4 Transpiration Gas Analysis

VOCs have been consistently detected in transpiration samples. In 1999 TCE and 1,1,2,2,-TCA were found at levels ranging from 14 to 840 parts per billion by volume (ppbv). Seasonal trends have been observed , with levels increasing during the warmer months and then decreasing again in the fall (Table 1).

Table 1 Seasonal Transpiration Gas and Water Results (ppbv)

	Spring		Summer		Fall	
VOC	**Gas**	**Water**	**Gas**	**Water**	**Gas**	**Water**
TCE	13.4	ND	210.0	6.3	99.0	1.8
1,1,2,2-TCA	170.0	56	2000	640.0	919.0	160.0

4.5 Nematode Sampling

The nematode population was found to increase in total abundance and specifically the fungivore community the first year after the trees were planted. It was believed that the presence of the trees may have enhanced the habitat for the nematode population. However, 1998 and 1999 showed a decrease in nematode population. It is speculated that this decrease may be related to the droughts which occurred during these two summers. In addition, sampling has been limited to only one sampling event per season. More data is needed.

4.6 Modeling

The performance of the phytoremediation technology was simulated using both analytical and numerical models. Currently, four years of data exist to develop the models. These models were used to estimate the amount to contaminant mass that the poplar trees may remove from the surficial aquifer over the lifespan of the plantation and to predict the time required to restore its water quality. Although such models have their limitations, they do provide some guidance to the feasibility of cleaning up a particular site.

A method of estimating contaminant uptake rate has been popularized by Schnoor(1997). The use of this equation as applied to this particular site can be summarized below.

The uptake rate is given by the equation:

$$U = (TSCF)(T)(F)$$

where	U=	Uptake rate of the contaminant in mg/day
	TSCF=	Transpiration Stream Concentration Factor (no units)
	T=	Transpiration rate of the vegetation (liters/day)
	C=	Aqueous phase concentration in soil or groundwater (mg/liter)

After solving for "U", contaminant uptake and clean-up time are given by:

$$k = U/Mo$$

where	k=	first order rate constant for uptake, yr^{-1}
	U=	contaminant uptake rate, kg/yr (calculated from above)
	Mo=	Mass of contaminant initially, kg

An estimate for the mass of contaminant remaining at any time is $M = Mo\ e^{-kt}$
Solving for the time required to achieve clean-up of a known action level:

$$t = -(\ln M/Mo)/k$$

where	t=	time required for clean-up to action level, yr
	M=	Mass allowed at action level, kg
	Mo=	initial mass of contaminant, kg

TCE

The total TCE at J-Field has been estimated at 215.86 kilograms (kg) in solution and an additional 593 kg associated with the soil. Concentration of TCE has been measured as 61mg/L. The J-Field hybrid poplar trees are estimated to be transpiring/removing 7500 L of H_2O/tree/year (at maximum). There are approximately 200 trees on the site, which covers an area of about 1 acre. TSCF for TCE is 0.74.

Calculating for 90% removal of the soluble TCE: t= 7.3 years. If it is assumed that all of the TCE (809.48 kg) on site will become soluble, then 90% removal is calculated: t= 27.52 years.

1,1,2,2-tetrachloroethane

The total 1,1,2,2-TCA at J-field has been estimated at 589.54 kg soluble and 1978.11 kg total. Concentrations have been measured at 170mg/L. TSCF is 0.79.

For 90% reduction of the soluble 1,1,2,2,-TCA: t= 6.73 years
If it is assumed that all of the 1,1,2,2-TCA (1978.11 kg total) on the site will become soluble in the aquifer, then 90% removal is calculated: t= 23.02 years.

regulatory guidelines prepared by Environment Canada] scheduled for release in the summer of 2000. Copies of the *PhytoPet*© database and associated reports will be available in CD format (free of charge) from the Department of Soil Science (University of Saskatchewan); Environment Canada; and the Petroleum Technology Alliance Canada (PTAC). Future updates of the database are expected on a biannual basis through a web site maintained by the University of Saskatchewan.

Table 4 Dominant or Codominant Plant Species Present at Oil Contaminated Sites in the Prairie and Boreal Plain Ecozones of Alberta (Plants Not Listed in the *PhytoPet*© Database)

Scientific Name	Common Name	Life Cycle & Growth Habit
*Bromus inermis**	Smooth brome	Perennial grass
*Poa pratensis**	Kentucky bluegrass	Perennial grass
Equisetum arvense	Common Horsetail	Perennial forb
*Galeopsis tetrahit**	Hemp nettle	Annual forb
Calamagrostis canadensis	Marsh reed grass	Perennial grass
*Taraxacum officianale**		Perennial forb
Phleum pratense		Perennial grass
Alnus crispa	Green alder	Perennial shrub

* Species exotic (non-native) to the Prairie and Boreal Plain Ecozones of Alberta.

4.2 Inherent Limitations of the *PhytoPet*© Database

The *PhytoPet*© database was developed as a tool to assist remediation specialists, site owners and managers, and environmental scientists in choosing candidate plants which may be suitable for the phytoremediation of petroleum hydrocarbons. Inevitably, however, some records which should have been included in the database were most likely missed during the initial computerized search of the literature. In addition, because the information entered into the database comes from a variety of sources – each with its own purpose – the specific information required to complete the various data fields (see Table 1) was not always available. With this in mind, several characteristics of the information provided in the database deserve closer attention. First, when considering phytoremediation as a reclamation strategy, stakeholders must consider the climate and soil type in the area they are reclaiming as these factors will influence the effectiveness of the phytoremediation effort (Jackson, 1999). However, the majority of studies included in the database (i.e., ca. 76%) involved only laboratory studies conducted under artificially controlled environmental conditions. Furthermore, only about 40% of the plant species listed in the database have been shown to produce enhanced degradation of the target contaminant; i.e., most of the plants listed in the database have been shown only to tolerate hydrocarbon contamination. Likewise, in only a few instances (i.e., ca. 35% of the 81 plant-hydrocarbon combinations) was there an attempt to determine the degradation mechanism involved in phytoremediation. Accordingly, although the *PhytoPet*© database provides a useful tool for helping to select plants with phytoremediation potential and prioritize the screening of candidate plant species, it

is intended to supplement, not supplant, region-specific botanical surveys. Moreover, before any plant species is used in a site remediation project, small-scale field trials should be conducted to validate a plant's phytoremediation potential under local conditions. Preliminary field trials also will help alert users to any possible confounding effects associated with salinity, wetability, and prior herbicide use on plant viability.

4.3 Native vs. Non-Native Plant Species

The U.S. government's Office of Technology Assessment has estimated that 4 to 19% of non-native organisms introduced into natural and agricultural ecosystems in the United States have had a severe negative impact on both the environment and the economy (OTA, 1993). Not surprisingly, therefore, there is much concern among ecologists and naturalists about the use of exotic species as vehicles for the phytoremediation of contaminated sites. Nevertheless, the use of exotic species should not be ruled out without due consideration of the threat they actually pose. (This should include discussions with appropriate regulatory agencies and concerned public organizations about species suitability.) For example, a species such as smooth brome (*Bromus inermis*) is a major threat to native plant communities in the moist grassland regions of the Canadian prairies. It is capable of invading native grass and shrub stands, greatly altering the stand's species composition and structure. However, brome is so widely spread now that it is found throughout the settled areas of the landscape. Thus, if its phytoremediation potential were to be established, it may be appropriate for use in areas where it is already ubiquitous in the landscape. Even an exotic species that could be considered a threat to native plant communities may still be useful if its use were restricted to areas not adjacent to native plant communities – e.g., the use of alfalfa in highly cultivated areas. Wherever possible, however, native plant species should be given preference over exotics.

5.0 Conclusions

The *PhytoPet*© database was developed as an inventory of plants with a demonstrated ability to phytoremediate or, at the very least, tolerate soils contaminated with petroleum hydrocarbons. As such, the database is expected to provide easy access to a wide range of information and assist in the pre-selection of plants appropriate for the phytoremediation of petroleum hydrocarbons in terrestrial and wetland environments.

The *PhytoPet*© database may prove especially useful when used in conjunction with the *Phytoremediation Decision Tree* (ITRC, 1999) – a tool which uses site-specific information and a flow chart layout to assist site managers in deciding whether phytoremediation is appropriate for a particular site. Once the suitability of a given site for phytoremediation has been established, the *PhytoPet*© database may be used to identify plants with phytoremediation potential for that site.

6.0 Acknowledgements

The *PhytoPet*© database was developed by researchers in the Department of Soil Science, University of Saskatchewan in co-operation with Environment Canada. Support for this project was provided through an initiative sponsored by the Petroleum Technology Alliance Canada (PTAC) and funded by Environment Canada, Quest–An Alliance Corporation & BP Amoco Canada Petroleum Co. Ltd., the

plant growth, reduce stress [Glick, 1995; Burd et al, 2000; Siciliano & Germida, 1997 Ajithkumar et al, 1998], including chemical toxicity. This allows vigorous plant growth, particularly in roots in the presence of chemical stressors [Burd et al, 2000; Siciliano & Germida, 1997; Walton et al, 1994; Walton & Anderson, 1992]. Precisely how plant growth promoting bacteria alleviate stress is unclear. However, some of these bacteria contain the enzyme 1-aminocyclopropane-1-carboxylic acid deaminase which can lower the levels of stress ethylene in plants [Shah et al, 1999]. It has previously been reported that plant growth promoting bacteria by lowering plant ethylene levels can reduce nickel toxicity to plants and can decrease the damage to plants from flooding and decrease the deleterious effects of certain pathogens [Glick, 1995].

Plant growth promoting bacteria have an important role to play in bioremediation. Plants are effective at removing large amounts of persistent organic contaminants if they can accumulate large amounts of root biomass. Plants are then able to generate a large amount of root biomass in soil thereby facilitating the bacterial growth and allowing for enhanced microbial degradation of contaminants. Plant roots are also capable of acting as a sink for contaminants from soil. Also, plant roots can release enzymes into the soil that can degrade contaminants. Moreover, plant roots are capable of taking large amounts of water from soil and this water movement in soil will bring contaminants in contact with roots and bacteria surrounding the roots. Therefore, phytoremediation can be effective at removing large amounts of contaminants from soil, as long as good conditions for plant growth are maintained. This combined strategy of using plants, bacteria, and land farming shows a great potential to remediate large amounts of persistent organic contaminants from soil.

4.0 References:

Alexander, M. 1999. *Biodegradation and Bioremediation.* Academic Press, Inc.

Ajithkumar, P.V., Gangadhara, K.P., Manilal, P. and Kunhi, A.A.M. 1998 *Soil Biolchem.* 30: 1053

Burd G.I., Dixon, D.G. and Glick, B.G. 2000. Plant growth promoting bacteria that decease heavy metal toxicity in plants. Can J. Microbiol. 46:237-245.

Burken, J.G.; Schnoor, J.L. 1997. Uptake and metabolism of atrazine by poplar trees. *Environ. Sci. Technol.* 31:1399-1406.

Cooke, M. and Dennis, A.J. 1983. *Polycyclic Aromatic Hydrocarbons: Formation, Metabolism and Measurement* Battelle Press Inc.

Cookson, J.T. 1995 Bioremediation engineering: design and application. McGraw-Hill, Inc.

Cunningham, S.D., Anderson, T.A., Schwab, A.P. and Hsu, F.C. 1996. *Advance in Agronomy.* 56: 55.

Drake, E. 1997. Phytoremediation of soil: current prospects and limitations for industrail application. *IBC Phytoremediation Conference*. Seattle, Washington. June 18.

Glick, B.R. The enhancement of plant growth by free living bacteria. *Can. J. of Microbiol.* 1995, 41, 109.

McConkey, B., Duxbury, C., Dixon, D.G. and Greenberg, B.M. 1997. Toxicity of a PAH photooxidation product to the bacteria *photobacterium phosphoreum* and the duckweed *Lemna gibba*: effects of phenanthrene and its primary product, phenanthrenequinone. *Eviron. Toxico. Chem.* 16: 892.

McCutcheon, S. 1996. Workshop on phytoremediation of organic contaminants. Fort Worth, Texas.

McIntire, T. and Lewis, G.M. 1997. The advancement of phytoremediation as innovative environmental technology for stabilization, remediation and restoration of contaminated sites *J. Soil Contam.* 6: 227.

Mcnicoll, D.M and Baweja A.S. 1995 *Bioremediation of petroluem- contaminated soils: an innovative, environmental friendly technology*, Environment Canada.

Neff, J.M. 1979. *Polycyclic Aromatic Hydrocarbons in the Aquatic Environments.* Appl. Sci. Pub. London.

Piver & Lindstrom. 1985 Environ. Health Perspect. 59:163.

Raskin, I., Smith, R.D. and Salt, D.E. 1997. Phytoremediation of metals: Using plants to remove pollutants from the environment. *Curr. Opin. Biotechnol.* 8: 221-226.

Rock, S. 1997. Phytoremediation of petroleum in soil and groundwater.In *12th Annual Conference on Contaminated Soils - Analysis, Site Assessment, Fate, Environmental and Human Risk Assessment, Remediation and Regulation*, P.T. Kostecki and E.J. Calabrese Eds.

Safe, S. 1984. Polychlorinated biphenyls and polybrominated biphenyls: biochemistry, toxicology and mechansims of action. CRC Crit. Rev. Toxicol. 13:319.

Shah, S., Li, J., Moffatt, B. A. and Glick, B.R.1999 Isolation and characatrization of ACC deaminase genes from tow different plant growth promoting rhizobacteria. *Can. J. of Microbiol.* In press.

Shann, J.R. and Boyle, J.J. 1994 Influence of plant species on in situ rhizosphere degradation In *Biorem. through rihzospere Technol.* Anderson & Coats Eds, ACS Series 563. Washington DC. 71-81

Siciliano, S.D. and Germida, J.J. 1997. Bacteria inoculants of forage grasses enhance degradation of 2-chlorobenzoiz acid in soil. *Environ. Toxico. Chem.* 16:1098-1104.

Phytoremediation of Chlorinated Solvents in a Surficial Aquifer by Hybrid Poplar Trees.

Harry R. Compton, Steven R. Hirsh
U.S. EPA
John G. Wrobel, Amy Burgess
U.S. Army Garrison, Aberdeen, MD, USA
William H. Schneider
Roy F. Weston, Inc., Philadelphia, PA, USA
Dale M. Haroski, Christopher D. Gussman
Lockheed Martin/REAC. Edison, New Jersey, USA
E-mail: Compton.Harry@epa.gov

Abstract

A pilot-scale phytoremediation study was implemented in the spring of 1996 at the Edgewood Area of Aberdeen Proving Ground in Harford County, Maryland. A portion of an approximately one acre area was planted with hybrid poplar (*Populus deltoides x trichocarpa* cv. HP-510) in an effort to intercept and contain volatile organic compounds (VOCs) in the groundwater originating from former disposal pits. Primary contaminants of concern include trichloroethene (TCE) and 1,1,2,2,-tetrachloroethane (TCA). Trees were initially planted two to eight feet below ground surface. Monitoring wells and lysimeters were also installed strategically throughout the site. Trees and wells have been monitored several times each year since this study has commenced. As of 1999, it was calculated that the trees were removing more than 4000 liters (L) of groundwater per day during the active growing season and it is estimated that this will increase to more than 7500 L per day as the trees fully mature. Corresponding data indicate that these trees have had an impact on the groundwater elevation during the growing season. Analysis of transpiration gases and condensate reveal site contaminants and their breakdown products. This particular site has provided much information for phytoremediation of VOCs.

1.0 Introduction

The J-Field Toxic Pits Site is located at the southernmost end of Gunpowder Neck Penninsula, in the Edgewood Area of Aberdeen Proving Ground, Harford County, Maryland. J-Field was historically used for the disposal of many types of chemical wastes and explosives. These materials were detonated or burned in open pits and trenches, often with the addition of hydrocarbon fuels to enhance combustion of the waste material. Two parallel pits approximately 3 meters (m) deep by 4.5 m wide by 60 m long are the main source of contaminants identified in the groundwater. The contaminants exist primarily in a surficial aquifer which slowly flows towards a freshwater marsh. Significant levels of VOCs, primarily TCE and 1,1,2,2,-TCA, have been detected in this surficial aquifer at levels up to 260 milligrams/liter (mg/L)(Figure 1). The water table is generally within 1- 1.5m of the ground surface.

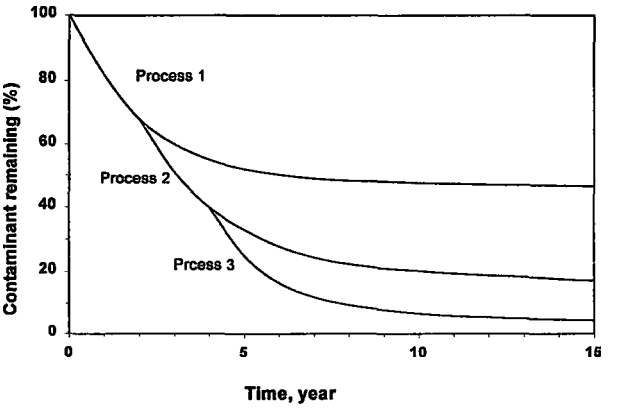


Figure 2. Kinetics of multi-process for contaminant remediation
Successive application of three processes can allow for pseudo-zero order kinetics.

To complicate matters, contaminated sites usually contain complex mixtures of contaminant chemicals. For example, PCBs are composed of 209 congeners and most PCBs contaminated sites contain more than 50 congeners. Petroleum hydrocarbon contaminants are also a large group of chemicals containing hundreds of different compounds. For instance, creosote, as a common source of polycyclic aromatic hydrocarbon (PAHs) contamination, contains more than 100 chemicals, most of which are aromatics. It is very difficult, if not impossible, to use a single technique to rapidly and completely remove all the components of such complex mixtures. Therefore, by knowing the contaminating components, and understanding their properties, and treating them strategically with selected multiple remediation processes, it may become feasible to remove them rapidly and completely. By combining multiple techniques, and optimizing each remediation process, the overall remediation process can be improved greatly and the time required for removal of persistent organic contaminants from soils can be shortened significantly.

3.0 A Case Study of Creosote (PAH) Contamination

Polycyclic aromatic hydrocarbons (PAHs) are a particularly recalcitrant group of contaminants [Neff, 1979, Cooke & Dennis, 1983]. There are many sources for soil contamination by PAHs including creosote, fossil fuels and steel production [Neff, 1979, Cooke & Dennis, 1983]. Not surprisingly PAHs are one of the most prevalent soil contaminants worldwide. At the present time, the techniques used to remediate PAH contaminated soils are inefficient and costly. [Rock, 1997; Cookson, 1991; McNicoll & Baweja, 1995]. PAHs are composed of hundreds of compounds. For instance, the regulated priority list of PAH compounds in the environment contains 16 compounds. They are different in size (2 to 6 benzene rings), shape, structure, and properties. Small compounds, such as naphthalene, acenaphthene, and acenaphthylene, are volatile or semi-volatile. Many are subjective to photooxidation. Many of the relative smaller and less hydrophobic PAHs are subject to microbial degradation. Others (i.e., benzo(a)pyrene, dibenzo(a,h)pyrene, benzo(g,h,i)perylene,

and indo(1,2,3-c,d)pyrene) are high hydrophobic and binding strongly to organic matter in soils. This later group is particularly recalcitrant to remediation.

To make remediation effective and efficient for PAHs, different techniques are required for removal of different classes of these compounds. Based on properties of these mixtures, a multiple technique remediation system was developed that involved land farming, light exposure(simulated solar radiation), microbial inoculation and plant growth with plant growth promoting rhizobacteria (PGPR). These are four remediation processes resulted in: volatilization, photochemical oxidation, microbial degradation and phytoremediation. They provide four complementary kinetic processes that we hoped to completely remove all classes of PAHs from soil. This multiple technique system was tested in the laboratory to assess its efficiency.

Table 1 PAH removal from soil by different methods

PAHs	Landfarming	MicroBiorem	Phytorem	System
Naphthalene	94.2	100.0	100.0	100.0
Acenaphthene	73.4	100.0	100.0	100.0
Acenathylene	75.5	100.0	100.0	100.0
Fluorene	92.2	100.0	100.0	100.0
Phenanthrene	87.8	98.3	99.8	98.2
Anthracene	84.3	93.8	90.4	94.5
Fluoranthene	79.2	90.5	98.2	95.4
Pyrene	45.2	83.2	99.5	96.7
Benzo(a)anthracene	24.1	55.7	60.4	81.4
Chrysene	6.3	21.7	22.3	75.2
Benzo(b)fluoranthene	11.6	0	11.5	59.2
Benzo(k)fluoranthene	4.7	39.4	44.6	63.9
Benzo(a)pyrene	0	0	19.9	51.8
Dibenzo(ah)pyrene	0	0	3.1	40.5
Benzo(ghi)perylene	0	0	9.9	41.6
Indo(123-cd)pyrene	0	0	5.1	32.4

Data were collected following a 120-day treatment in the greenhouse and presented as percentage of chemical removal relative to the control that contains 2 g/kg of 100% creosote.

Land farming was chosen because it is a fast and effective method for removal of volatile chemicals such as naphthalene, acenaphthene, and acenaphthylene [Table 1]. It also aerates the soil, resulting in an increase in the potential for redox reactions in the soil. Further, it exposes buried chemicals to sunlight for photooxidation. One problem with degrading intact PAHs is that the first oxidation step is difficult for most biological organisms. This is because the π-orbital structures of intact PAHs provide great thermodynamic stability. However, PAHs are readily photooxidized by sunlight to quinones and hydroxyl quinones [McConkey, et al 1997]. Therefore, the soil was tilled before bioremediation treatment so a new layer of soil was exposed to light. Land farming was performed by turning the soil for weeks. When this is done, approximately 40% of the PAHs are lost from the soil due to volatilization and photooxidation to new products [Table1 and Figure 3].

Weather data was utilized to estimate the overall evapotranspirational potential demand on a daily basis for a three year period. A Campbell Scientific Meteorological Station was used to collect wind speed, relative humidity, precipitation, temperature, and net solar radiation. The evapotranspirational potential and sap flow data were used to generate a tree and site specific crop index for the planted region. Leaf area measurements were also collected in July of 1999 and compared to trunk areas to estimate the progression of leaf area index.

3.2 Groundwater Sampling.

Fourteen wells and four lysimeters are located within the vicinity of the phytoremediation area. In addition, numerous Geoprobe microwells have been installed throughout the site. Groundwater levels are monitored and the effect of the poplar trees on the groundwater levels can be closely observed. Groundwater sampling for VOCs are regularly performed.

3.3 Tree Tissue Sampling.

Tree tissue (leaf and bud) extract samples are analyzed seasonally using GC/MS following methanol extraction using U.S. EPA standard methods.

3.4 Transpiration Gas Analysis.

Samples were taken utilizing a clear, 2 mil, 100 liter Tedlar(TM) bag with dual stainless steel fittings, manufactured by SKC (TM) Inc. and placed over the end of two or three healthy branches. Several modifications were made by varying sampling location on the tree, experimentally cooling the collecting bag, and sampling method.

Condensation formed in the Tedlar bag after sealing over a tree branch. This condensate was sampled after the transpiration gas was sampled but before the sampling bag was removed from the tree.

3.5 Nematode Sampling

Soil samples were collected for nematode extraction once each year since 1997. Three soil samples were taken from around each tree at approximately 45 centimeter (cm), 30 cm, and 15 cm increments perpendicular to the base of the tree. All three samples were then combined and sent to a sub-contracting laboratory. The samples were split into three 20 gram (g) subsamples, placed onto Baerman funnels and extracted for 48 hours. Nematodes encountered were placed into functional groups based on esophageal morphology and known feeding habits. The following trophic groups were identified: bacterivores, fungivores, herbivores, omnivore/predators, hatchlings, and unknowns.

3.6 Modeling

Flow and contaminant transport modeling was performed to estimate the capacity for the poplar trees to remove contaminant mass and to predict the time to restore the surficial aquifer. Two methods of modeling have been utiilized at J-Field, one based on analytical methods of Schnoor (1997) and the other utilizing numerical methods based on a 3D-groundwater flow (MODFLOW) and contaminant transport (RT3D) model. (McDonald and Harbaugh, 1988; Clement, 1998).

4.0 Results

4.1 Evapotranspiration Rates and Groundwater Removal

The trees have grown considerably since they were first installed. Correspondingly the evapotranspiration rates and associated groundwater removal have increased and it is predicted that they will continue to increase as the trees further develop and mature.

Stem diameter initially increased by 2.5 cm year but declined to 1.9 cm increase/year between July 1998 and July 1999. Leaf Area Index (LAI) was calculated to be an average of 2.59 and a maximum or 3.16 as of the 1999 growing season. A canopy closure is predicted to occur at a LAI of 4 and may occur during the 2000 growing season. Sap flow estimates for 1999 indicate that the poplar plantation is removing more than 4000 L of water per day (based on a 200 day growing season) with individual trees removing more than 26 L per day on average (Figure 1). It is predicted that the amount of water use will increase to 7500 L/day for the entire poplar plantation (48 L/Tree/day). Note that these values are averages and that transpiration rates vary by individual tree, season, and weather patterns.

4.2 Groundwater Sampling

Continued monitoring of groundwater levels indicate a depression in groundwater at the phytoremediation plot. A groundwater depression of 12 centimeters or more has been recorded during the growing season.

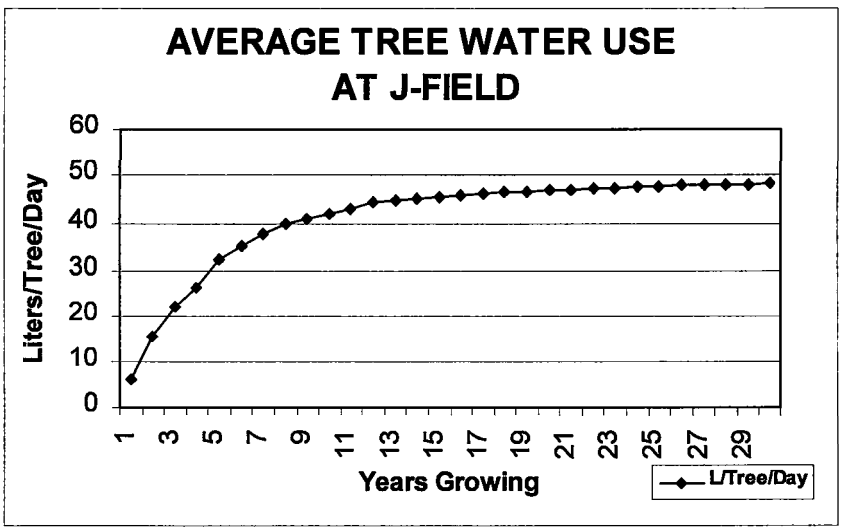


Figure 2: Average Tree Water Use at J-Field

Results of lysimeter sampling 2.2 m below ground surface (bgs) have detected both TCE and 1,1,2,2,-TCA at the tree root zone. TCE ranged from 5.2 to 29 ug/L and 1,1,2,2-TCA was found at a concentration of 14- 36 ug/L.

Table 2 Plants Native to Western Canada and with a Demonstrated Ability to Phytoremediate Petroleum Hydrocarbons: Results of a Multiple Queries Search of the *PhytoPet*© Database

Plant Common Name (*Genus, Species*) [Family – Growth Form]	Petroleum Hydrocarbons	Mechanism of Phytoremediation
Western wheatgrass (*Agropyron smithii*) [Gramineae – grass]	chrysene, benzo[*a*]pyrene, benz[*a*]anthracene, dibenz[*a,h*]anthracene	unknown
Big bluestem (*Andropogon gerardi*) [Gramineae – grass]	chrysene, benzo[*a*]pyrene, benz[*a*]anthracene, dibenz[*a,h*]anthracene	unknown
Side oats grama (*Bouteloua curtipendula*) [Gramineae]	chrysene, benzo[*a*]pyrene, benz[*a*]anthracene, dibenz[*a,h*]anthracene	unknown
Blue grama (*Bouteloua gracilis*) [Gramineae – grass]	chrysene, benzo[*a*]pyrene, benz[*a*]anthracene, dibenz[*a,h*]anthracene	unknown
Common buffalograss (*Buchloe dactyloides*) [Gramineae – grass]	naphthalene, fluorene, phenanthrene	unknown
Prairie buffalograss (*Buchloe dactyloides* var. Prairie) [Gramineae – grass]	naphthalene, fluorene, phenanthrene	unknown
Canada wild rye (*Elymus canadensis*) [Gramineae – grass]	chrysene, benzo[*a*]pyrene, benz[*a*]anthracene, dibenz[*a,h*]anthracene	unknown
Red fescue (*Festuca rubra* var. Arctared) [Gramineae – grass]	crude oil and diesel	rhizosphere effect (suspected)
Poplar trees (*Populus deltoides* x *nigra*) [Salicaceae – deciduous tree]	potential to phytoremediate benzene, toluene, *o*-xylene	rhizosphere effect
Little bluestem (*Schizchyrium scoparious* or *Andropogon scoparious*) [Gramineae – grass]	chrysene, benzo[*a*]pyrene, benz[*a*]anthracene, dibenz[*a,h*]anthracene	unknown
Indiangrass (*Sorghastrum nutans*) [Gramineae – grass]	chrysene, benzo[*a*]pyrene, benz[*a*]anthracene, dibenz[*a,h*]anthracene	unknown

Though more than 70 plant species were catalogued at the contaminated sites, there were only four matches to plants listed in the *PhytoPet*© database: alfalfa (*Medicago sativa*), common cattail (*Typha latifolia*), quack grass (*Agropyron repens*), and red fescue (*Festuca rubro*). However, an additional 21 plant species (including 18 native species) catalogued at the contaminated sites were found to be related at the genus level to plants listed in the database (Table 3).

Table 3 Plant Species Present at Oil Contaminated Sites in the Prairie and Boreal Plain Ecozones of Alberta and Related Plants Listed in the *PhytoPet*© Database

Genus	Species	
	***PhytoPet*©**	**Site Surveys**
Agropyron	*A. repens, A. smithii*†, *A. desertorum*	*A. repens, A. subsecundum, A. trachycaulum*
Carex	*C. aquatilis, C. rupestris, C. rotundra*	*C. bebbii, C. rostrata, C. siccata*
Elymus	*E. canadensis*†	*E. innovatus*
Hordeum	*H. vulgare*	*H. jubatum*
Medicago	*M. sativa*†, *M. lupulina*†	*M. falcata*, M. sativa**†
Melilotus	*M. altissima*†	*M. alba*, M. officianalis**
Phalaris	*P. arundinacea*	*P. arundinacea*
Pinus	*P. banksiana*	*P. contorta*
Populus	*P. deltoides*†, *P. nigra*†	*P. balsamifera, P. tremuloides*
Salix	*S. arctica*	*S. bebbiana, S. discolor, S. petiolaris*
Scirpus	*S. pungens*	*S. microcarpus*
Trifolium	*T. hybridum, T. pratense,T. repen*	*Trifolium spp.*
Vicia	*V. fabia*	*V. americana*

* Species exotic (non-native) to the Prairie and Boreal Plain Ecozones of Alberta.

† Plant species with a previously demonstrated phytoremediation potential.

In all, the *PhytoPet*© database was used to identify 33 plant species (29 native and four introduced species) that may have applications for the phytoremediation of hydrocarbon contaminated sites in the Prairie and Boreal Plain Ecozones of western Canada. This list of candidate plants includes 11 species with a previously demonstrated phytoremediation potential (see Table 2) and 22 related species (see Table 3) selected from a catalogue of plant species found growing at hydrocarbon contaminated sites in western Canada. In addition, eight species found to be dominant or codominant at one or more sites (Table 4) – but which were not related to any plant listed in the *PhytoPet*© database – also were added to the list of candidate plants. We are currently in the initial stage of a multi-phase study to assess the phytoremediation potential (and elucidate degradation mechanisms) of these candidate plants under simulated local environmental conditions.

4.0 Availability and Limitations of the *PhytoPet*© Database

4.1 Availability of the *PhytoPet*© Database

A beta version (ver. 2.0) of the *PhytoPet*© database is currently available from the authors. Testing of the beta version is scheduled to be completed by late spring 2000, with release of an updated version of the database [ver. 2.1; including the companion reports by Frick et al. (1999b) and Godwin et al. (2000) and

A more comprehensive numerical model was constructed to evaluate the performance of an integrated remedial system. The system is designed to hydraulically contain and ultimately reduce the VOC plume and consists of groundwater circulating wells or extraction wells located in the core of the plume to provide active source control. The source control is combined with monitored natural attenuation (MNA) and phytoremediation instituted to further reduce dissolved-phase contaminants. The more detailed modeling effort was conducted to examine the effectiveness and optimal configuration of the integrated remedial technologies. The additional level of modeling was warranted based on field evidence that indicates the hybrid poplars are withdrawing VOCs from the shallow aquifer. Furthermore, field data indicates that natural attenuation (NA) and groundwater extaction/treatment are capable of reducing the VOC mass. Monitoring of natural attenuation parameters indicates that abiotic and biotic degradation is actively occurring and a 90 day pilot test of a circulating well providid 21 lbs of VOC removal (WESTON, 2000).

A 3D-groundwater flow (MODFLOW) and contaminant transport (RT3D) model was constructed to estimate the capacity of the remedial system to satisfy the remedial objective. Model results indicate that the integrated remedial system is capable oremoving up to 85% of the total 1,1,2,2,-TCA mass after 30 years. NA was determined to be the predominant mass removal mechanism unless four or more wells were employed. Sensitivity analyses indicate that variations in the rate constants impact these estimates and additional NA monitoring is needed to verify the results. Phytoremediation emerged as a favorable contributor to the remedial program by providing 7.5% of the total mass removal. Model results support field evidence that show the poplar trees generating partial hydraulic containment of the 1,1,2,2-TCA plume during the peak growing season (Schneider *et al.* 2000)

5.0 Conclusions

The results obtained over several years thus far indicate that the project objectives are being met and that phytoremediation is a feasible remediation method for this particular site. The detection of VOCs and their degradation products in transpiration gas, condensate, and leaf tissue indicate that the trees are removing or degrading these contaminants of concern. Although the mechanism and rate of VOC removal are not known, the detection of these compounds offer strong evidence that the trees are actively withdrawing VOCs from the aquifer. Sap flow rates and surficial ground water levels provide evidence that containment and interception of groundwater flow is also occurring. In addition, it is possible that the trees may also be enhancing the soil community although further investigation is needed. Finally, models can be used to estimate contaminant removal at this site. Based on the two models presented, the site contaminants may be reduced by up to 85% in 30 years. This study provides evidence that phytoremediation can be successfully applied to sites that satisfy the application criteria and comprise similar hydrogeologic settings.

6.0 References

Clement, T.P., *RT3D- A Modular Computer Code for Simulating Reactive Multi-Species Transport in 3-Dimensional Groundwater Aquifers,* Version 1.0. 1998.

Chappell, J., *Phytoremediation of TCE in Groundwater Using Populus.* U.S. EPA Technology Innovation Office. 1998.

Dynamax, *EPA Phytoremediation Study- Aberdeen Proving Grounds J-Field.* Version 3.0, 2000.

McDonald, M.G. and A.W. Harbaugh, *A Modular Three-Dimensional Finite-Difference Ground-Water Flow Model, Techniques of Water Resources Investigations, Book 6, Chapter A1,* U.S. Geological Survey, Reton, Va., 1998.

Quinn, R. L., Johnson, T.L., and L.E. Martino, *An Optimized Groundwater Extraction System for the Toxic burning Pits Area of J-Field, Aberdeen Proving Ground, Maryland.* Environmental Assessment Division, Argonne National Laboratory. Argonne, Il., 1996.

Schneider, W.H., Wrobel, J.G., Hirsh, S.R., Compton, H.R., and D. Haroski, *The Influence of an Integrated Remedial System on Groundwater Hydrology.,* 2000.

Schnoor, J.L., *Environmental Modeling Fate and Transport of Pollutants in Water, Air, and Soil.* John Wiley & Sons, Inc., Wiley-Interscience Publication, 1996.

Schnoor, J.L, *Phytoremediation.* Ground-Water Remediation Analysis Center, Pittsburgh, Pa, 1997.

Weston, Roy F. (Inc.), *A Three-Dimensional Groundwater Flow and Contaminant Transport Model to Evaluate Remedial Alternatives at J-Field. Aberdeen Proving Ground, Maryland.* West Chester, Pa., 2000.

It is generally agreed that the key processes involved in phytoremediation include (i) the stimulation of rhizobacterial transformations by root exudates and decaying plant matter and by affecting the oxygen regime in the rhizosphere, (ii) the slowing of contaminant transport from the rooting zone as a result of adsorption and/or increased evapotranspiration, and (iii) plant uptake, followed by metabolism, volatilization, or accumulation (Cunningham et al., 1995; Schnoor et al., 1995; Siciliano & Germida, 1998). Despite the flexibility and adaptability that these various plant-associated remediation pathways provide, it is the interactions between these pathways as well as the biochemical and ecological interactions between the plant/microbe/environment continuum that give rise to the complexity surrounding phytoremediation. Nevertheless, because of its cost effectiveness, adaptability, and potential as a final *polishing* step to close out sites after other cleanup technologies have been used to treat hotspots, phytoremediation science remains an area of intense interest.

2.0 Database Organization and Search Capabilities

PhytoPet© was compiled using Microsoft Access 97. This platform was chosen because of its widespread use among the various stakeholder groups involved in this project and because of its interchange capability with other database and spreadsheet formats. The purpose of the *PhytoPet*© database is to serve as an inventory of plant species that phytoremediate (or, at the very least, tolerate) petroleum hydrocarbons in terrestrial and wetland environments. Information in the database was compiled by first conducting an extensive computerized search of several public access databases and commercial abstracting services. Key search words and phrases included: phytoremediation, hydrocarbons, petroleum hydrocarbons, polycyclic aromatic hydrocarbons (PAH), BTEX compounds, organic contaminants, bioremediation, biodegradation, biotransformation, rhizosphere biodegradation, phytoextraction, phytovolatilization, and natural attenuation. Only published studies reporting a demonstrated ability of one or more plants to phytoremediate or tolerate petroleum hydrocarbons were included in the database.

Information presented in the database is grouped into one of three categories: *summary information*, *experimental data*, and *plant specific data* (Table 1). *Summary information* provides a brief description of the plant and its mechanism of phytoremediation. The *experimental data* sections provide a detailed summary of the experimental conditions found in each case study included in the database. (NOTE: as of November 9, 1999 information from 34 such cases had been compiled.) The *plant specific data*, include information on the taxonomy, habitat, biology, and distribution of each plant in the database.

Upon opening the phytopet.mdb file in Microsoft Access 97 (ver. SR-2 or later), the user is presented with the main menu window (Figure 1). Four option buttons (i.e., search filters) in the main menu allow the user to search the experimental data by selecting either a specific *petroleum hydrocarbon*, an *individual plant species* (using either the common or scientific name), a *plant group* (based on whether the species phytoremediate or only tolerate petroleum hydrocarbons), or the primary *phytoremediation mechanism* of the plant (e.g., accumulation, rhizosphere degradation, containment, or phytovolatilization). In addition, species-specific data on each of the 62 plants included in the database can be accessed through the *plant details* option button. The complete list of *references* used to compile the database

Table 1 Information Contained in the *PhytoPet*© Database

Summary Information	Experimental Data	Plant specific Data
▪ Common name of plant	----- *Experimental Data (1)* -----	----- *Plant Description & Habitat* -----
▪ Scientific name of plant	▪ Laboratory or field study	▪ Common & scientific names
▪ Cultivar, strain, or code	▪ Initial hydrocarbon concentration	▪ Synonym
▪ Demonstrated ability of plant to phytoremediate or tolerate hydrocarbon	▪ Length (duration) of experiment	▪ Family
▪ Mechanism of phytoremediation	▪ Post-experiment concentration and/or conditions	▪ Demonstrated ability of plant to phytoremediate or tolerate hydrocarbon
▪ Types of microorganisms associated with plant	▪ Soil characteristics	▪ Growth form
	▪ Age of plant at first exposure	▪ Morphology
		▪ Growth duration
	----- *Experimental Data (2)* -----	▪ Primary habitat
	▪ Storage sites in plant	▪ Western Canadian occurrence
	▪ Special requirements for phytoremediation	--- *Additional Information & References* ---
	▪ Additional notes	▪ Salinity tolerance
	▪ Reference	▪ Cultural information
		▪ Impact description
		▪ Natural history notes
		▪ North American occurrence
		▪ World range
		▪ Other species in genus
		▪ Additional notes
		▪ References

researched extensively. For instance, "bioreactors" have been attempted, but the contaminated soils must be brought to the reactor for clean up. This is expensive and can damage the soil. Alternatively, *in situ* bioremediation, usually inoculation of contaminant degrading microorganisms at contaminated sites, has been attempted. However, it is difficult to generate sufficient biomass in natural soils to allow an acceptable rate of sequestration and degradation of hydrophobic molecules [Alexander, 1999; Mcnicoll & Baweja, 1995]. A further problem is that few microorganisms can use high molecular weight contaminants as a sole carbon source, therefore, a readily degradable organic carbon source must be supplied for co-metabolism of high molecular weight compounds [Alexander, 1999; Cookson, 1997; Rock, 1997].

For bioremediation to be effective, the throughput must be very high [Alexander, 1999; Cookson, 1997; Rock, 1997; Cunningham et al, 1996]. A route for achieving this is by increasing biomass. For this reason, phytoremediation has received considerable attention recently [McIntire & Lewis, 1995; Rock, 1997; McCutcheon, 1996; Raskin et al, 1997]. Plants have extensive root systems that explore a large volume of soil and assimilate contaminants over a wide area. As well, roots can enhance microbial activity by supplying substrates and nutrients. Phytoremediation has been successfully used to remediate a variety of contaminants in soil and groundwater. For instance, *Brassica* plants have been used to effectively take up heavy metals such as cadmium, zinc, copper and selenium [Burd et al, 2000; Raskin et al, 1997]. Hybrid poplar trees have been used for removal of herbicides, such as atrazine [Buren & Schnoor, 1997]. Many other plants have been used to take up and/or degrade various organic contaminants in soils [McIntire and lewis, 1997; Siciliano & Germida, 1997; Cunningham et al, 1996; Shann & Boyle, 1994]. The advantages of phytoremediation are: 1) it preserves the natural structure and texture of soil; 2) it is driven by solar energy and suitable to most regions and climates; 3) it is low in cost and technically feasible; 4) it has the potential to be rapid by providing a large amounts of biomass.

Although using plants for remediation of persistent organic contaminants holds advantages over other methods, many limitations exist for current application on a large scale [McIntire & Lewis, 1997; Rock, 1997; McCutcheon, 1997; Drake, 1997]. For instance, when contaminant concentrations in the soil are high, many plants will not grow enough to provide sufficient biomass for successful remediation. In many cases, contaminated soils are poor in nutrients, which will limit plant growth, slowing the remediation process. Further, microbial populations in contaminated soils are often depressed both in diversity and abundance. Contaminated soils do not contain the appropriate microorganisms for the efficient degradation of the contaminants. This further limits the effectiveness of remediation. Therefore, phytoremediation processes are, in general, slow and the time scale for complete remediation is often unacceptably long [McCutcheon, 1997; Cunningham et al, 1996]. To address this problem, we have developed a multi-component phytoremediation system for the removal of recalcitrant organic contaminants from soil.

2.0 Multi-process Strategy for Remediation

Three common types of kinetics may be used to describe remediation process. They are zero order, first order and second order kinetics [Figure 1]. In zero order kinetics, contaminant concentration decreases by linear relation with time. That is the rate of contaminant removal is concentration independent (i.e., -dC/dt=k). In first order kinetics, an exponential decay of contaminant concentration is observed as a function of time(i.e., -dC/dt=kC). In this case, the rate of contaminant uptake is proportional to contaminant concentration. In second order kinetics, a higher order exponential decay is observed. This means the rate of contaminant removal is proportional to the square of contaminant concentration or on the product of two contaminant concentrations (i.e., $-dC/dt=kC^2$ or $-dC/dt=kC_1C_2$).

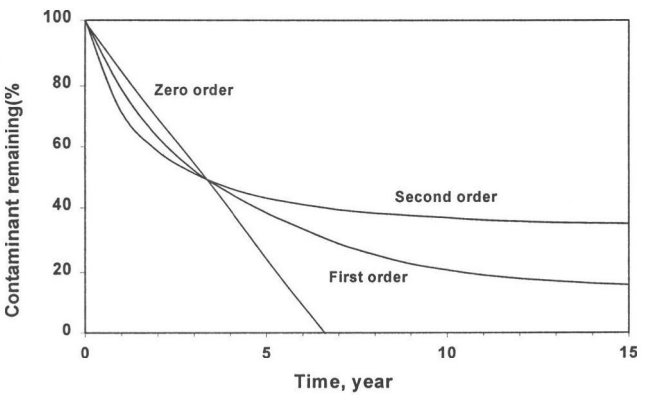


Figure 1. Three common types of kinetics observed for contaminant remediation
Zero order: -dC/dt/=k; first order: -dC/dt=kC; second order: $-dC/dt=kC^2$.

Remediation rates for *in situ* bioremediation of persistent organic contaminants usually follow first or second order kinetics [Alexander, 1999]. Because of the exponential relationship between time and contaminant concentration in soil, it takes a long time for a single remediation process to completely remove persistent organic contaminants. However, the initial remediation rates are nearly linear (zero order) for all three types of kinetics. For first and second order kinetics, the exponential decrease in remediation rate makes a single process for complete remediation of persistent organic contaminants unacceptably slow. Although remediation rates can be accelerated by optimizing environmental factors for a single process, it is very difficult, if not impossible, to change the overall kinetics of degradation. However, if the initial remediation rates are combined in a multi-process system, the remediation kinetics can remain approximately linear (i.e., pseudo zero order) and faster for a greater fraction of the degradation process [Figure 2]. Therefore, the time required for complete remediation can be shortened by several fold. Furthermore, it might even become possible for rapid and complete removal of the persistent organic contaminants from soils.

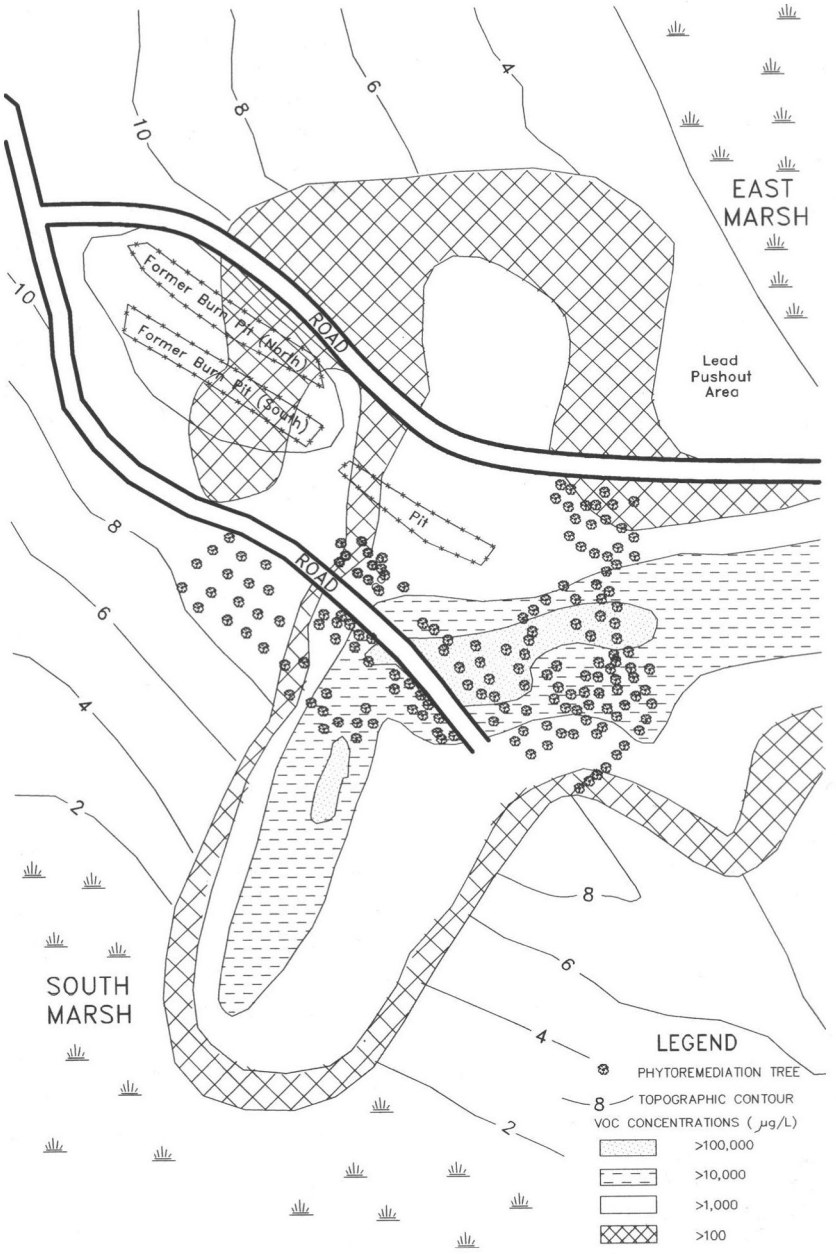


FIGURE 1: Total VOC Concentration at J-Field.

Phytoremediation using trees was determined to be a feasible option at this site due to lack of time limitations, a sensitive environment, high groundwater, design flexibility, and proven ability of poplar trees to remove the contaminants of concern. In addition, other technologies investigated proved inappropriate or impractical for this site. It has been estimated that a 23.66 L/minute groundwater extraction system would be enough to control the flow of groundwater in the area (Quinn *et al.* 1996). Poplar trees were chosen because they are phreatophytic and the contaminated groundwater at this site is known to be relatively shallow. Hybrids were chosen because the leaf area of hybrids are considerably larger than either parent species potentially allowing for much greater evapotranspiration combined with a faster rate of growth (Chappell, 1998).

A pilot-scale phytoremediation study was implemented in the spring of 1996. The planted area is approximately 2039 m^2 and originally consisted of 183 hybrid poplar trees (*Populus deltoides x trichocaarpa* cv. 510) This site has been continuously monitored since the beginning and it appears that the use of trees is meeting the objectives for this site. In addition, the site is providing useful phytoremediation data for a contaminated site spanning over several years.

2.0 Objectives

The objectives of this particular site is to demonstrate that phytoremediation is a viable alternative for remediation of shallow groundwater contaminated with VOCs. The study must show that the surficial aquifer can be intercepted and contained due to evapotranspiration from the tree plantation, and that the volatile organic compounds in the groundwater can be removed and/or destroyed through natural mechanisms.

The effectiveness of specific mechanisms, as well as the optimal methods to monitor them, are the subjects of ongoing research. In order to show that these objectives are being met, it is necessary to:

1) Determine aquifer drawdown within the planted area as related to its zone of influence and seasonal fluctuations.
2) Estimate groundwater removal rates by the hybrid poplars to determine the extent at which the trees are removing groundwater and to model future water use of the trees.
3) Determine that VOCs are being removed and or destroyed through natural mechanisms.
4) Model the time it will take to reduce the contaminants of concern.

3.0 Materials and Methods

3.1 Evapotranspiration Rates and Groundwater Removal

The evapotranspiration rates of individual, mature trees were estimated by measuring sap flow using the Dynamax Dynagage TM Flow 32 system (Dynamax, 2000). Sap flow, tree size, and on-site weather conditions were examined seasonally over a three-year period. Sap flow and data on tree growth have been used to calculate current and future groundwater removal rates by the poplar plantation after generating a crop index specific for this site. Tree size was measured using a manual dendrometer tape to record diameter of the trees approximately 1.5 meters from the ground. Leaf area was calculated using a Dynamax leaf area meter (AM100).

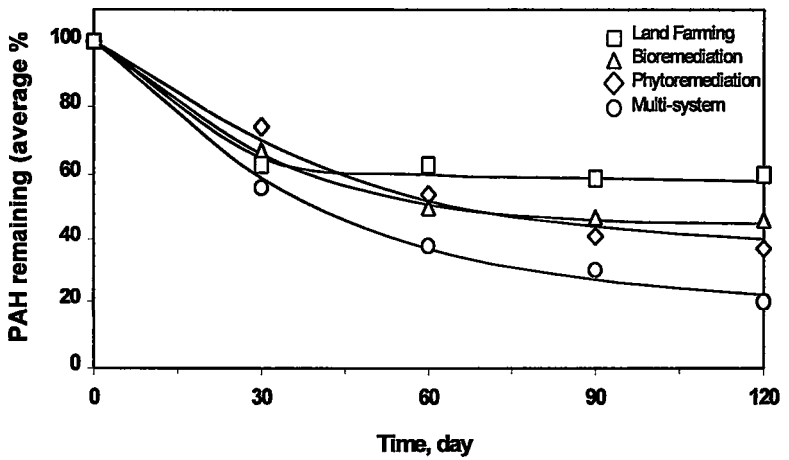


Figure 3 Comparison of PAH Removal Rates of Single Method with Multi- component System

Land farming: the soil was tilled twice a week for a period of 120 days; Bioremediation, inoculation of PAH degrading bacteria; Phytoremediation, plant growth (Tall fescue) on contmainated soil for 120 days; Multi-component system, plant growth (Tall fescue) with PGPR in land farmed and PAH degrading bacteira inoculated soil.

Microbial remediation with bacteria might be more efficient if some of the PAHs have first been photooxidized making them more amendable to metabolism. The bacterial species that were used to inoculate soil were selected from an old creosote contaminated site and acclimated with PAHs in the laboratory for 10 weeks. This bacterial mixture contains strains of *Pseudomonas putida, Flavobacterium sp.*, *Pseudomonas aeruginosa* and an unknown. The soil was inoculated with these bacteria following the land farming treatment. Inoculation with PAH degrading bacteria enhanced removal of PAHs from soil [Table 1 and Figure 3]. In particular, fluoranthene, pyrene and benzo(a)anthracene which can be used as a reduced carbon source for these bacteria[Trzesicka-Mlynarz,1995] were readily remediated [Figure 3].

Growth of plants in soil without land farming or degradative bacteria resulted in removal of PAHs on par with bacteria [Table1 and Figure 3]. However, removal of more of the higher molecular weight PAHs was observed [Table 1]. It was observed that plant growth was poor on the contaminated soil, which impaired remediation (see below). However, when a multi-component system was used, the plants grew much better (see below) and PAH removal was greatly improved as well [Figure 3]. This system included land farming and light exposures, followed by inoculation of the soil with the PAH degrading bacteria, followed by stimulation of plant growth with plant

growth promoting rhizobacteria. In this case, plant growth was vigorous (see below) and efficient remediation was achieved [Figure 3].
To summarize, a comparison of remediation rates of the multi-component phytoremediation system with the individual methods is shown in Table 1 and Figure 3. Land farming is the least effective technique used in the experiments and the overall remediation rate for 16 PAHs was only 35%. The compounds removed by land farming are limited to the small PAH compounds such as naphthalene, acenaphthene, acenathylene, fluorene, phenanthrene, anthracene and benzo(a)anthracene. They are either volatile or subject to photooxidation. Land farming combined with bioremediation by inoculation with PAH degrading bacteria is more effective than land farming alone. Here, the total removal rate of PAHs was about 50%. This is comparable with phytoremediation following landfarming treatment (55%)[Figure 3]. The advantage of phytoremediation over bacterial treatment was that was more effective at removing the larger, more tightly soil bound PAHs. The multi-component remediation system had the great level for removal of PAH contaminants from soil, with an average removal for 16 PAHs at 80% and the total material removed was 95%. The greatest improvement was for the strongly soil bound PAHs. In the multi-component system, where the kinetics overall are first order, the pseudo-linear range is much longer than with any single method. Thus, one can estimate that if it takes 15 to 20 years to remediate a highly contaminated soil site by bioremediation or phytoremediation alone, it will only take the multi-component system 3 to 6 years to achieve the equivalent level of remediation.

One important reason for inoculation of plants with plant growth promoting bacteria is that growth of plants in contaminated soil is much improved with inoculation of PGPR. This allows rapidly and greater accumulation of biomass, particular for roots in the soil [Table 2 and 3]. These bacteria are known to increase

Table 2 Germination efficiency of Alfalfa grown on creosote contaminated soil

Creosote, g/kg	Untreated soil	Land Farmed soil	Land Farmed soil with PGPR
0	100.0	100.0	100.0
0.5	2.9	93.4	103.7
1.0	0	75.3	86.0
2.0	0	17.9	72.0
3.0	0	3.9	12.8

Untreated soil, plant growth in contaminated soil without landfarming and PGPR Landfarmed soil, plant grwoth in the contaminated soil that was landfarmed twice a week for a month. Landfarmed soil with PGPR, plant growth with PGPR in the soil that was land farmed for a month.

Table 3 Germination efficiency of grass species grown on creosote contaminated soil

Creosote	Wild Rye		Kentucky Blue Grass		Tall Fescue	
g/kg	without	with PGPR	without	With PGPR	without	with PGPR
0	100.0	100.0	100.0	100.0	100.0	100.0
0.5	39.5	102.3	104.6	99.2	101.6	98.8
1.0	7.6	35.0	99.2	107.7	102.1	103.7
2.0	9.1	24.6	30.5	61.2	39.4	86.9
3.0	2.1	1.5	15.5	39.2	17.0	67.4

Canadian Association of Petroleum Producers (CAPP), and the Saskatchewan Agriculture & Food strategic research program in Soil Biology & Conservation.

Comments and suggestions from the PTAC Phytoremediation Technical Steering Committee (and especially Sandra Blenkinsopp, Stuart Lunn, and Terry McIntyre) are gratefully acknowledged. The authors also would like to acknowledge the *W.P. Fraser Herbarium* for access to its extensive library collection. Compilation of the database was made easier by the assistance of Jay Booth and Melissa Forster who helped in resource recovery and data entry. The *PhytoPet*© database was programmed by Scott Gelowitz of SG Systems Development, Regina, SK.

7.0 References

Acton, D.F., G.A. Padbury, and C.T. Stushnoff, *The Ecoregions of Saskatchewan*, Canadian Plains Research Center: Regina, SK, 205 p., 1998.

Anderson, T.A., E.A. Guthrie, and B.T. Walton, "Bioremediation in the Rhizosphere", *Environmental Science and Technology 27 (13)*: 2630-2636, 1993.

Bailey, V.L. and W.B. McGill, "Assessment of the Role of Plants in the Bioremediation of Two Hydrocarbon-Contaminated Soils", *Proceedings of the First Phytoremediation Technical Seminar*, Environment Canada, Ottawa, ON, pp. 87-97, 1999.

Biederbeck, V.O., R.M. St. Jacques, D. Curtin, H.J. Geissler, F. Selles, and J. Waddington, *Use of Heavy Oil Waste Sludge for Protection and Improvement of Sandy Soil*, Report prepared for the Oil, Gas, and Energy Division, Industrial Programs Branch, Environmental Protection,Environment Canada, Ottawa, ON, Publ. No. 379M0091, 191 p, 1993.

Cunningham, S.D., W.R. Berti, and J.W. Huang, "Phytoremediation of Contaminated Soils", *TIBTECH 13*: 393-397, 1995.

Cunningham, S.D., T.A. Anderson, A.P. Schwab, and F.C. Hsu, "Phytoremediation of Soils Contaminated with Organic Pollutants", *Advances in Agronomy 56:* 55-114, 1996.

Erickson, L.E., L.C.Davis, and N. Muralidharan, "Bioenergetics and Bioremediation of Contaminated Soil, *Thermochimica Acta* 250: 353-358, 1995.

Frick, C.M., J.J. Germida, and R.E. Farrell, "Assessment of Phytoremediation as an In-Situ Technique for Cleaning Oil-Contaminated Sites", *Proceedings of the First Phytoremediation Technical Seminar*, Environment Canada, Ottawa, ON, pp. 105-124, 1999a.

Frick, C.M., J.J. Germida, and R.E. Farrell, *Assessment of Phytoremediation as an In-situ Technique for Cleaning Oil-contaminated Sites*, Report prepared for the Petroleum Technology Alliance Canada (PTAC), University of Saskatchewan, Saskatoon, SK, 82 p., 1999b. Available on-line (in pdf format – 375K) at:
http://www.ag.usask.ca/departments/scsr/department/research/index.html.

Godwin, R., J. Thorpe, and R.E. Farrell, *Phase II Assessment of Phytoremediation as an In-situ Technique for Cleaning Oil-contaminated Sites: Botanical Survey Results*, Report prepared for the Petroleum Technology Alliance Canada (PTAC), University of Saskatchewan and Saskatchewan Research Council, Saskatoon, SK, 35 p., 2000.

Interstate Technology and Regulatory Cooperation (ITRC) Work Group – Phytoremediation Work Team, *Phytoremediation Decision Tree*, 1999. Available on-line (in pdf format – 139K) at: http://clu-in.org/techpubs.htm.

Jackson, L.A, "Phytoremediation: An Industry Partner's Perspective", *Proceedings of the First Phytoremediation Technical Seminar*, Environment Canada, Ottawa, ON, pp. 1-14, 1999.

Office of Technology Assessment (OTA), *Harmful Non-indigenous Species in the United States*, U.S. Government Printing Office, Washington, DC, 1993.

Schnoor, J.L., L.A. Licht, S.C. McCutcheon, N.L. Wolfe, and L.H. Carreira, "Phytoremediation of organic and nutrient contaminants", *Environmental Science and Technology 29 (7)*: 318-323, 1995.

Shimp, J.F., Tracy, J.C., Davis, L.C., Lee, E., Huang, W., Erikson, L.E. and Schnoor, J.L. 1993. Beneficial effects of plants in the remediation of soil and groundwater contaminated with organic materials. *Critical Reviews in Environmental Science and Technology. 23 (1)*: 41-77.

Siciliano, S.D. and J.J. Germida, "Mechanisms of Phytoremediation: Biochemical and Ecological Interactions Between Plants and Bacteria", *Environmental Review 6*: 65-79, 1998.

United States Environmental Protection Agency (USEPA), *A Citizen's Guide to Bioremediation - Technology Fact Sheet*, Office of Solid Waste and Emergency Response, (5102G) EPA 542-F-98-011, 6 p., 1998.

Trzesicka-Mlynarz D. 1993. *Biodegradation PAHs by A mixed culture of bacteria isolated from contaminated soil.* Thesis of University of Waterloo, Waterloo, ON Canada.

Walton, B.T.; Guthrie, E.A.; Hoylman, A.M. 1994. In *Biorem. through rihzospere Technol.* Anderson & Coats Eds, ACS Series 563. Washington DC. Chapter 2.

Walton, B.T. and T.A. Anderson. 1992. Plant-microbe treatment systems for toxic waste. *Curr. Opinion Biotechnol.* 3:267-270

The Use of Forage Grasses and Bacterial Inoculants as Phytoremediation Agents in Soils Contaminated with Heavy Metals and Aliphatic Hydrocarbons

[1]Patrick H. Duxbury, [2]Steven D. Siciliano, [1]Shiv O. Prasher, [2]Charles W. Greer
[1]Department of Agricultural and Biosystems Engineering,
McGill University, Macdonald Campus
Ste-Anne-de-Bellevue, Quebec, Canada
[2]National Research Council - Biotechnology Research Institute
Montreal, Quebec, Canada
pduxbu@Po-box.mcgill.ca

Abstract

Contaminated sites often contain a complex mixture of contaminants that require remediation. Yet, little is known about phytoremediation systems capable of remediating mixtures of heavy metals and organic contaminants. Plant and microbial biota that were suitable for the treatment of soils contaminated with heavy metals in combination with hydrocarbons were identified. Twenty-seven forage plant species, grown in heavy metal contaminated hydroponic solution, were screened for metal tolerance. Six forage grass species were selected from these screenings because they were exceptionally tolerant of heavy metals. Seven strains of root-associated bacteria, with hydrocarbon degrading capacities were isolated. One isolate, M2 Rhizo4, promoted the growth of tall oatgrass (*Arrhenatherum elatius* L.) in soil contaminated with creosote and chromated-copper-arsenate (CCA). Tall oatgrass was grown in 8 levels of soil contamination with or without M2Rhizo4 inoculation. Inoculated plants had significantly greater biomass at several levels on contamination than non-inoculated plants. The results from this study indicate that combinations of forage grasses and bacterial inoculants are able to promote the growth of metal-tolerant plants in contaminated soil. A phytoremediation system comprising metal-tolerant plants inoculated with hydrocarbon-degrading bacteria may therefore be suitable for sites contaminated with a mixture of petroleum hydrocarbons and heavy metals.

1.0 Introduction

Many sites requiring remediation contain a complex mixture of toxicants. Combinations of contaminants are common, with 37 % of the U.S. sites contaminated with organic compounds, as well as inorganic pollutants such as heavy metals (Springael *et al.*, 1993). Contaminant mixtures are difficult to remediate because remediation techniques are not always compatible between organic and inorganic compounds (Reddy *et al.*, 1999). Cost-effective and ecologically friendly methods of remediating soils having mixtures of contaminants need to be investigated. Phytoremediation is a technology that is being applied in the treatment of heavy metal and organic compound contaminated soils (Flathman and Lanza, 1998). However, little research has been conducted on the potential of phytoremediation systems to remediate soils contaminated with a mixture of organic and heavy metals contaminants.

For this study, combinations of heavy metals, polycyclic aromatic hydrocarbons (PAHs) and aliphatic hydrocarbons were examined. These contaminants are found at industrial sites, particularly at wood-treatment facilities,

which employ creosote and chromated-copper-arsenate (CCA) to protect their products against deterioration (Mueller *et al.*, 1989).

1.1 Selection of Suitable Plant Species

The phytoremediation of contaminant mixtures requires the establishment of plant species with the capacity to tolerate and/or accumulate heavy metals while promoting enhanced biodegradation in the rhizosphere. Perennial grass species have been suggested as good phytoremediation candidates (April and Sims, 1990; Reilley *et al.*, 1996). These species possess a perennial growth pattern, thus reducing disturbance of contaminated soil. Such plants also have fibrous root morphology that allows greater interaction between root and soil particle surfaces. They tend to tolerate stress well, have a wide distribution in North America, and are easy to cultivate (Fletcher and Hedge, 1995).

A number of metal-tolerant grasses have been identified and established in projects related to environmental restoration. Metal-tolerant perennial grass species, such as common bentgrass (*Agrostis capillaris)* and red fescue (*Festuca rubra*) have been used in the revegetation of mine tailings (Patra *et al.*, 1994). Metal-tolerant forage grasses result in increased microbial activity by the release of soluble carbon and energy sources from their roots. This effect has been reported by Boon *et al.* (1998), who noted that planting a copper-tolerant grass species, *Agrostis capillaris,* in a copper-contaminated soil resulted in faster bacterial growth than in non-vegetated control plots. Plants can also reduce metal solubility and toxicity in contaminated soils (Romkens *et al.*, 1999).

1.2 Role of Contaminant-Degrading Bacterial Inoculants in Contaminant Mixtures

Bacteria are involved in the degradation of hydrocarbons in soil (Wilson and Jones, 1993). Bacterial inoculants of plants have been used to stimulate contaminant degradation during phytoremediation (Siciliano and Germida, 1998). Aside from the role that bacteria play as contaminant degraders in the rhizosphere, microbial communities also protect plants from chemical injury (Krueger *et al.*, 1991; Pfender, 1996) which can lead to improved phytoremediation activity.

1.3 Objective of study

The purpose of this study was to evaluate the potential of forage grass and contaminant-degrading bacterial inoculants in remediating soils contaminated with heavy metals, PAHs, and aliphatic hydrocarbons.

2.0 Materials and Methods

2.1 Screening of Metal-Tolerant Plant Species

Hydroponic studies were conducted to evaluate heavy metal tolerance in selected forage species. A hydroponic system was constructed to test for heavy metal tolerance in 27 species (25 grasses, 2 legumes) of forage crops (see Table 2). The system consisted of 6, 16 L polypropylene tubs aerated with sparging tubes attached to the bottom of the tubs and connected to an air compressor. The plants were grown in 2.4-cm-diameter wells cut out of 1cm thick styrofoam sheets which were floated on the tubs. The plant seeds were pre-germinated and 6-8 seedlings were placed in each well. Each plant species was replicated twice per tub. The nutrient solution

consisted of the following compounds: 6.0 mM KNO_3; 4.0 mM $Ca(NO_3)_2$; 0.1 mM $NH_4H_2PO_4$; 1.0 mM $MgSO_4$; 25 μM $CaCl_2$; 12.5 μM H_2BO_3; 1.0 μM $MnSO_4$; 1.0 μM $ZnSO_4$; 0.5 μM $CuSO_4$; 0.1 μM H_2MoO_4; and 0.1 μM $NiSO_4$. The nutrient solution was buffered to pH 6.5 with 3-(N-Morpholino) propanesulfonic acid (MOPS) buffer. The plants were grown in the system for 10 days and the nutrient solution was changed after 5 days. The plants were grown at temperatures between 21-25°C. The photoperiod was 16 hrs/day. The system was established in the greenhouse facilities of Macdonald Campus of McGill University, Sainte-Anne-de-Bellevue, Québec.

This experiment was designed to evaluate the response of plants to a mixture of copper, cadmium, and zinc. Copper is a component of the wood preservative chromated-copper-arsenate (CCA), and it was tested instead of chromium because it is more toxic to plants (Wong and Bradshaw, 1982). Arsenic is less phytotoxic to plants than either chromium or copper and thus it was not examined.

The hydroponic screening occurred in three tubs contaminated with metals and three non-contaminated control tubs. The initial level of contamination was set at 100 μM Zn, 5 μM Cu, and 1 μM Cd. A root elongation tolerance index (TI) was used to compare plant heavy metal resistance (Patra *et al.*, 1994). The formula for the tolerance index is the following:

$$TI(\%) = \frac{R \text{ in solution with metal}}{R \text{ in solution without metal}} \times 100$$

R is the length of the longest root. The hydroponic screening test was repeated twice. The nine most metal tolerant plants, of the 27 species that were screened, were tested further to determine their capacity to tolerate increasing levels of heavy metal contamination. The following levels of heavy metal contamination were assessed:

Level 1 - Control
Level 2 - 200 μM Zn, 10 μM Cu, and 2 μM Cd
Level 3- 400 μM Zn, 20 μM Cu, and 4 μM Cd
Level 4- 600 μM Zn, 30 μM Cu, and 6 μM Cd
Level 5 - 800 μM Zn, 40 μM Cu, and 8 μM Cd

A hydroponic tub was assigned for each level of contamination. Each selected plant was placed randomly in 6 wells on the styrofoam float with 6-8 pre-germinated seeds in each well. After a 10-day growing period, the plant samples were oven-dried for 36 hr at 40°C and measured for root and shoot biomass.

2.2 Selection of Bacterial Inoculates - Isolation and Identification of Alkane-Degrading Organisms

Bacterial stains were isolated from rhizosphere soil obtained from a petroleum hydrocarbon phytoremediation study. Viable soil bacteria were spread-plated in triplicate onto medium containing yeast extract, tryptone and starch (250 mg/L each) solidified with 15 g/L Bacto Agar. The plates were incubated at room temperature for one week at which time the bacterial colonies were counted.

The soil bacterial colonies were lifted onto nylon membranes, cells were lysed and the bacterial DNA was denatured and fixed to the membranes. The membranes were hybridized and probed with a labeled *alkB* gene probe. The membranes were sealed in plastic blotting bags and photographed at –80°C to detect positive colonies (Greer *et al.*, 1993). The *gene* probe is an 870 nucleotide (nt) fragment from the coding sequence of the *alkB* gene derived from the biodegradation pathway for aliphatic hydrocarbons with 6 to 12 carbons from *Pseudomonas oleovorans* ATCC 29347 (Kok *et al.*, 1989). The gene probe was prepared by the polymerase chain reaction (PCR) using primers specific for the *alkB* gene fragment. Two PCR primers were added to a 50 µl reaction mix containing template DNA, deoxyribonucleotide triphosphates (dNTPs), reaction buffer (1.5 mM $MgCl_2$ at pH 8.3) and Taq DNA polymerase. The PCR was performed using a Perkin Elmer Cetus DNA Thermal Cycler. PCR reaction conditions were 1 min at 94°C (melting) and 2 min at 72°C (annealing and elongation) for 30 cycles. After completion the probes were labelled with [^{32}P] dATP.

2.3 PCR Analysis of M2Rhizo4 for the *alkB* Gene.

Genomic DNA was extracted from a liquid culture of the rhizosphere bacterial strain, M2Rhizo4, grown in 1/10 tryptone soy broth (TSB), to accurately confirm or reject the isolate's hydrocarbon catabolizing properties. A PCR was conducted to generate the single-stranded catabolic gene probe fragments associated with *alkB*. The 30-cycle PCR was performed with a Perkin Elmer Cetus DNA Thermal Cycler. The reaction conditions were 1 minute at 96°C (melting) and 2 minutes at 72°C (annealing and elongation). The resulting probe fragments were visualized by electrophoresis in a 1.2-% agarose gel. DNA from an *alkB*-positive organism was included in the gel as a comparison to M2Rhizo4.

2.4 Selection of Plant-bacterial Combinations - Growth Survival Test

Plant-bacterial combinations were assessed for their capacity to promote plant growth in soil mixtures contaminated with creosote and CCA. The soil in which these plant-bacterial combinations were established was composed of 50% creosote contaminated soil, 20% CCA contaminated soil, and 30% sand. The contaminant composition of these soils is listed in Table 1.

Table 1. Contaminant Composition of Experimental Soils

Soil	Contaminant	Concentration (mg/kg)
Creosote	- Low molecular weight (<3 rings) polycyclic aromatic hydrocarbons	2482
	- High molecular weight (≥3 rings) polycyclic aromatic hydrocarbons	2859
	- Hydrocarbons $C_{10} - C_{50}$	21500
CCA	- Copper	180
	- Chromium	550
	- Arsenic	550

The plant-bacterial combinations were visually observed for germination and growth in the contaminated soil over a period of 10 days. Following the first plant survival assay, a second assay identified which plant-bacterial combinations best tolerated the contaminated soil. The plants were grown longer, for 30 days, to better determine the effect of the rhizobacterial inoculants on growth promotion.

2.5 Growth of Plants in Creosote and CCA Contaminated Soil

Tall oatgrass and the bacterial isolate M2Rhizo4 were established in a number of contaminated soil mixtures to assess the potential for growth. Seeds of tall oatgrass, with and without M2Rhizo4 inoculation, were sown into seeding trays containing 8 soil mixtures with varying proportions of creosote contaminated soil: CCA contaminated soil: and garden soil. For each soil mixture, tall oatgrass, with and without M2Rhizo4 inoculation, was replicated 3 times in individual seeding tray pockets (approximately 70 g soil/pocket). The soil mixtures contained the following concentrations of contaminants:

Mixture 1 - 10736 mg/kg hydrocarbons
Mixture 2 - 10736 mg/kg hydrocarbons; 36 mg/kg Cu; 110 mg/kg Cr; 110 mg/kg As
Mixture 3 - 10736 mg/kg hydrocarbons; 72 mg/kg Cu; 220 mg/kg Cr; 220 mg/kg As
Mixture 4 - 10736 mg/kg hydrocarbons; 108 mg/kg Cu; 330 mg/kg Cr; 330 mg/kg As
Mixture 5 - 72 mg/kg Cu; 220 mg/kg Cr; 220 mg/kg As
Mixture 6 - 5368 mg/kg hydrocarbons; 72 mg/kg Cu; 220 mg/kg Cr; 220 mg/kg As
Mixture 7 - 16104 mg/kg hydrocarbons; 72 mg/kg Cu; 220 mg/kg Cr; 220 mg/kg As
Mixture 8 – control (non-contaminated)

The plants were grown with a photoperiod of 16 hrs/day, at a temperature between 21-25°C for 10 weeks in a greenhouse at the Macdonald Campus of McGill University. . After this growth period, the plants were harvested, cleaned and oven-dried at 40°C for 36 hours, after which their biomass measurements were taken.

3.0 Results and Discussion

3.1 Screening of Metal-Tolerant Plant Species

Nine of the 27 examined species were selected as the most metal tolerant species examined in the initial screening study (see Table 2). Three of these nine species, (small fescue, sweet vernal grass and strawberry clover) were rejected. Small fescue and sweet vernal grass were low biomass producers, and therefore not suitable for phytoremediation applications. Strawberry clover, though apparently metal-tolerant, did not grow well in the hydroponic system. The germination of strawberry clover was extremely inconsistent, thus resulting in fewer viable plants relative to the other forage species tested. The accepted species were meadow bromegrass, crested wheatgrass, tall oatgrass, hard fescue, red fescue (vars. Reptans and Molate native). These six species were tested in the contaminant range experiment. The 3 largest biomass producers at all levels of contamination were meadow brome, tall oatgrass and crested wheatgrass. The biomass results for these three species are given in Figures 1-3. For all the plants tested, biomass decreased as the heavy metal concentration increased. The effect of heavy metal contamination on shoot biomass is most dramatically observed in the case of crested wheatgrass (Figure

2) between treatments 1 and 5. Crested wheatgrass was the least heavy metal-tolerant species, as indicated by shoot biomass. Meadow bromegrass (Figure 1) and tall oatgrass (Figure 3) were both similar in their response to the various levels of heavy metal contamination.

Table 2. List of Forage Species Screened for Metal Tolerance

Species Name	Tolerence Index (%)	Metal Tolerant Species
1. Streambank wheatgrass - *Elymus lanceolatus*	83	
2. Tall fescue var. Apache – *Festuca arundinacea*	78	
3. Dahurian wildrye – *Elymus dahuricus*	76	
4. Altai wildrye – *Leymus angustus*	79	
5. Meadow bromegrass – *Bromus bierbersteinii*	88	*
6. Tall fescue var. Rebel 3-D – *Festuca arundinacea*	84	
7. Russian wildrye – *Elymus farctus*	81	
8. Slender wheatgrass – *Agropyrum trachyculus*	79	
9. Tall wheatgrass – *Agropyrum elongatum*	80	
10. Crested wheatgrass – *Agropyrum cristatum*	87	*
11. Sweet vernal grass – *Anthoxanthum odoratum*	88	B
12. Tall oatgrass – *Arrhenatherum elatius*	90	*
13. Meadow fescue – *Festuca pratensis*	86	
14. Hard fescue – *Festuca trachyphylla*	89	*
15. Redtop – *Agrostis gigantea*	76	
16. Colonial bentgrass – *Agrostis tenuis*	84	
17. Red fescue var. Reptans – *Festuca rubra*	91	*
18. Creeping wildrye – *Leymus triticoides*	A	
19. Rose Clover – *Trifolium Hirtum*	A	
20. Blando brome – *Bromus hordeaceus*	83	
21. California brome – *Bromus carinatus*	84	
22. Small fescue – *Vulpia microstchys*	87	B
23. Purple needlegrass – *Nassella pulchra*	85	
24. California barley – *Hordeum californicum*	71	
25. Strawberry clover – *Trifolium fragiferum*	93	C
26. Blue wildrye – *Elymus glaucus*	84	
27. Red fescue var. Molate native – *Festuca rubra*	90	*

* - Indicates tolerant species

A – Creeping wildrye and rose clover did not germinate properly

B – Sweet vernal grass and small fescue are low biomass producers, thus not suitable for phytoremediation

C – Due to germination problems, strawberry clover was rejected

3.2 Selection of Bacterial Inoculates - Isolation and Identification of Alkane-Degrading Organisms

Seventeen isolates tested positive for the *alkB* gene. Preliminary tests indicated that 7 of these isolates mineralized a C^{14} tracer compound mixture of 50% phenanthrene and 50% hexadecane in the presence of chromated-copper-aresenate (data not shown). Isolates capable of hydrocarbon mineralization in soil were M2Rhizo8, M2Rhizo6, TFEndo10, M2Rhizo5, TF2Endo9, M2Rhizo4 and P5-4.

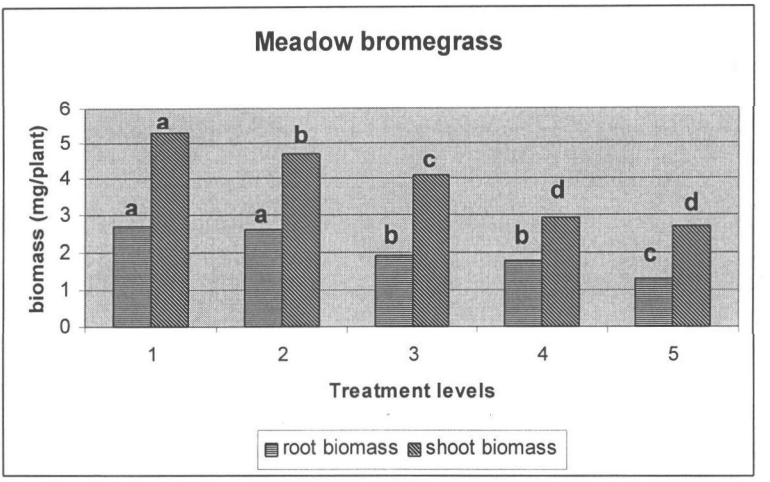


Figure 1. Root and Shoot Biomass of Meadow Bromegrass at 5 levels of Heavy Metal Contamination

Analysis of variance procedure was conducted with Duncan's multiple range test at a confidence interval of α =0.01. The letter associated with the value indicates a significant difference between treatment levels. Different letters indicate a significant difference between treatment levels; same letter indicates no significant difference. Root biomass is compared to root biomass at other treatment levels, not shoot biomass

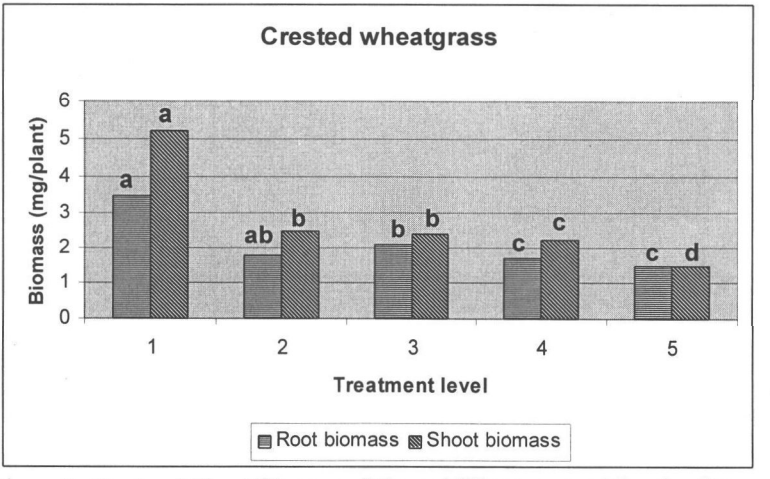


Figure 2. Root and Shoot Biomass of Crested Wheatgrass at 5 levels of Heavy Metal Contamination

Analysis of variance procedure was conducted with Duncan's multiple range test at a confidence interval of α =0.01. The letter associated with the value indicates a significant difference between treatment levels. Different letters indicate a significant difference, same letter indicates no significant difference. Root biomass is compared to root biomass at other treatment levels, not shoot biomass.

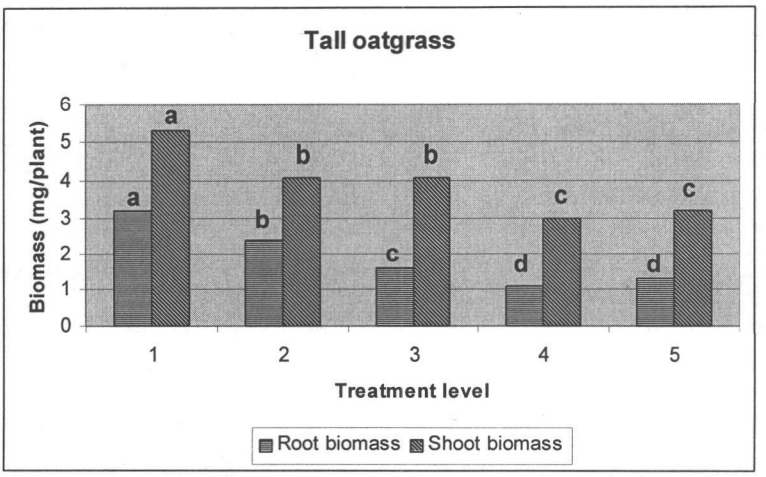


Figure 3. Root and Shoot Biomass of Crested Wheatgrass at 5 levels of Heavy Metal Contamination

Analysis of variance procedure was conducted with Duncan's multiple range test at a confidence interval of $\alpha = 0.01$. The letter associated with the value indicates a significant difference between treatment levels. Different letters indicate a significant difference, same letter indicates no significant difference. Root biomass is compared to root biomass at other treatment levels, not shoot biomass

3.3 Analysis of M2Rhizo4's Ability to Biodegrade Hydrocarbons

PCR amplification of the *alkB* gene from total genomic DNA of M2Rhizo4 was positive, as indicated by the presence of an *alkB*-size fragment following agarose gel electrophoresis. Therefore, this bacterium has the potential to degrade aliphatic hydrocarbons.

3.4 Selection of Plant-bacterial Combinations – Results of the Growth Survival Tests

The growth responses of the plant-bacterial combinations (Table 4.) are indicated by a "yes", "no" or "slight" growth response. Following this first plant survival assay, the second simplified assay was conducted with crested wheatgrass and tall oatgrass; which were the two species that most successfully germinated and grew in the contaminated soil. At the end of the 30-day period it was observed that tall oatgrass inoculated with M2Rhizo4 had the most visually significant growth promotion (Table 5), having much more substantial shoot growth compared to all other combinations. Crested wheatgrass was rejected, as its growth was very poor in comparison to tall oatgrass. The combination of M2Rhizo4 and tall oatgrass was selected for implementation into creosote and CCA contaminated soil mixtures.

Table 4. Growth promotion of selected forage grasses by bacterial inoculants capable of hydrocarbon mineralization

	Meadow bromegrass	Crested wheatgrass	Tall oatgrass	Hard fescue	Red fescue Var. Reptans	Strawberry clover	Red fescue var. Molate native
M2Rhizo8	No	No	Yes	No	No	No	No
M2Rhizo6	Yes	Slight	No	No	No	No	No
TF2Endo8	Yes	Yes	Yes	No	No	Slight	No
M2Rhizo5	No	No	Yes	No	No	No	No
TF2Endo9	No	Yes	Yes	No	No	No	No
M2Rhizo4	No	Yes	Yes	No	No	No	No
P5-4	Slight	No	Yes	No	No	No	No

Table 5. Growth Promotion of Crested Wheatgrass and Tall Oatgrass by bacterial inoculants capable of hydrocarbon mineralization

	Crested wheatgrass	Tall Oatgrass
M2Rhizo8	No	Slight
M2Rhizo6	No	No
TF2Endo8	No	Slight
M2Rhizo5	No	Slight
TF2Endo9	Slight	Slight
M2Rhizo4	Slight	Yes
P5-4	No	No
Control	No	No

3.5 Growth of Plants in Soil Contaminated with Creosote and CCA – Biomass Results

The tall oatgrass biomass values are displayed as mg biomass/plant in Table 6. In a number of soil mixtures (refer to Section 2.5 for soil concentrations of contaminants), significant differences between inoculated and non-inoculated treatments were observed. At Mixtures 1–3, where creosote contaminated soil was 20% of the soil mixture; M2Rhizo4-inoculated plant treatments had more biomass, in both root and shoot, than non-inoculated plants. This effect may be explained by the fact that contaminant-degrading bacterial inoculants can protect plants and promote their growth (Pfender, 1996). Bacteria-mitigated detoxification of organic contaminants in the root zone is a possible explanation for the difference in plant growth between inoculated and non-inoculated plants. This effect has been experimentally observed by Siciliano and Germida (1998) who found that bacterial inoculation of Daurian wild rye (*Elymus dahuricus)* promoted plant growth in soil contaminated with a mixture of chlorobenzoic acids.

Oddly, the plant-growth promotion of inoculated tall oatgrass in Mixtures 1-3 was not observed in Mixture 4, where creosote contaminated soil was also 20%. The factor of difference in Mixture 4 may have been that the soil of Mixture 4 was composed of 30% CCA-contaminated soil. This level of heavy metal contamination may have had an inhibitory effect on the capacity of M2Rhizo4 to promote plant growth. CCA has been observed to inhibit the organic contaminant biodegradation capacity of bacteria and is known to be toxic to bacterial growth (Wall and Stratton, 1994; Edgehill, 1996). There was no difference in root or shoot biomass between

inoculated and non-inoculated treatments in Mixture 5, where only CCA was present as a toxicant. A difference in shoot biomass was observed in Mixture 6, where creosote contaminated soil was present at 10% in the soil mixture. A very obvious difference in biomass was observed in Mixture 7, where the 30% proportion of creosote-contaminated soil in the soil mixture had a lethal effect on non-inoculated plants. This growth response at Mixture 7 suggests that the presence of a hydrocarbon-degrading bacterial inoculant can have a major role in phytotoxicity prevention at high concentrations of hydrocarbons in the rhizosphere. In Mixture 8, there were no differences in biomass between plant treatments in the non-contaminated control soil.

Table 6. Biomass Results from Creosote and CCA Soil Plant Growth Study

Levels	Roots (mg / plant)		Shoots (mg / plant)	
	Inoculated	Non- inoculated	Inoculated	Non-inoculated
Mixture 1	16.3a	11.2b	13.9a	7.9b
Mixture 2	12.4a	9.8b	10.6a	7.8b
Mixture 3	15.3a	8.7b	6.9a	9.9b
Mixture 4	7.5a	6.3a	6.8a	13.1a
Mixture 5	20.3a	20.4a	23.9a	23.9a
Mixture 6	12.4a	11.9a	16.9a	13.6b
Mixture 7	6.4	killed	5.7a	killed
Mixture 8	29.19a	25.95a	28.84a	25.95a

Significant differences between inoculated and non-inoculated treatments were determined with a two-tail t-test assuming unequal variance. A significant difference between inoculated and non-inoculated treatments is indicated by the letter combination a – b. No significant difference is indicated by the combination a – a.

4.0 Conclusions

The results from this study indicate that rhizosphere bacteria, capable of degrading hydrocarbons, are also able to promote the growth of metal-tolerant plants in creosote and CCA contaminated soil at varying contaminant concentrations. This effect was achieved by systematically selecting specific plant-inoculant combinations that had the strongest plant growth responses in contaminated soil. Significant differences in plant biomass were observed between inoculated and non-inoculated plants. These results suggest that plant inoculation may provide more advantage in the phytoremediation of heavy metal and hydrocarbon contaminated soil than a system where no inoculation occurs, particularly during the period of plant establishment and early growth. However, this effect must be examined in longer-term field studies to prove conclusively. The difference in the roles of plant growth promotion between indigenous soil bacteria and introduced inoculates may be minimized in actual field conditions over several growing seasons. A phytoremediation system comprising of metal-tolerant plants inoculated with plant-growth promoting hydrocarbon-degrading bacteria may be suitable for sites contaminated with a mixture of petroleum hydrocarbons and heavy metals provided that the level of either contaminant does not drastically affect the function of either the plant or the inoculated bacteria.

5.0 Acknowledgements

Special thanks are extended to the staff of the Biotechnology Research Institute's Environmental Microbiology Group for their assistance in this project. Special thanks are also extended to Marc-David Andrade for his work in constructing the hydroponic screening system and to Richard Smith, greenhouse technician at Macdonald College for his help.

6.0 References

April, W., and Sims, R.C., Evaluation of the Use of Prairie Grasses for Stimulating Polycyclic Aromatic Hydrocarbon Treatment in Soil", *Chemosphere,* Vol. 20, pp. 253-265, 1990.

Boon, G.T., L.A. Bouwman, J.Bloem and P.F.A.M. Romkens, "Effects of a Copper-tolerant Grass (*Agrostis capillaris*) on the Ecosystem of a Copper-contaminated Arable Soil", *Environmental Toxicology and Chemistry,* Vol. 17, pp. 1964-1971, 1998.

Edgehill, R.U., "Effects of Copper-chrome-aresenate (CCA) Components on PCP Degradation by *Arthrobacter* Strain ATCC 33790", *Bulletin in Environmental Contamination and Toxicology,* Vol. 57, pp. 258-263, 1996.

Flatman, P.E., and G.R. Lanza, "Phytoremediation: Current Views on an Emerging Green Technology", *Journal of Soil Contamination,* Vol. 7, pp. 415-432, 1998.

Fletcher, J.S. and R.S. Hedge, "Release of Phenols by Perennial Plant Roots and their Potential Importance in Bioremedation", *Chemosphere,* Vol. 31, pp. 3009-3016, 1995.

Greer, C., L. Masson, Y.Comeau, R. Brousseau, and R. Samson, "Application of Molecular Biology Techniques for Isolating and Monitoring Pollutant-degrading Bacteria", *Water Pollution and Resource Journal of Canada,* Vol. 28, pp. 275-287, 1993.

Kok M, R., Oldenhuis, M.P.G. van der Linden, P. Raatjes, J. Kingma, P.H. van Lelyveld and B. Witholt, "The *Pseudomonas oleovorans* Alkane Hydroxylase Gene: Sequence and Expression", *Journal of Biological Chemistry,* Vol. 264, pp. 5435-5441, 1989.

Krueger, J.P., R.G. Butz and D.J. Cork, "Use of Dicamba Degrading Microorganisms to Protect Dicamba Susceptible Plant Species", *Journal of Agriculture and Food Chemistry*, Vol. 39, pp. 1000-1003, 1991.

Mueller, J.G., P.J. Chapman and P.H. Pritchard, "Creosote-contaminated Site: Their Potential for Bioremediation. *Environmental Science and Technology,* Vol 23, pp. 1197-1201, 1989

Patra J., M. Lenka and B.B. Panda, "Tolerance and Co-tolerance of the Grass *Chloris barbata Sw.* to Mercury, Cadmium and Zinc", *New Phytologist,* Vol. 128, pp. 165-171, 1994.

Pfender, W.F., "Bioremediation Bacteria to Protect Plants in Pentachlorophenol-contaminated Soil", *Journal of Environmental Quality,* Vol. 25, pp. 1256-1260, 1996.

Reddy, K.R., J.A. Adams, and C. Richardson, "Potential Technologies for Remediation of Brownfields", *Practice Periodical of Hazardous, Toxic, and Radioactive Waste Management,* pp. 61-68, 1999.

Reilley, K.A., M.K. Banks and A.P. Schwab, "Dissipation of Polycyclic Aromatic Hydrocarbons in the Rhizosphere", *Journal of Environmental Quality,* Vol. 25, pp. 212-210, 1996.

Romkens, P.F.A.M., L.A. Bouwman and G.T. Boon, "Effect of Plant Growth on Copper Solubility and Speciation in Soil Solution Samples", *Environmental Pollution,* Vol. 106, pp. 315-321, 1999.

Siciliano, S.D., and J.J Germida, "Degradation of Chlorinated Benzoic Acid Mixtures by Plant-bacteria Associations", *Environmental Toxicology and Chemistry,* Vol 16, pp.728-733, 1998.

Springael, D., L. Diels, L. Hooyberghs, S. Kreps and M. Mergeay, "Construction and Characterization of Heavy Metal-resistant Haloaromatic-*degrading Alcaligenes eutrophus* Strains", *Applied and Environmental Microbiology,* Vol. 59, pp. 334-339, 1993.

Wall, A.J., and G.W. Stratton, "Effects of a Chromated-copper-arsenate Wood Preservative on the Bacterial Degradation of Pentachlorophenol", *Canadian Journal of Microbiology* Vol. 40, pp. 388-392, 1994.

Wilson, S.C., and K.C. Jones, Bioremediation of Soil Contaminated with Polynuclear Aromatic Hydrocarbons (PAHs): A Review", *Environmental Pollution,* Vol. 81, pp. 229-249, 1993.

Wong, M.H., and A.D. Bradshaw, "A Comparison of the Toxicity of Heavy Metals Using Root Elongation of Rye Grass, *Lolium perenne", New Phytologist* Vol. 91, pp. 255-261, 1992.

Preliminary Results of Field Trials Testing Plants for Phytoextraction Capability in a Multi-metal Contaminated Environment Near a Lead Zinc Smelter

A.G. Mattes, Nature Works Remediation Corporation*
W. F. A. Duncan, Cominco Limited
*Winfield, British Columbia, Canada
mattes@cablelan.net

Abstract

Screening of more than 100 members of the *Brassica* family and other species was completed at a University of Guelph greenhouse. Based on an extensive review of published reports plants were selected for future phytoremediation work on a site close to a smelter in Trail affected by particulate and plume deposition from stack emissions. The area chosen for research had been assayed and found to have high concentrations of many metals.

Twelve plants were selected for field trials. Six replicates of five treatments were used: control; addition of biosolid residuals in a 50% mix with existing soil; addition of 25% peat, 25% biosolid residuals and existing soil; and the same two treatments with the addition of *Penicillium bilaii*.

Soil was sampled, and re-sampled after amendment addition. Plants were harvested at 6 & 12 weeks or when dead and assayed for metal content using ICP-MS. At harvest, a soil sample was taken from below the plant and assayed. Final harvest took place in October and plants were dried and weighed to provide an estimate of biomass production.

Results show several plants that have potential for phytoremediation in this area and that metal concentration in the soil for the four major contaminants was reduced from 10 – 25% in a year.

1.0 Introduction

Soil and water contamination can be a concern in areas near mining and smelting. Production processes have changed to reduce and/or eliminate further negative environmental impacts and problems associated with long-term activity are being addressed. The effects of 50-100 years of deposition of fine metal particulate coupled with acidification due to plume effects have resulted in acidic soil that has high levels of heavy metals.

Researchers and scientists have turned their attention to a promising new technologies – rhizofiltration and phytoremediation (Salt et al, 1995, Dushenkov et al, 1995). It is gaining favour amongst industries, regulatory agencies and the general public as it is very low impact and utilizes processes that are easily understood. The process rapidly returns the environment to a normal appearance. Special cultivars able to withstand the toxic effects of metals can be used to stabilize or remove metals. Such plants are found growing in areas that are known to be high in metals or plants are developed (genetically or by hybridization) to maximize their ability to safely sequester metals.

This process is safe, relatively inexpensive compared to other methods and potentially very cost effective. The affected soil may require amendments to support plant growth and careful plant selection is also a prerequisite. Instead of removing soil and replacing with purchased topsoil suitable plants are grown on the site and subsequently harvested. The resultant metal containing biomass can be treated to remove metals (smelted) or disposed of in a much smaller area (say by ashing). However, no site has yet been decommissioned using this technology alone.

The ideal plants for purposes of phytoextraction are hyperaccumulators. For Zn, Pb, Ni, Cu or Mn a plant is described as a hyperaccumulator that can safely store more than 1% dry weight while for Cd the level is 0.01% (Baker et al, 1991). To be most cost effective the plants should store the metal in an easily harvestable part.

To date research has concentrated on removal of one, or at most two elemental metals of concern. However, sites near smelters pose particular problems. Generally, the soil has numerous heavy metal contaminants ranging from levels similar to normal background levels to levels that require remediation to meet Provincial regulations. Metals of primary concern at Trail are Pb, Zn, Cd and As.

2.0 Method

2.1 Greenhouse Research

In fall 1997, soil samples were taken from areas around Trail and shipped to the University of Guelph. Initially, 100 *Brassica* family members were screened using hydroponics systems to assess their abilities to grow in metal-contaminated water. Two areas were then investigated:

1) The potential of seeds of specific species said to be heavy metal resistant to germinate and establish successful seedlings on soil found in the Trail area.
2) The potential of germinated seedlings of the same species successfully being transplanted into soil that was either as found *in situ* or modified using a number of amendments.

2.2 Field Studies

From greenhouse research potential candidates were selected for field trials during the summer of 1998. Plants were grown in a local greenhouse and transplanted in late May. The majority were *Brassicaceae* but other species were investigated: a native grass; *Agrostis stolonifera*; two native trees: horse chestnut, (*Aesculus hippocastanum*) and silver maple, (*Acer saccharinum*); a non-native tree species – hybrid poplar (*Populus deltoides)*; lemon scented geraniums (*Pelargonium* reported by Saxena et al, 1998); and *Eruca sativa* or arugula.

The *Brassica* planted were: kale (*Brassica oleracea*), flowering kale (*Brassica oleracea*), flowering cabbage (*Brassica oleracea*), BCN 3483 (mizuna) (*Brassica rapa, japonica group*), turnip greens (shoigun) (*Brassica napa*), Cime di rapa broccoletti (*Brassica rapa*), wild wallflower (*Cheiranthus cheiri*), radish (Mino summer cross) (*Raphanus spp.*)

There were 5 treatments: Addition of 50% biosolid residuals; Addition of 25% peat & 25% biosolid residuals; Addition of 50% biosolid residuals & *Penicillium bilaii*; Addition of 25% peat, 25% biosolid residuals & *Penicillium bilaii*; and a Control (no amendments). Six replicates were prepared with treatments distributed randomly in each replicate. Each single plot was thoroughly tilled. *Penicillium bilaii*

was added per manufacturer's instructions to investigate its potential as a natural chelator. Nine plants of each species (except for trees) were sown into each plot (330 of each species). Sub-plots were randomly laid out in each of the 30 plots and the area fenced. Soil was assayed in each plot before and after amendments were added. A random sample (top 8 cm) was taken from three places in the plot and mixed together in a plastic labeled bag. A generous amount of calcium nitrate was added to each plot, including controls, after sampling was completed.

Weekly, plots were monitored and plant growth, colouration and physical changes noted. Watering was carried out regularly. A water-soluble fertilizer was twice added according to manufacturer's instructions. In June and August, a single plant was harvested from each sub-plot. Plants were separated into root and shoot, placed in labeled paper bags, dried at 80°C for 24 hours, digested (Campbell and Plank, 1998) and assayed. At final harvest, a soil sample was collected below the root area where the plant had grown and placed in labeled paper bags, air-dried, digested (Soong, 1998) in Nitric Acid and assayed. One complete plant of each species from each plot was harvested as above. Biomass was determined and used to calculate total plant uptake potentials.

3.0 Results

Soil amendments increased plant growth and biomass while control plots with no amendments had plants that barely survived with some growing slowly but most plants in control plots died over the course of the summer.

Table 1 Final biomass determinations (dry grams per individual) of each species in each treatment. Roots and shoots were assayed separately and metal concentrations combined except for maple and poplar where only leaves were harvested.

Species	Control		Soil, Biosolid 50:50		Soil, Biosolid plus *Penicillium b.*		Soil, Peat & Biosolid		Soil, Peat, Biosolid plus *Penicillium b.*	
	mean	S.E.	mean	S.E.	mean	S.E.	mean	S.E	mean	S.E.
Cabbage	1.48	0.46	26.38**ab**	3.75	31.82**a**	10.06	33.11**a**	7.54	26.5**ab**	6.22
Eruca sativa	0.76	——	12.35	6.29	9.71	4.16	10.06	3.28	15.28	4.75
Geranium (l)	——	——	222.88	38.58	204.6	52.22	177.49	36.16	166.32	43.13
Geranium (s)	3.15**b**	0.86	9.38**ab**	2.49	7.77**ab**	1.55	14.62**a**	4.21	8.40**ab**	2.21
Kale	1.64	0.53	17.58	6.12	17.92	3.07	18.27	4.33	20.41	5.67
Flowering Kale	1.49**b**	0.34	11.53**b**	1.10	19.81**ab**	3.07	38.20**a**	11.12	22.06**ab**	5.56
Maple, silver	0.17	0.05	2.03	0.13	0.37	0.29	1.15	0.73	——	——
Poplar, hybrid	0.05	——	3.48	0.88	2.65	0.64	2.34	0.42	2.63	0.64
Radish (Mino)	15.82	1.80	10.45	2.22	32.03	8.44	14.89	4.74	21.10	8.26
Rapa	——	——	3.77	1.97	5.39	1.63	4.73	1.73	3.33	2.52
Redtop	15.82	1.80	15.97	3.78	22.36	5.71	13.80	3.41	15.61	8.25
Shoigun	6.36	——	7.76	1.41	9.65	2.82	5.80	3.36	6.64	1.75
Wallflower	0.78	0.04	3.58	1.30	7.08	1.96	4.24	1.55	2.60	0.95

F ratio for the specified treatment is significant at the 95% confidence level if Prob>F is less than or equal to 0.05. a,b,c, means any given species and plant part sharing the same letter are not significantly different at the p=0.05 level as determined using the Tukey multiple comparison test.

Treatment with 25% biosolid residuals and 25% peat was best for growth of flowering cabbage, small geraniums and flowering kale (Table 1). The treatment with only biosolid residuals produced the highest biomass for wild wallflower. All other species showed no significant biomass differences among treatments.

Table 2 Elemental concentrations in all species under different amelioration treatments; root shoot combined.

Treatment	Number of Samples	As, µg/g mean	S.E.	Cd, µg/g mean	S.E.	Pb, µg/g mean	S.E.	Zn,µg/g mean	S.E.
Garden	12	6.51	1.42	9.26	1.48	97.93	22.12	663.26	100.81
Control	51	16.48	1.76	33.61	4.50	407.09	59.52	2511.26	233.31
Soil, Biosolids 50:50	184	9.39	0.90	24.83	1.14	179.61	21.72	1265.42	45.68
Soil, Biosolids plus *P.b.*	175	7.82	0.54	24.79	1.77	121.24	10.52	1190.35	72.67
Soil, Peat & Biosolids	181	11.86	1.19	26.49	1.23	217.78	25.24	1651.89	60.60
Soil, Peat, Biosolids, *P.b.*	166	8.80	0.98	25.27	1.21	166.87	20.65	1603.96	71.10
Anova Results									
Random Block Design									
Treatment Effects F		3.36		0.95		4.58		8.72	
Prob>F*		0.0293		0.4563		0.0087		0.0003	

Notes: divide concentration in µg/g by the element's atomic weight to give its molecular concentration in µmol/g
analysis of variance results remain identical except for combinations of several elements.
a,b,c, means for any given element sharing the same letter are not significantly different at the p=0.05 level as determined using the Tukey multiple comparison test.
*F ratio for the specified treatment effect is significant at the 95% confidence level of Prob>F is less than or equal to 0.05

The effect of each soil amendment treatment on the total metal accumulated across all species was calculated with individual assay results for As, Cd, Pb and Cd given (Table 2). Total accumulation in all species for these four metals was also calculated (Table 3).

There were some differences in mean plant uptake due to treatment effects:

- For As the 50:50 biosolid treatment had a significantly lower plant uptake than in control plants, as did the treatment that utilized peat diluted biosolid residuals and *Penicillium bilaii.*
- There were no differences for Cd in plant uptake between controls and any treatment
- The highest plant uptake of Pb was in the control and the total was significantly different than for plants grown in any of the treatments. However, there were no significant differences in plant Pb uptake between any of the treatments.
- Plant uptake of Zn was highest in control plots and this was statistically significantly different than for any of the treatments. There were differences between some of the treatments with the lowest level obtained with the 50:50 biosolids treatment plus the addition of *Penicillium bilaii.*
- *Penicillium bilaii* did not appear to increase metal uptake, as there were no significant differences.

Table 3 Concentrations of four elements (As, Cd, Pb, Zn) in all species under different amelioration treatments; root and shoot combined.

Treatment	Number of Samples	As, Cd, Pb, Zn μg/g mean	S.E.	As, Cd, Pb, Zn μmol/g mean	S.E.
Garden	12	776.97	109.64	10.79	1.59
Control	51	2968.44	237.54	40.90	3.58
Soil & Biosolid (50:50)	184	1479.24	56.76	20.57	0.75
Soil, Biosolid, & *P.b.*	175	1344.20	76.39	19.12	1.15
Soil, Peat & Biosolid	181	1908.30	71.81	26.71	0.98
Soil, Peat, Biosolid, *P.b.*	166	1804.90	80.76	25.68	1.13
Anova Results					
Random Block Design					
Treatment Effects F		8.87		8.82	
Prob>F*	0.0003	0.0003			

Mizuna (*Brassica rapa, japonica* group) sequestered the highest concentrations of As, and Pb (Table 4). *Brassica oleracea,* (Cime di rapa broccoletti) sequestered the highest concentrations of Cd and Zn. The highest total metal concentration was found in Cime di rapa broccoletti *(Brassica rapa)* and *Eruca sativa* (Table 5). Shoigun (*Brassica napa*) and mizuna followed with no differences between these two and *Eruca sativa* at less than 0.3% in terms of dry weight. While *Eruca sativa* had low variability from plant to plant, other plants displayed large variability in the total metals sequestered.

Plant uptake by all species varied significantly with treatment (Table 6). Soil amended with biosolid residual diluted with peat supported the highest plant uptake of As, Pb, and Zn and the sum of the four metals - μg or μmol (Table 7) . Highest loading of Cd was found in 50:50 biosolids with *Penicillium bilaii* treatment.

Total element loading among species across all treatments varied with plant biomass. The large biomass produced by the geraniums resulted in relatively high metal loading in all treatments (data not shown). The greater biomass of geraniums means that three times the total metals were removed than by Mizuna (ranked second). This is an important consideration in determining plants for future research.

Total elemental loading: metals accumulated in root or shoot (or both) are multiplied by the biomass of the respective plant part resulting in values for an entire plant (Table 8). The calculation factors in biomass as the larger a plant grows the higher the total metals taken up are for the plant. The metal value data is taken from the second harvest. Values are given for whole plants.

Table 4 Elemental concentrations in different species across all amelioration treatments; root and shoot combined. Mean levels of metal concentration as determined by ICP - AES analysis were computed for As, Cd, Pb and Cd.

Species	Number	As,μg/g		Cd,μg/g		Pb,μg/g		Zn,μg/g	
		Mean	S.E.	Mean	S.E.	Mean	S.E.	Mean	S.E.
Cabbage	51	3.73 de	0.63	27.67 cde	4.79	76.84 cde	13.70	1551.20cde	194.69
Eruca sativa	52	14.16ab	1.40	38.77 ab	2.94	261.96 a	37.38	2140.79 ab	120.00
Geranium	123	10.44 bc	0.89	17.73 ef	1.45	222.48 abc	29.05	1041.54 fg	82.78
Kale	50	4.24 de	0.50	26.24 cde	1.49	104.23 bcd	15.09	1405.53 def	62.31
Kale (flowering)	49	2.55 e	0.39	19.45 de	0.93	54.43 d	9.91	1135.34 efg	46.10
Mizuna	99	19.41a	2.23	29.06 bcd	1.82	282.79 a	38.89	1653.61 cd	86.38
Hybrid Poplar	22	3.06 de	0.34	30.93 bc	3.29	48.14 d	8.81	1319.17 def	86.67
Radish (Mino)	103	8.69 bcd	0.84	19.83 de	1.34	182.59 abcd	27.25	1241.66 defg	85.29
Rapa	46	10.12 bc	1.1	46.28 a	3.41	251.50 ab	35.53	2494.73 a	142.95
Redtop	24	5.2 cde	0.6	8.45 f	1.55	100.24 bcd	19.67	837.19 g	70.23
Shoigun	96	13.57 b	1.52	29.10 bcd	1.82	221.12 abc	39.90	1910.33 bc	112.07
Wallflower	51	5.60 cde	0.94	21.61 cde	1.21	140.48 abcd	32.04	1104.38 efg	69.69
Anova Results									
Random Block Design									
Treatment Effects	F	13.75		18.24		5.28		30.65	
	Prob>F	0.0001		0.0001		0.0001		0.0001	

Notes: divide concentration in μg/g by the element's atomic weight to give its molecular concentration in μmol/g analysis of variance results remain identical except for combinations of several elements.

a,b,c, means for any given element sharing the same letter are not significantly different at the p=0.05 level as determined using the Tukey multiple comparison test.

*F ratio for the specified treatment effect is significant at the 95% confidence level of Prob>F is less than or equal to 0.05

Table 5 Concentrations of four elements (As, Cd, Pb, Zn) in all species under different amelioration treatments; root and shoot combined.

Species	Number of Samples	As, Cd, Pb, Zn μg/g		As, Cd, Pb, Zn μmol/g	
		Mean	S.E.	Mean	S.E.
Cabbage	51	1659.43 cde	298.10	24.40 cde	3.07
Eruca sativa	52	2455.67 ab	134.85	34.55 ab	1.90
Geranium	123	1292.29 ef	90.11	17.30 ef	1.29
Kale	50	1540.23 de	68.75	22.29 de	0.98
Kale (flowering)	49	1211.77 ef	49.28	17.84 ef	0.72
Mizuna	99	1984.87 bcd	106.57	27.18 bcd	1.41
Hybrid Poplar	22	1401.30 ef	88.25	20.73 def	1.34
Radish (Mino)	103	1452.77 def	99.02	20.17 def	1.37
Rapa	46	2802.63 a	161.59	39.92 a	2.28
Redtop	24	951.08 f	82.78	13.44 f	1.14
Shoigun	96	2174.12 bc	125.13	30.73 bc	1.76
Wallflower	51	1271.77 ef	96.10	17.84 ef	1.19
Anova Results					
Random Block Design					
Treatment Effects	F	26.15		29.31	
	Prob>F	0.0001		0.0001	

Table 6 Total element sequestration in all species under different amelioration treatments; root and shoot combined. Values are based on assays of plants harvested at the end of the summer only.

Treatment	Number of Samples	As, μg/g mean	S.E.	Cd, μg/g mean	S.E.	Pb, μg/g mean	S.E.	Znμg/g mean	S.E.
Control	9	30.4 a	9.7	29.6 b	8.2	802.0 a	218.0	3515.6 b	1045.5
Soil, Biosolids 50:50	60	194.3 a	63.3	481.0 ab	108.9	5202.6 a	1921.1	31805.1 ab	8318.4
Soil, Biosolids plus *P.b.*	56	264.2 a	74.1	709.2 a	132.4	5474.4 a	1630.5	42642.5 ab	8376.2
Soil, Peat & Biosolids	62	294.7 a	101.4	697.6 a	215.1	8969.4 a	3662.3	52644.9 a	14770.7
Soil, Peat, Biosolids, *P.b.*	61	167.0 a	50.3	460.8 ab	100.9	4172.8 a	1424..3	37178.9 ab	8391..3
Anova Results									
Random Block Design									
Treatment Effects	F	6.71		4.01		4.38		3.93	
	Prob>F*	0.0014		0.0150		0.0105		0.0163	

Notes: divide concentration in μg/g by the element's atomic weight to give its molecular concentration in μmol/g
analysis of variance results remain identical except for combinations of several elements.
a,b,c, means for any given element sharing the same letter are not significantly different at the p=0.05 level as determined using the Tukey multiple comparison test.
*F ratio for the specified treatment effect is significant at the 95% confidence level of Prob>F is less than or equal to 0.05

Table 7 Combined total element sequestration of As, Cd, Pb and Zn in all species under different amelioration treatments; root and shoot combined. Values are based on assays of plants harvested at the end of the summer only.

Treatment	Number of Samples	As, Cd, Pb, Zn μg/g mean	S.E.	As, Cd, Pb, Zn μmol/g mean	S.E.
Control	9	4377.6	1266.9	58.3	17.2
Soil & Biosolid (50:50)	60	37693.0	10076.5	518.7	136.4
Soil, Biosolid, & *P.b.*	56	49090.0	10119.9	688.6	137.6
Soil, Peat & Biosolid	62	62606.6	17993.7	858.8	242.6
Soil, Peat, Biosolid, *P.b.*	61	41979.5	9900.9	595.2	136.4
Anova Results					
Random Block Design					
Treatment Effects	F	4.86		4.29	
	Prob>F*	0.0066		0.0115	

While the effectiveness of specific plants and their abilities to remove and sequester metals from the metal contaminated soil can be seen, soil response is not as clear due to the extreme heterogeneity of soil. Sampling from different plots shows wide variability and even in each plot the sub-samples following amendments exhibit much the same trait.

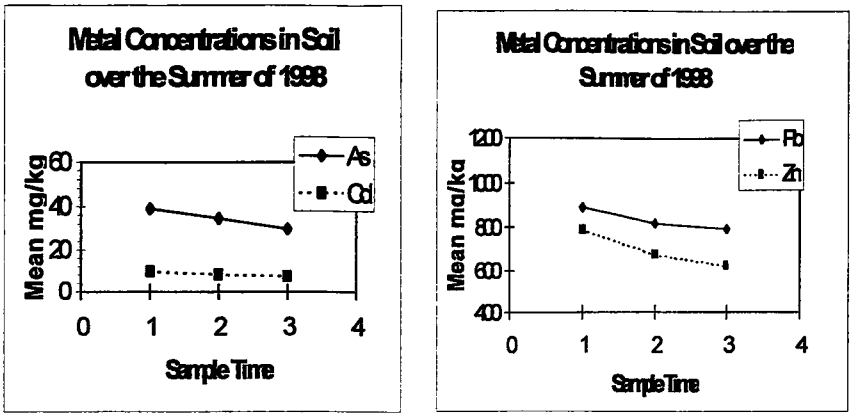


Figure 1 Graphs of metal reduction of elements (Cd and As; Pb and Zn) during 8-week growth period during summer 1998. Initial sample was taken prior to amelioration additions and prior to all planting. Sample 2 was taken mid summer, sample 3 was taken at the end of the summer following all harvesting.

The data in Table 8 clearly shows the accumulation ability of the tested species. As samples of soil prior to planting were assayed, then re-assayed immediately following the growing season reduction in soil metal presence could easily be determined. It can be seen that all metals of interest were reduced in the soil over the course of the summer (Figure 1). However, it is not clear from the assays whether or not the metals were taken up by plants or were simply removed as they were dissolved in either rain or irrigation water. Table 8 provides a partial answer to this question. It is derived by calculation using the presence of the metal in the soil as assayed prior to planting and presenting this as a ratio to the presence of the metal in plant tissue parts when these were assayed at the end of the summer. If the value of metal concentration is greater than 1, then it indicates that there is an accumulation or concentration of the metal in question in the plant tissue.

The data clearly shows that none of the plants we used were concentrating Pb in their tissues. However, this cannot rule out the potential that some of these might be better accumulators than shown as the Pb in the soil in the area is not present in a soluble form and therefore it is not bioavailable.

For Zn and Cd there are many plants with high accumulation rations. Since both metals are much more soluble in the soil conditions under study, this is expected. Zn, a metal that is a required trace element for plant growth can accumulate to high levels in plants without plant phytotoxicity, whereas, Cd, with no known biological function in plants often leads to phytotoxic plant reactions. Some plants are able to withstand high levels of Cd due to the formation of phytochelatins that effectively bind the metal thereby removing it from plant vital functions.

Eruca sativa, demonstrated an ability to concentrate As in its tissues to a level that is higher than that found in background soil levels. The relatively low value combined with the low general level in terms of As concentration in plant tissue

(Table 4) indicate that although it shows an ability to concentrate the metal it is not a hyperaccumulator.

The reduction of metal concentration in the soil over the duration of the experimental process shown as the mean concentration of all metals in the research plot decreases over the course of the first two harvests (Figure 1). Decline over initial values of 23.3% for As, 22.9% for Cd, 10.9% for Pb and 21.5% for Zn occurred during the study period. Metal levels are reduced in soils with no significant differences between treatments.

Table 8 Accumulation of metals in plant tissue; values are mean ratios of plant concentration to soil concentration. Species are listed in order; in descending order of the overall greatest to lowest accumulation of metal relative to that found in the associated soil. Trees are maple and poplar combined. Letter following plant name identifies plant part R: root; S: shoot; B: both.

Species		Number	As	Cd	Pb	Zn
Rapa	B	26	0.290 a	5.802 ab	0.414 abc	4.362 b
Eruca sativa	S	1	0.261 ab	7.422 a	0.135 a	6.066 a
	R	1	0.102 b	2.908 ab	0.091 a	2.375 a
	B	26	1.576 a	5.150 abc	0.676 a	4.300 b
Mizuna	S	26	0.358 ab	4.573 ab	0.418 a	3.536 ab
	R	26	0.740 a	2.718 ab	0.272 a	1.927 ab
	B	5	0.489 a	3.822 bcd	0.464 ab	2.506 bc
Shoigun	S	26	0.238 ab	4.025 ab	0.339 a	3.630 ab
	R	26	0.511 ab	2.642 ab	0.169 a	2.439 a
	B	6	0.259 a	7.570 a	0.194 bc	6.681 a
Radish Mino	S	25	0.340 ab	3.373 ab	0.431 a	2.706 b
	R	24	0.242 ab	1.465 ab	0.144 a	1.341 ab
	B	7	0.265 a	2.636 cde	0.265 bc	2.658 bc
Kale	S	2	0.553 a	2.371 b	0.617 a	1.711 b
	B	25	0.117 a	2.905 cde	0.142 bc	2.262 bc
Geranium	S	31	0.317 ab	1.010 b	0.481 a	2.295 a
	R	32	0.262 ab	3.919 a	0.353 a	2.295 a
	B	6	0.231 a	1.986 de	0.369 abc	1.953 c
Trees	S	23	0.115 b	4.606 ab	0.110 a	2.601 b
	R	1	0.017 b	0.191 b	0.008 a	0.094 b
Cabbage	B	27	0.121 a	3.764 bcd	0.152 bc	2.955 bc
Wallflower	B	26	0.203 a	2.468 de	o.249 bc	1.719 c
Flowering Kale	B	26	0.077 a	2.612 cde	0.091 c	2.121 c
Agrostis Stolonifera	B	23	0.170 a	1.103 e	0.160 bc	1.5222 c
Anova Results for Shoots						
F			6.13	8.88	4.20	10.52
Prob.>F			0.0009	0.0001	0.0068	0.0001
Anova Results for Roots						
F			21.65	6.41	4.20	10.30
Prob.>F			0.0001	0.0022	0.9576	0.0002
Anova Results for Both						
F			1.03	12.70	10.24	9.09
Prob.>F			0.4360	0.0001	0.0001	0.0001

If Prob.>F is less than 0.05 then treatment effects are significant at the 95% confidence level. Results sharing the same letter (abcde) when in the same row are not significantly different at the 95% confidence level.

By combining information on soil metal reduction with plant uptake insights into the potential of using plants tested to remove metals from highly affected soil can be observed (Figure 1; Table 8). It is possible that treatments that took the form of repeated annual cropping using metal sequestering plants would result in sufficient reductions to meet soil regulatory standards. However, the potential offsite migration of metals dissolved in water needs to be determined to provide a definitive answer. By capturing ground water and assaying it for dissolved and suspended metals it would be possible to complete a thorough mass balance assessment to determine what percentage of the soil metal reduction was due to plant uptake and which due to removal from the test area due to water flow.

Agrostis stolonifera, the ubiquitous grass species in the region, surviving in all areas except those most affected by smelter plume deposition, shows the lowest ability to concentrate metals of any species tested. This ability to keep metals out of both root and shoot indicates a protective ability. When the metal accumulating data was considered it was suspected that the plant might have a mycorrizal association that inhibited the metal uptake. However, when plants were examined at Okanagan College and University by Dr. D. Durrall, there was no evidence of mychorizae.

4.0 Conclusions

The highest metal uptake for all species across all treatments occurred in controls. However, most were dead or exhibited only poor growth. What could be happening in control plants is a 'soda straw' effect in which plants take up large amounts of metals from their surroundings simply because soluble metals are present in soil water and are therefore available. This severely limits their ability to grow or results in death. In examining the results for control plants it is important to consider Al loading, high levels of which are phytotoxic. Besides diluting metal concentration one effect of the addition of the biosolid residual is to increase the pH of the soil. The reduced levels of Al found in plants grown in treatments other than controls is an indication that low pH could be a contributing factor to plant death in controls.

Harvests were made after one and two months growing time. In the case of controls, due to early death, plants were often harvested sooner. Results for plants in control plots are best used as indicators of a plant's potential to sequester metals – corroborated by results in treatments.

In general no plants approached the desired level that defines a hyperaccumulator for Zn, Pb or Cd. Levels set for As that would characterize a plant as a hyperaccumulator have not been reported. However, a level of 0.01% has been suggested and this level was used in our research (McIntyre, 1999). No plant investigated in this research achieved this level of accumulation for As. The obtained results do not eliminate the potential shown by some of these plants. Four individual plants several showed marked promise by accumulating better than 0.6% dry weight total for the four metals.

Geranium was not one of the highest accumulators (Table 4) and was surpassed by many other plants. The species exhibited a very large range of metals sequestered. This species included the specimen with the highest level and many of those with very low values (18 of lowest 25) that could be attributed to extreme soil heterogeneity or cultivar differences (two sources of plant used). Due to this wide variability and the

concentration of many samples at the lowest end of sequestration levels, the mean value for geranium is substantially lower than the highest potential indicated. But, it produces a large biomass and also has an ability to survive in a low pH environment.

Screening at the University of Guelph had indicated that Mizuna had high phytoremediation potential. This was confirmed in field trials. Shoigun has a large potential root storage organ in its tuber, field results indicated that the plant divides the metals almost equally between root and shoot and that total metal concentrations are high. Cime di rapa broccoletti (*Brassica rapa*) was the best plant in terms of its tissue metal concentrations, however, it produced a lower amount of biomass than many other plants (Table 1) as it was not always harvested when peak biomass was produced. If irrigated, it could easily produce more than one crop in the Trail environment and therefore, it will be included in future investigations. *Eruca sativa* (Arugula) was good at extracting metals and it had shown an ability to survive in high metal concentrations when tested at the University of Guelph. The growing period for this plant is relatively short and it could also produce multiple crops in a single growing season in the Trail region.

The local grass species used in this research, *Agrostis stolonifera* (redtop) grows well throughout the area indicating drought tolerance and ability to withstand an environment in which soil pH is low and metals are present. It had been found in areas where water high in Cd and Zn leaching through a landfill site seeps from a hillside. However, as can be seen in the tables, it is not an accumulator of metals. While metal tolerant it does not sequester large amounts. Of all species tested it demonstrated the least ability to take up metals. For the cumulative total of the four metals the mean value (n= 24) was only 951.08 μg/g. Its ability to grow well in low pH, high metal environments indicates a potential use for this species in areas where phytostabilization, not metal uptake is the aim of the remediation process.

Field studies showed soil metal concentrations are reduced in all treatments over the 8-week experimental duration. Additionally, several of the plants tested are capable of sequestering relatively large amounts of metals in their tissues. While no plants could be considered as hyperaccumulators several plants were able to accumulate high levels of metals based on plant concentrations. Four plants are considered worthy for further study (*Eruca sativa,* Mizuna, Cime de rapa broccoletti, and geranium). For the fourth plant (geranium) the results obtained in this report suggest that it is perhaps only average in its abilities to concentrate metals. However, due to the extreme variability in size of plants originally transplanted and that some of the plants achieved truly large biomass proportions in comparison to all other plants, they will be used in further testing as well as the other three. The intent of the preliminary work was to establish protocols, assess various plant capabilities and to ensure that subsequent work was based on understanding the particularities of the site's growth environment. This was done and as a result a second year's study with an experimental design based on these results was completed during the summer of 1999.

5.0 Acknowledgments

Dr. W. Rauser, University of Guelph, Dr. B Husband, University of Guelph, Dr. L Peterson, University of Guelph for assistance with greenhouse and lab preparations of initial screening protocols and materials. Dr. Susan Warwick, Agriculture Canada for provision of seeds and plants of *Brassica* species. Dr. Phil Burton, Symbios Research and Restoration, for statistical analysis. Dr. Dan Durrell, Okanagan College and University for examination of roots of *Agrostis stolonifera* for mychorrizae. National Research Council (IRAP) for assistance with funding for field work. Ulrike Sliworski, for daily maintenance of field site.

6.0 References

Baker, A.J.M., Reeves R.D. and S.P. McGrath, In Situ-Decontamination of Heavy Metal Polluted Soils Using Crops of Metal-Accumulating Plants – A Feasibility Study, in *In Situ Bioreclamation* eds. R.E. Hinchee and R.F. Olfenbuttel, Butterworth-Heinemann, Boston MA., pp: 600 – 605, 1991

Campbell C.R., and Plank C.O., Preparation of Plant Tissue for Laboratory Analysis in *Handbook of Reference Methods for Plant Analysis*, eds. Yash. P. Kalra, Soil and Plant Analysis Council, Inc., CRC Press, Boca Raton USA, pp: 37-49, 1996.

Dushenkov, V., Nanda Kumar, Motto H. and I. Raskin, Rhizofiltration: The Use of Plants to Remove Heavy Metals from *Aqueous Streams, Environmental Science and Technology*, Vol. 29, pp: 1239 – 1245, 1995

McIntyre T., Development of a Worldwide Data Base on Metal Tolerant and Metal Accumulating Plants for Contaminated Site Remediation", in *Proceedings of the Phytoremediation Technical Seminar,* Calgary Alberta, May 31 – June 1 1999, pp: 33-59, 1999

Salt D.E., Blaycock, M. Kumar, N.P. B.A., Dushenkov, V., Ensley, B.D., Chet, I., and I. Raskin, Phytoremediation: A Novel Strategy for the Removal of Toxic Metals for the Environment Using Plants, *Biotechnology* Vol. 13, pp: 468-475,1995,

Saxena, P. K., and Sankaren, Krishnaraj, On the 'Scent' of Soil Remediation: Scented Geraniums for Phytoremediation of Metal-Contaminated Soils, *PBI Bulletin, National Research Council of Canada*, 1998.

Soong, Y.K., Determination of Cadmium, Chromium, Cobalt, Lead and Nickel in Plant Tissue, *Handbook of Reference Methods for Plant Analysis*, eds. Yash. P. Kalra, Soil and Plant Analysis Council, Inc., CRC Press, Boca Raton USA, pp: 193 - 198, 1998.