PROCEEDINGS OF THE THIRTEENTH TECHNICAL SEMINAR ON CHEMICAL SPILLS

COMPTE RENDU: 13ᵉ COLLOQUE TECHNIQUE SUR LES DÉVERSEMENTS DE PRODUITS CHIMIQUES

JUNE 10 AND 11, 1996
LBERT

LES 10 ET 11 JUIN, 1996
CALGARY (ALBERTA)
CANADA

ement

Canada

PROCEEDINGS

Thirteenth Technical Seminar
on Chemical Spills

June 10 and 11, 1996
Sandman Hotel
Calgary, Alberta, Canada

Seminar sponsored by

Environmental Protection
Service
Environmental Technology
Advancement Directorate

Environment Canada

COMPTE RENDU

Treizième colloque
technique sur les
déversements de produits
chimiques

10 et 11 juin, 1996
Hôtel Sandman
Calgary, Alberta, Canada

Colloque commandité par

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

NOTICE

The materials and information contained herein are published in the exact form as presented to the sponsors by conference speakers. Any statements or views presented here are those of the speakers and are neither condoned nor rejected by the sponsors. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

Inquiries related to the technical contents 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
Environmental Technology
Centre
Ottawa, Ontario, Canada
K1A 0H3

Phone: (613) 998-9622

Cover Photograph
Spill Excercise
Port of Montreal, Quebec
September 1995.

AVIS

Les textes et renseignements contenus dans le présent document sont publiés tels qu'ils ont été présentés aux commanditaires par les conférenciers.
Les déclarations et opinions apparaissant dans ce document sont celles des conférenciers; elles ne sont ni approuvées ni rejetées par les organisateurs. La mention de marques de commerce ou de produits commercialisés ne constitue ni une approbation ni une recommandation d'emploi.

Toute demande d'information relativement au contenu des conférences 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
Centre de technologie
environnementale
Ottawa, Ontario, Canada
K1A 0H3

Tél: (613) 998-9622

Photographie de la couverture
Exercice de déversement
Port de Montréal, Québec
Septembre 1995.

TABLE OF CONTENTS
TABLE DES MATIÈRES

Countermeasures
Mesures d'intervention

Fate and Effects
Sort et Effets

Analytical
Analytique

The Spill Problem
Les Contraintes des déversements

Poster Session
Session d'affiches

Development of Treatment Trains for A Remediation Demonstration Project at Former Missile Sites

by

Janis Avotins*, Valdis Kokars*, Laura Ouellette**, Harry Whittaker**

*Faculty of Chemical Technology
Riga Technical University
Azenes st. 14
Riga, Latvia

**Emergencies Engineering Division
Environmental Technology Centre
Environment Canada
3439 River Road
Ottawa, Ontario
K1A 0H3

Introduction

Activities carried out at former Soviet military bases in Latvia have resulted in the discharge of various toxic substances into the environment (Whittaker, 1994). Since the abandonment of these bases, local residents have been able to access these lands for agriculture, forestry and recreation. Consequently, there is a high risk for exposure to the soil and water which is contaminated with toxic chemicals with the resultant impacts to human health. Large scale clean-up operations are required in order to return this land to profitable or safe use. A joint project was set up in Canada and Latvia to carry out the environmental assessment and remediation of sites at former military bases at Barta and Tasi, located in the coastal zone near Liepaja (Latvia).

During the site assessment conducted at former military bases at Barta and Tasi, soil and water samples were found to be contaminated with varying concentrations of the xylidine-based missile fuel SAMIN and oil products (Ladanowski, 1996). The estimated level of oil product contamination (by mineral oil and grease analysis) reaches 6,000-7,000 ppm, while the xylidine contamination reaches a few thousand ppm (in some places more than 20,000 ppm). Xylidines have been found to be toxic at concentrations as low as 2 ppm by inhalation and skin contact; however xylidines are valuable intermediates in many industry processes. Therefore, the main research objective of this project is to improve the quality of these coastal sites by focussing on the development of remediation technologies to clean-up the xylidine contaminated soil and water through the development of a nondestructive xylidine concentration and recovery process.

Latvian and Canadian researchers began research in the autumn of 1995 to investigate different treatment technologies with the goal of developing an optimized treatment process for remediating these sites. Based on this research, a pilot-scale treatment train is being built and is planned for use during a remediation demonstration project to be carried out in Latvia in August 1996.

Background

The treatment technologies investigated for the remediation of contaminated soil were soil washing, solvent extraction, and low temperature thermal desorption. Steam stripping and advanced oxidation were investigated to remediate the contaminated ground water.

Soil washing is a physical treatment method in which contaminants are removed from the soil by solubilizing them, or suspending them in a fluid such as water with or without surfactants or detergents. The soil is separated from the washing fluid with the contaminants, fine soil particles and soluble components of the soil staying in the washing fluid (Intera Kenting, 1990). Ultimately the contaminants are concentrated in the washing fluid and the "cleaned" soil is tested to ensure the contaminants have reached target levels and then returned to its original site (Kendall, 1991). In some cases, soil washing alone can reduce the contaminant concentrations to acceptable levels and therefore serve as a stand-alone technology (USEPA, 1990). In other cases, it can be a cost-effective pre-processing step in reducing the quantity of material to be processed. It is important to note that this process does not destroy but rather concentrates the contaminants for further processing. Although this treatment method is suitable for a wide range of contaminant problems, it is most effective on coarse material (Traver, R.P., 1992, Kendall, 1991, USEPA, 1990).

Solvent extraction is differentiated from soil washing because it utilizes organic solvents or critical fluids to remove hydrophobic contaminants from the soil (Intera Kenting, 1990). The extracting fluid is then separated from the soil by a physical method such as filtration. The soil may require additional treatment to remove any residual extracting fluid (CPPI, 1991). The extracting fluid may then be treated and recycled back into the process (Kendall, 1991, CPPI, 1991). The effectiveness of this process is dependent upon the nature of the contaminant, soil type and extracting agent used. Several methods of enhancing solvent extraction (Punt, 1994) and proprietary processes (Kenting, 1990, Robbins, 1990) have been developed.

Low temperature desorption is a process by which either direct or indirect heating is used to raise the temperature of a contaminated soil to volatilize the organic contaminants and water into an exhaust gas. The contaminants in the exhaust gas are either destroyed in an afterburner (Ouellette, 1994) or recovered by condensation into a liquid form (Bogzaran, 1994). The condensate may then be separated into organic and water fractions. Thermal desorbers generally operate at relatively low soil discharge temperatures, typically in the range of 150°C to 500°C (Troxler, Goh et al, 1993). This process can be used for the remediation of a wide range of contaminants such as petroleum products and pesticides (Troxler, Cudahy et al., 1993; Toxler, Goh et al., 1993)

Steam stripping allows steam to come into contact with the contaminated water causing the contaminants to volatilize and transfer from the water to the steam. Although the contact between the two phases may be achieved by a variety of methods, most traditional units are counter-current packed columns (Sundstrom, 1979, Punt, 1991). The driving force for the contaminant transfer is the concentration differential between the liquid and vapor phase. The vapor outlet stream is condensed and the contaminant is recovered in a concentrated water stream. The stripping temperature is important since Henry's law constant (ratio of the contaminant concentration in the water and vapor phase) is temperature dependent. Other important system operating parameters are the steam to feed ratio, and the pH of the feed stream.

The advanced oxidation process is a technique that may be used to degrade organic contaminants in ground water and in some cases mineralize them to undetectable levels. Advanced oxidation processes are applicable for treatment of low concentration contaminated ground waters and as a post-treatment step. Ultra-violet light in conjunction with powerful oxidants such as hydrogen peroxide and Fenton's reagent treatment generate powerful hydroxyl radicals. The hydroxyl radicals oxidize the organic contaminants which are kept in an excited state and vulnerable to attack by the UV/oxidant system. In the absence of ultra-violet light, Fenton reagent (dark Fenton's reaction) produces hydroxyl radicals by the interaction of hydrogen peroxide with ferrous salts (Walling, 1975). The reaction is retarded after complete conversion of the ferrous ions (Fe^{2+}) to ferric ions (Fe^{3+}). The irradiation of this solution (photo-Fenton's reaction) includes the photoreduction of Fe^{3+} to Fe^{2+} ions allowing the generation of hydroxyl radicals to continue (Ruppert, 1993). The irradiation of hydrogen peroxide solution involves a single step dissociation of the hydrogen peroxide to form two hydroxyl radicals (Venkatadri, 1993, Paul, 1990).

Materials and methods

This research project used contaminated soil and water samples from the former Soviet military bases in Latvia in addition to spiked soil and water samples. The contaminated soil and water samples received were refrigerated until use. The spiked samples were used to narrow the range of operating parameters for these tests before the actual soil and water samples were used for parameter optimization.

Spiked water samples were produced by adding specific amounts of 2,4 xylidine or 2,5 xylidine to deionized water. A soil comparable to that at the site in Latvia, was produced by mixing 70 wt% sand, 10 wt% black earth, 10 wt% peat and 10 wt% water in a ball mixer. This soil was then spiked by adding a xylidine/methanol solution. The methanol was then evaporated by air drying at room temperature.

The analyses of the xylidine and oil products were performed by gas chromatography /FID. A rapid analytical method for spiked sample determination using a UV-VIS spectrometry was also developed. This method is based on the reaction of xylidine with a reagent to shift the absorbance signal from the UV region towards the visible zone of the spectrum. The colouring agents used were para-dimethyl-aminobenzaldehyde (DMBA) and trisodium pentacianoamino ferroate (TPF).

Results and discussion

The technologies investigated for the decontamination of the soil were soil washing, solvent extraction, and low temperature desorption (LTD).

As mentioned previously, in soil washing an aqueous solution is used to solubilize and separate contaminants from soil. Although soil washing is technically easy to conduct and comparably cost effective, its application is limited. Table 1 shows the low solubility of xylidine in water and its slow dissolution rate. As a result, it is necessary to use large volumes of water and to repeat the washing process several times to reach acceptable target levels of xylidine in the processed soil. In addition, Barta's soil contains a large amount of fine dispersion silt, whose presence renders the outlet stream very difficult to filter and causes interference with the subsequent concentration process. For these reasons, the use of soil in Latvia will be soil matrix dependent.

Table 1

Final concentrations and efficiency of removal of xylidines from soil

Water/soil ratio L/kg	Conc. of xyl. in the soil(ppm) at the washing time			Efficiency of removal of xylidines, %		
	30 min	120 min	24 h	30 min	120 min	24 h
3	5512	3624	1958	11.5	41.8	68.6
4	4354	2832	1710	30.1	54.5	72.6
5	3870	2544	1295	37.9	59.2	79.2
6	3642	2068	866	41.5	66.8	86.1
7	2768	1831	847	55.6	70.6	86.4
8	2685	1565	710	56.9	74.9	88.6

Solvent extraction from the soil matrix using methanol permits a greater than 90% recovery of the xylidine, but solvent recovery from the soil is costly and the processed soil often requires further treatment such as LTD to remove the solvent. For these reasons, solvent extraction was therefore not pursued further.

Although xylidine's boiling point is between 213 °C and 228 °C, our research indicates, as shown in table 2, that effective and relatively fast xylidine removal may be possible by heating the soil to temperatures which are lower than the boiling point. For these temperatures, bioremediation may be necessary as a polishing step. For the xylidine recovery optimization of this low temperature desorption (LTD) process, it is necessary to have have at least 10% water in the soil. Steam acts as a carrier gas which serves to enhance the xylidine desorption and also lessens its destruction/oxidation by reducing the oxygen concentration in the desorption unit. The gaseous emissions from the LTD process can be condensed to obtain a relatively concentrated xylidine-water solution/emulsion without the carry-over of the finely dispersed silt from the soil. By applying a partial vacuum, it is possible to desorb the oil contamination in addition to the xylidine.

Table 2
Removal of xylidine from soil using LTD

time of exposure, min.	conc. of xylidines(ppm) in the soil at different temperatures					
	140 C	160 C	180 C	200 C	220 C	240 C
0	4806	4806	4806	4806	4806	4806
5	3456	2503	2147	1018	479	87
10	1531	717	428	222	63	7
15	834	441	93	20	13	2
30	332	103	22	6	2	0

For ground water remediation, research was done utilizing steam-stripping. Good results have been obtained by this process for concentrating xylidine. More complete xylidine recovery and higher xylidine concentrations, as shown in Table 3, are achieved with higher initial concentrations and higher feed/steam ratio values. A pH adjustment step is required before the steam-stripping process in order to maximize the recovery of the xylidine in the column tops stream. Also, enhanced recovery of the xylidine is possible by preheating the feed stream. A full description of this research is available elsewhere (Avotins, 1996). The residual xylidine in the column bottoms stream may be destroyed using AOP.

Table 3
Concentration of xylidine using steam-stripping

Feed/steam ratio, L/kg	Final xylidine concentrations at the top of column at different initial conc.			
	1098 ppm	692 ppm	239 ppm	133 ppm
1.9	2434	1252	599	305
3.6	4200	1916	1062	507
5.3	5158	2341	1285	617
8.5	6044	3611	1537	1055

Advanced oxidation research was conducted on spiked 2,4 xylidine and 2,5 xylidine solutions utilizing UV photolysis, UV/hydrogen peroxide, photo Fenton's reaction and Fenton's reaction. The results of the photolysis research indicate that the oxidation of 2,4 and 2,5 xylidine requires a similarly prohibitively long residence time to obtain non-detect levels. The results of the hydrogen peroxide-UV experiments indicate a trend of decreasing exposure time required to achieve non-detect levels of xylidine with increasing hydrogen peroxide concentrations. The Fenton's reagent research indicates the enhancement of Fenton's reagent with UV light and faster oxidation of both 2,4 and 2,5 xylidine with increasing Fe^{2+} ion concentration. The best results, as shown in Table 4, have been achieved with UV/hydrogen peroxide and photo-Fenton's reaction.

Table 4

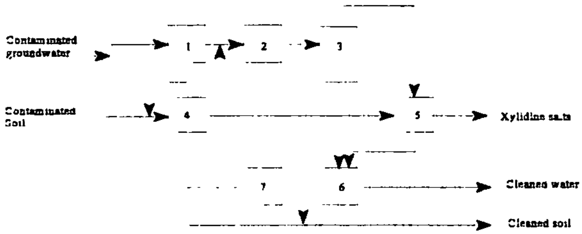
Advanced oxidation of 2,5xylidine water solutions

Time of exposure, min	Options of treatment						
	UV*	UV HP**-100	UV HP-200	UV HP-500	UV HP-1000	HP-1000 FR***-50	UV HP-1000 FR-50
0	94	123	123	131	156	90	90
2	88	84	103	85	81	77	58
4	80	55	62	45	46	76	48
6	74	42	44	0	0	70	0
8	71	36	36	0	0	67	0
10	67	30	29	0	0	63	0
15	58	24	0	0	0	0	0

* UV - ultraviolet light; **HP - hydrogen peroxide, ppm; ***FR - Fenton reagent, ppm

The remediation process of xylidine-contaminated soil and ground water will be based on the flow diagram shown in figure 1:

Figure 1



1. Filtration 2. pH control 3. Steam- stripper 4. Low temperature desorption
5. Chemical treatment 6. Advanced oxidation process 7. Bioremediation

The diagram illustrates the processing of the solids from the ground water filtration in the LTD unit and the processing of the condensate from the soil treated by LTD using the steam-stripper. The product stream from LTD and steam stripping processes is a concentrated xylidine and oil product solution. The oil products are removed in the chemical treatment process by solvent extraction and xylidine is recovered in the form of xylidine salts. An advanced oxidation process is used as a destructive technology to eliminate residual xylidine and oil products from both the column bottoms flow stream and in the post chemical treatment water. As the xylidine concentration in the soil will be significantly lower after low temperature thermal desorption, bioremediation can be used as a polishing step for the contaminated soil.

A method has been developed for recovery of the xylidines in concentrated form from the process water which accumulates after the soil has been treated by low temperature desorption or after the ground water has been treated by steam stripping. The method is based on the ability of the xylidine to form salts with various organic dicarboxylic acids. These salts have variable solubilities in water and other polar solvents depending on the xylidine isomer. The best results have been obtained by using phthalic acid. The solubility of 2,5-xylidine phthalic acid salt in water has more than 10 times the solubility 2,4-xylidine phthalic acid salt, and this allows the two isomers to be separated.

Conclusion

The research conducted under this joint Latvian-Canadian project has led to the development of a novel multi-stage treatment process for xylidine-contaminated soil and water. The outputs for this process are xylidine salts, cleaned water and cleaned soil.

The developed method, producing xylidine phthalic acid salts, allows the recovery of xylidine in a concentrated form and their separation into isomers after treatment of the xylidine-contaminated soil and water.

References

Avotins, J., Kokars, V., Ouellette, L., Whittaker, H., `Evaluation of Steam Stripping for Recovery of Xylidine at Former Missile Sites', to be published in Proceedings of 13th Technical Seminar on Chemical Spills, Calgary, Alberta, 1996

Bogzaran, F., Proceedings of 11th Technical Seminar on Chemical Spills, Vancouver, B.C., pp 51- 61, 1994.

CPPI, Manual of Petroleum Contaminated Soil Treatment Technologies, report no. 91-9, 1991.

Intera Kenting, Final Report on Current and Innovative Excavate and Treat Technologies for the Remediation of Contaminated Soils, prepared for the National Ground water and Soil Remediation Program Excavate and Treat Technical Sub-Committee, 1990.

Kendall, P.R.W., Technical Report: Identification of Potential Environmental and Health Concerns of Soil Remediation Technologies, Environmental Protection Office, Department of Public Health, City of Toronto, 1991.

Ladanowski, C. et al., 'Results of Environmental Site Assessment in Latvia', to be published in Proceedings of 13th Technical Seminar on Chemical Spills, Calgary, Alberta, 1996.

Ouellette, L., Razbin, V., Proceedings of the Seventeenth Arctic and Marine Oilspill Program Technical Seminar, Vancouver, B.C., pp 569-580, 1994.

Paul, D., Canter, L.W., J. Environ. Sci., Health, A25(8), pp 953-985, 1990.

Punt, M., Cooper, D., Fourth Annual Conference on Contaminated Land, London, England, 1994.

Punt, M., Whittaker, H., Proceedings of the Eighth Technical Seminar on Chemical Spills, Vancouver, B.C., pp 117-132, 1991

Robbins, L.C., Proceedings of the EPA/A&WMA International Symposium, Hazardous Waste Treatment: Treatment of Contaminated Soils, pp 314-324, 1990.

Ruppert, G., Bauer, R., Heisler, G., J. Photochem. Photobiol. A: Chem., 73, pp 75-78, 1993.

Sundstrom, D.W., Klei, H.E., Wastewater Treatment, Prentice-Hall, 1979.
Traver, R.P., O'Brien, S., Clean-up of Contaminated Sites, Insight Press, Article VII, 1992.

Troxler, W.L., Cudahy, J.J., Zink, R.P., Yezzi, Jr., J.J., Rosenthal, S.I., Air & Waste, Vol. 43, 1993, pp 1512-1525, 1993.

Troxler, W.L., Goh, S.K., Dicks, L.W.R., Air & Waste, Vol. 43, 1993, pp 1610-1619, 1993.

USEPA, Engineering Bulletin: Soil Washing Treatment, September, 1990.

Venkatadri, R., Peters, R.W., Hazardous Waste and Hazardous Materials, Volume 10. No. 2, pp 107-149, 1993.

Walling, C., Accounts of Chemical Research, Vol. 8, pp 125-131, 1975.

Whittaker, H., Valtere, S., 2nd International Symposium and Exhibition on Environmental Contamination in Central and Eastern Europe. Budapest, Hungary, 1994, pp 971-973.

RECOVERY OF SELENIUM FROM WATER USING A MEMBRANE PROCESS

Anne Legault, Martin Canuel
Environment Canada - Environmental Technology Centre
Emergencies Engineering Division
3439 River Road, Ottawa, Ontario
K1A 0H3 (613) 997-2904

Selenium recovery from water has been investigated using a binding process followed by a membrane separation. In this process, binding first occurred between the selenium contaminant and the binding agent, forming a macromolecule which is then retained by an ultrafiltration membrane. The presence of salts, the solution's pH, and the use of different binding agents were factors affecting the retention of selenium. Although additional studies are necessary to determine more suitable binding agents in the presence of a high salts concentration, the data obtained to date seem promising. The use of the polymeric/membrane technique results in a significant reduction of the total selenium present in water, and is a promising method to produce water that meets the selenium Canadian discharge limits for drinking water

INTRODUCTION

Environmental effects resulting from water contaminated by selenium species represent an environmental concern in todays society. In the human body, selenium has been found to act as an anti-oxidant and seemed to prevent cancer through several interactions; however, a high concentration of selenium is toxic to humans and animals [Glenn, 1991]. These high concentrations create important health hazards that lead to severe sicknesses [IPCS, 1987]. Diseases arising from selenium intoxication include alkali disease, which is responsible for lameness, loss of hair and hoof in animals, "blind staggers" that attacks the central nervous system, and "white muscle disease" which causes a degeneration of muscle tissue [NAS, 1976; Krehl, 1970; Underwood, 1977].

Environmental water remediation limits set by the Canadian Council of the Ministers of the Environment (CCME) were reported to be among the most severe criteria in the world [Canuel, 1996], and were set for different types of water as reported in Table 1. The drinking water guideline established a maximum acceptable level of 10 ppb, which represents the target selenium concentration for this study.

Table 1 Selenium Remediation Criteria for Different Water [CCME, 1991]

Type of Water	Concentration (μg/L)
Freshwater - Aquatic Life	1
Irrigation	20-50
Livestock Watering	50
Drinking Water	10

Through an extensive literature review, several treatment methods were found to reduce selenium concentration in water [Peräniemi et al., 1994; Ramana et al., 1992; Nurdogan et al., 1994; Koren et al., 1992; Saisho and Fujimura, 1990; Nurdogan et al., 1994; Itoh et al., 1989;]. The broad range of methods developed is a direct result of the efforts taken to date to deal with the selenium toxic waste problem. Each of these methods contain major drawbacks which could include high complexity, high cost, and non-selectivity that limit their industrial application.

In the early 1990s, scientists from Environment Canada investigated the used of a polymeric binding/membrane separation technique to effectively remove heavy metals from contaminated water. This technique was effective in treating metals contamination, such as arsenic and chromium, reaching retention levels as high as 99% at the bench-scale [Legault and Tremblay, 1994; Legault, 1995]. Results obtained during previous research demonstrated that the removal of arsenic from contaminated groundwater was affected by various factors: salinity, initial arsenic concentration, pH of the solution, type of polymer and concentration of polymer used [Legault, 1994]. Considering these results and the numerous chemical similarities between selenium and arsenic, this process was selected for a study to remove selenium at the laboratory scale. This publication reports the results obtained using this technique and three binding agents, namely poly(ethylenimine), chitosan, and copper oxide.

ANALYSIS

The analysis of selenium solution was achieved using an atomic absorption spectrometer, combined with a hydride generator. Additional analysis were carried-out using a polarograph. This method, developed by Environment Canada, determines the validity of the results obtained with the hydride generator. Both methods had a detection limit below 1 ppb.

EXPERIMENTAL

Synthetic groundwater was produced for all the experiments by preparing solutions containing 1.5 ppm of selenium (IV) and 1.5 ppm of selenium (VI). All tests were performed at room temperature and a working pressure of 40 psi(g). Three binding agent were used at a concentration of 1,000 ppm: poly(ethylenimine) [PEI], chitosan, and copper oxide (CuO). The system was allowed to reach steady state for a period of ten minutes, after which the permeate collected was remixed with the feed solution. An initial feed sample of 2.5 ml was taken at the beginning of the experiment, and after 5, 10, 15 minutes of operation. All samples were refrigerated until they were analyzed. Each test was performed using three 50 ml magnetically stirred batch cells run in parallel. Each stirred-cell contained the polymeric solution composed of 3.0 ppm of the selenium species, 1,000 ppm of polymer and either 0 or 1,000 of mixed salts (NaCl, Na_2SO_4, $MgSO_4$, $Ca(NO_3)_2$, Na_2CO_3) at a pH of 3.0 or 7.5. A polyethersulphone ultrafiltration membrane, with a molecular cut-off of 10,000 Daltons (FPI-Separations and Systems, Inc.) was used for the study. The membrane sample was replaced every time a polymer being tested was changed. The initial and concentrate solutions were sampled once per test while the permeate was sampled at regular time intervals (5, 10 and 15 minutes). The time of collection and weight of each sample was recorded.

The selenium retention on the high pressure side (feed side) of the membrane (R_{Se}) was used to characterize the efficiency of the metals removal [Volchek et al, 1992] using the equation (1):

$$R_{Se} = 1 - C_p/C_f \qquad (1)$$

where C_p and C_f are the concentration of selenium in the permeate and the feed respectively.

RESULTS

As stated earlier, three binding agent were used for the retention of selenium from contaminated water. Problems were encountered using the last binding agent, copper oxide (CuO). The used of this specific chemical created a slurry which caused plugging of the membranes under normal experimental conditions. Difficulties also arose during the chemical analysis due to interference from CuO which altered the selenium characteristic which in turn affected the selenium hydride produced. For these reasons the CuO results were determined not to be indicative of actual performance and are not reported in this paper.

Furthermore, due to budget constraints, analyses were performed only for Se(IV). The authors are aware that the measured concentrations of Se(IV) could be higher than the actual experimental concentrations due to the possible oxidation of Se(IV) to Se(VI) caused by the addition of HCl during analysis. Based on the problems encounter during these trials, the results reported in this publication must be considered as preliminary in nature. The results obtained using PEI and Chitosan as binding agents are reported in Table 2 and Table 3 respectively.

Table 2 Selenium Retention Using 1,000 ppm of PEI
for Two Different pH and Salts' Concentrations.

Time (Minute)	pH	Retention (%) at Salts' Concentration		Average Retention(%) at Salts' Concentration	
		0 ppm	1,000 ppm	0 ppm	1,000 ppm
0:00	3.0	79.7*	---	75.5	3.5
5:00	3.0	72.0*	0.2*		
10:00	3.0	74.9*	6.8*		
0:00	7.5	93.1*	21.1*	96.4	26.9
5:00	7.5	98.1*	31.3*		
10:00	7.5	97.9*	22.6*		
15:00	7.5		32.4*		

*Value based on three replicates.

The percentages of selenium removed during the experiment using PEI as the binding agent revealed an average of 75.5 % at a pH of 3.0 compared to 96.4 % obtained at a pH value of 7.5. These results demonstrate that pH affects the selenium retention using PEI, with better retentions being obtained at higher pH, i.e., 7.5. This can be attributed to a higher pH causing an increase in the number of charged nitrogen sites available for polymeric binding [Legault and Tremblay, 1994]. The results obtained also showed that PEI was more effective for selenium retention in the absence of salts. At a salts concentration of 1000 ppm, the retention of selenium species decreased, obtaining a value of 3.5 % and 26.67 % respectively. This demonstrated the general lack of selectivity for the selenium species using the PEI binding agent at both pH values. The pH of the test solution also had an effect, as the retention increased when the selenium solution had a neutral pH. The competitive effect between the five salts (NaCl, Na_2SO_4, $MgSO_4$, $Ca(NO_3)_2$, Na_2CO_3) and the selenium contaminant was obvious, and further research should be performed to determine the exact and magnitude effect of each salt on the retention.

A slight increase in the selenium retention was also noticed with time, in the absence of salts. These observations could possibly be explained by the formation of a polymeric gel at the surface of the membrane as reported by Legault and Tremblay [1994]. As the experiments proceed, the polymer being recirculated accumulates at the surface of the membrane, increasing its local concentration. This higher polymer concentration increases the likelihood that the contaminant will bind with the polymer.

Table 3 Selenium Retention Using 1,000 ppm of Chitosan and Two Different pH and Salts' Concentrations.

Time (Minute)	pH	Retention (%) at Salts' Concentration		Average Retention (%) at Salts' Concentration	
		0 ppm	1,000 ppm	0 ppm	1,000 ppm
15:00	3.0	--	28.2*	60.6	26.0
30:00	3.0	58.7*	25.7*		
45:00	3.0	62.5*	25.7*		
60:00	3.0		24.4*		
15:00	7.5	7.3*	27.1*	12.2	28.5
30:00	7.5	4.8*	29.5*		
45:00	7.5	3.8*	27.1*		
60:00	7.5	32.8*	30.4*		

*Value based on three replicates

The results shown in Table 3 were obtained using chitosan, the second binding agent. Selenium retention values obtained were not as high as in the case of PEI, as it reaches a maximum of 60.6 %. A lower pH value of the solution gave more promising results in the absence of salts, but did not seem to have the same affect when salts were present. Retentions reaching 60.6 % and 12.2 % were achieved in the absence of salts, compared to 26% and 28.5 % in the presence of 1,000 ppm of salts. Based on this experiment, better retention results are expected when both low salts' concentration and low pH are combined. Once again, the results showed that this water-soluble polymer was not selective for the selenium since high salts' concentration affected the retention obtained, from an average high of 60.6 % (in the absence of salts) down to 26.0 %.

Further studies will have to be performed to determine the interaction between salts concentration and the solution pH. Tests performed to date are only preliminary in nature and additional studies should be conducted to determine reliable conclusions on this subject.

CONCLUSIONS

1. Neither of the two water-soluble polymers studied were very selective toward selenium species in the presence of high salts' concentration;
2. PEI is a superior binding agent than chitosan in the absence of salts;
3. PEI was affected by the pH of the solution;
4. Chitosan achieved, in the absence of salts, higher retention at a lower pH;
5. Interactions seemed to occur between variables studied, i.e., salts concentration and pH of the solution when chitosan is used in this process;

RECOMMENDATIONS

1. Proper analysis of all selenium species should be performed;
2. Additional investigation should be carried-out to determine all factors affecting the separation;
3. A second level factorial design should be performed to determine the interactions occurring between variables during the selenium retention;
4. More selective binding agents should be selected or outlined using computational chemistry software.

ACKNOWLEDGMENTS

The authors will like to express their thanks FPI-Separations and Systems, Inc. for the supply of membrane samples.

REFERENCES

Canuel, M., "A Literature Review for the Extraction of Selenium Species From Aqueous Solution", Environment Canada - The Emergencies Engineering Division, In-house Student Report (1996)

Canadian Council of Ministers of the Environment, Interim Canadian Environmental Quality Criteria for Contaminated Sites, Report CCME EPC-CS34 (1991)

Glenn, W.M., "Selenium : This Poison Fights Cancer", OH&S Canada, Vol.7, No.2 (1991) pp.32, 34-37

IPCS International Programme on Chemical Safety, Environmental Health Criteria 58: Selenium , World Health Organization, Geneva, (1987)

Itoh, K., Chikuma, M. and M. Nishimura, "Determination of Selenium (IV) and Other Forms of Selenium Dissolved in Sea Water by Anion-exchange Resin Loaded with Sulfuric Acid Derivative of Bismuthiol-II and Hydride Generation Atomic-absorption Spectrometry", Fresenius' Zeitschrift Fur Analytische Chemie, Vol.333, No.2 (1989), pp.102-107

Koren, D.W., Gould, W.D. and L. Lortie, "Selenium Removal From Waste Water", Proceedings of the International Symposium on Waste Processing and Recycling in Mineral and Metallurgical Industries, Edmonton, Alberta (1992)

Krehl, W.A., "Selenium: The Maddening Mineral", Nutrition Today, Vol.5 (4) (1970) pp.26-32

NAS, Selenium, National Academy of Sciences, Washington D.C., (1976), pp. 203

Nurdogan, Y., Schroeder, R.P. and C.L. Meyer, "Selenium Removal from Petroleum Refinery Wastewater", Proceedings of the 49th Industrial Waste Conference, Purdue University (1994)

Legault, A., "Comparison of Two Membrane Processes for Toxic Metal Removal", Proc. of 12th Tech. Seminar on Chemical Spills, Edmonton (1995) pp.11-20

Legault, A.S. and A.Y. Tremblay, "Arsenic Removal by Polymeric Binding and Ultrafiltration Separation", Proc. 11th Tech. Seminar on Chemical Spills, Vancouver (1994) pp. 15-23

Legault, A.S., "Etude de la rétention d'arsenic de solutions aqueuses utilisant un traitement au polymère suivi d'une séparation par membrane d'ultrafiltration", submitted to the Department of Graduate Studies of the University of Ottawa, Ottawa (1994)

Legault, A.S., Volchek, K., Tremblay, A.-Y. and H. Whittaker, "Removal of Arsenic from Groundwater Using Reagent Binding/Membrane Separation", *Environmental Progress*, Vol.12, No.2, pp.157-159 (1993), " First Separation Division Topical Conference on Separations Technologies: New Developments and Opportunities, AIChE, Miami Beach, Florida (1992) pp. 751-753.

Peräniemi, S., Hannonen, S., Mustalahti, H. and M. Ahlgren, "Zirconium-loaded Activated Charcoal as an Adsorbent for Arsenic, Selenium and Mercury", Fresenius Journal of Analytical Chemistry, Vol.349 (1994) pp.510-515

Ramana, A. and A. Sengupta, "Removing Selenium(IV) and Arsenic(V) Oxyanions with Tailored Chelating Polymers", Journal of Environmental Engineering, Vol.118, No.5 (1992) pp.755-775

Saisho, H. and Y. Fujimura, "Lanthanum Coprecipitation Method for the Determination of Selenium in Environmental Water", Analytical Sciences, Vol. 6 (1990) pp.619-621.

Underwood, E.J., Trace Elements in Human and Animal Nutrition, Fourth Edition, Academic Press, New York, (1977), pp.302-346

Volchek, K., Keller, L. and D. Velicogna, "Polymer Binding/Ultrafiltration as a Method for Concentration and Separation of Metals", Journal of Membrane Science, Vol.79 (1993) pp.253-272

Volchek, K., Legault, A.S. and L. Keller, "Reagent Membrane Separation as a Method of Metal Removal from Water: The Case of Competitive Binding", Proc. 9th Technical Seminar on Chemical Spills, Edmonton (1992) pp. 49-51

EVALUATION OF STEAM STRIPPING FOR THE RECOVERY OF XYLIDINE AT FORMER MISSILE SITES

By

Janis Avotins*, Valdis Kokars*, Laura Ouellette**, Harry Whittaker**

* Riga Technical University, Riga, Latvia
**Environmental Technology Centre, Environment Canada, Ottawa, Ontario

Introduction

Since 1994, work has been conducted on a Canadian-Latvian joint project, one of whose purposes is to conduct site assessment and remediation research for the clean up of two former soviet military bases in Latvia. The results of the site assessment conducted in August 1995 indicate that soil and ground water on these bases are contaminated with missile fuel SAMIN. The main toxic component of SAMIN is a 2,4-xylidine and 2,5-xylidine mixture present in a 3:1 ratio respectively. The xylidine contamination levels varied from a few hundred to a few thousand ppm (in some places more than 20,000 ppm). Due to the high levels of contamination and the industrial value of these products, a focus of this project has been to recover the xylidine through the development of a non-destructive xylidine concentration and recovery process (Avotins, 1996).

A xylidine separation technology has been developed which, preliminary studies have shown, is able to remove xylidines from a water matrix in the form of xylidine organic acid salts. The effectiveness of the xylidine separation increases if the feed to this process is a concentrated xylidine-water solution.

The main soil decontamination technologies proposed in this process are a low temperature desorption (LTD) process and soil washing (Avotins, 1996). The condensates recovered from the low temperature desorption of xylidine-contaminated soil typically have a large xylidine content which can form emulsions when the xylidine concentrations are above 10,000 ppm. These solutions are sufficiently concentrated for use in the xylidine separation process. As the LTD process can be quitely costly, an alternate soil decontamination method was proposed, namely, soil washing. However, in the soil washing process large quantities of contaminated water are generated which contain a relatively low concentration of xylidines. The groundwater at these contaminated sites may also have relatively low concentrations of xylidines. In order to effectively recover the xylidines, it is therefore necessary to concentrate these xylidine-water solutions.

Steam stripping is effective for separating volatile compounds with low solubility in water and relatively low boiling points. Although xylidines have boiling points over 210°C (Chemical Safety Data Sheets), it was predicted that as these compounds have a low solubility in water that the xylidine contaminants could be effectively recovered and concentrated using steam stripping.

Background

For many years air stripping has been used to remove volatile organic contaminants (VOCs) from water. Although steam stripping can be costly to operate, the range of contaminant types that can be treated with stream stripping is much greater than with air stripping (Punt, 1991). In addition, the off-gases from an air stripper must be treated to prevent the release of volatile contaminants to the air (Tchobanoglous, 1987). Steam stripping has been successfully used in the field to remediate VOC contaminated groundwater (Punt 1991; Ladanowski, 1993).

Steam stripping allows steam to come into contact with the contaminated water causing the contaminants to volatilize and transfer from the water to the steam. Although the contact between the two phases may be achieved by a variety of methods, most traditional units are counter-current packed columns (Sundstrom, 1979; Punt, 1991). The driving force for the contaminant transfer is the concentration differential between the liquid and vapour phases. The vapour outlet stream is condensed and the contaminant is recovered in a concentrated water stream. The stripping temperature is an important parameter since Henry's law constant (ratio of the contaminant concentration in the water and vapor phases) is temperature dependent (Sundstrom, 1979, Tchobanoglous, 1987). Other important system operating parameters to consider are the steam to feed ratio, the pH of the feed stream and the initial contaminant concentration.

Methods and Materials

This research project used both spiked water samples and contaminated water samples. The contaminated water samples were produced from soil washing experiments conducted with soil samples collected from a former military base in Barta, Latvia. Spiked water samples were produced by adding specific amounts of 2,4 xylidine and/or 2,5 xylidine to deionized water. The pH of the samples were adjusted using sulphuric acid.

The analysis of the xylidine and oil products were performed by gas chromatography/FID and UV-VIS spectrometry.

Results and Discussion

Spiked water samples were utililized to assess the feasibility of steam-stripping as a method of xylidine extraction and concentration. The spiked samples consisted of water solutions containing 300 ppm of pure 2,4-xylidine, pure 2,5-xylidine, and a mixture of 2,4 and 2,5-xylidine prepared in 3:1 proportion. The spike xylidine mixture was prepared to better simulate the contaminants found on the sites as described above.

The results obtained, as shown in table 1, indicate that there is practically no difference in the results of experiments conducted with spike solutions of 2,4-xylidine and 2,5-xylidine. The slightly lower concentration obtained in the column tops stream for the 2,4 xylidine spike solution experiments can be attributed to its greater solubility in water.

Table 1

Final concentrations and removal efficiency of xylidines from contaminated water with initial concentration of 300 ppm

Feed/steam ratio, L/kg	Concentrations of xylidine, ppm				
	2,4 xylidine			2,5 xylidine	mixture*
	tops	bottom	removal, %	tops	tops
1.9	199	60	74.2	191	197
2.5	526	79	66.1	518	515
4.1	836	97	60.3	851	843
5.1	1108	131	48.4	1149	1121

* - mixture of 2,4 and 2,5 xylidines in a ratio 3:1

The experiments conducted with the 3:1 xylidine isomer mixture, also had similar results to the 2,4- and 2,5-xylidine experiments. It was noted that the xylidines which were collected in the column tops and the bottom streams retained their original isomer proportions.

As discussed previously, the column tops stream will undergo further treatment in the xylidine extraction/precipation process. As its effectiveness is highly dependent upon the concentration of the xylidine solution entering this process, it was considered expedient to determine the operating parameters that maximize the effectiveness of steam-stripping. The parameters that were examined are the initial xylidine feed concentration, feed/steam ratio, feed pH, and feed temperature.

The results of the research on the effect of initial xylidine concentration and feed/steam ratio on the xylidine concentration in the column tops, and on the removal efficiency are shown in Table 2. These results indicate that a greater effect can be obtained for lower initial xylidine concentration feed solutions. This effect can been seen by noting that the concentration factor of xylidines in the tops stream is as high as approximately eight times for 25 ppm feed stream while it is approximately five times for 508 ppm feed stream. Although a marked increase is noted in the column top stream concentration with increasing feed/steam ratios, a decrease is observed in the removal efficiency. This indicates that the absolute quantity of xylidine extracted from the water has decreased. This may be attributed to resultant increase in the bottoms stream flowrate when compared to the steam flowrate.

Table 2
Removal Efficiency and Final Concentration of Xylidine at the Different Initial Concentrations and Feed/Steam Ratio

Feed/steam ratio, L/kg	Final conc. at the column tops(ppm) and removal efficiency(%)					
	initial conc.- 25 ppm		initial conc.-112 ppm		initial conc.- 508 ppm	
	ppm	removal,	ppm	removal,%	ppm	removal,%
1.4	16	93.4	67	90.9	237	70.3
1.9	21	89.1	90	85.9	333	69.7
2.4	43	83.6	174	78.1	683	67.2
3.6	63	77.2	263	73.1	1,035	63.2
4.5	96	67.6	392	63.0	1,602	56.5
5.6	143	58.1	565	52.4	2,242	45.7
7.2	199	40.6	799	37.3	2,506	31.2

Xylidine solubility in water is dependent on the pH of the solution. Increasing the solution acidity causes the xylidines to protonate and their solubility increases dramatically. Consequently, the steam-stripping effectiveness is very much dependent on the pH of the feed stream. By decreasing the feed pH from 8.2 to 2.7, as shown in Table 3, the concentration of xylidine in the column tops stream is more than four times lower. As the terrain of the former military bases in Latvia from which the contaminated samples were taken are swampy, the soil and water are acidic. It is therefore expected that for the field demonstration to be conducted in August, 1996 pH adjustment of the groundwater will be necessary.

Table 3
Effect of pH on Xylidine Concentration in Steam Stripper Column Tops with Initial Feed Concentration of 774 ppm

Feed/steam ratio, L/kg	Final xylidine concentrations (ppm) at the top of column at different pH			
	pH 2.7	pH 5.3	pH 6.1	pH 8.2
1.9	734	1165	1752	1768
3.6	834	2438	3288	3294
5.3	962	3172	4061	4058
8.5	1053	3551	4661	4682

As expected the volatility of xylidines are temperature dependent. Therefore, experiments were conducted to determine the effects of preheating the feed stream on the concentration of xylidines recovered in the column tops stream. As shown in Figure 1 below, an increase in the feed stream temperature increases the concentration of the xylidine solution in the column tops stream. The removal efficiency for the steam stripping of contaminated water samples, as shown in Figure 2, behaves in a similar manner to the spiked solutions as it decreases with increasing feed/steam ratios. However, the effect of the steam/feed ratio for the contaminated water samples is less pronounced with the higher feed stream temperatures. As less steam in the process is lost to heating the feed stream, the flowrate of the tops stream is increased which results in a corresponding increase in recovery.

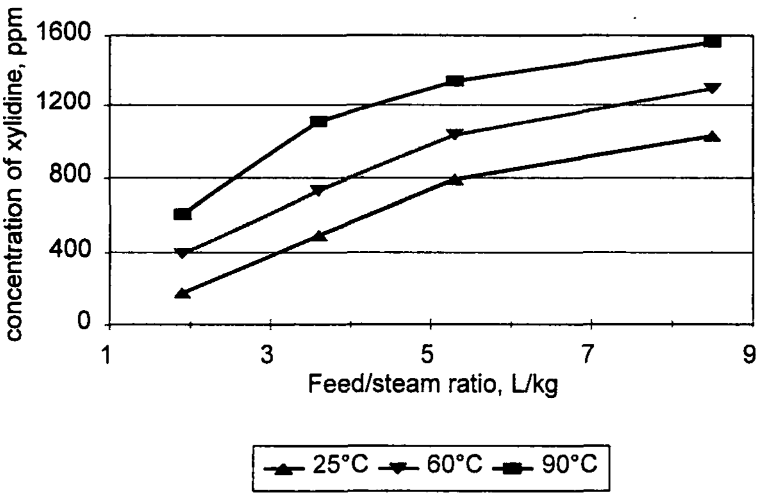


Figure 1 Concentration of xylidine from contaminated water experiments (initial concentration - 245 ppm) in the steam stripper column tops

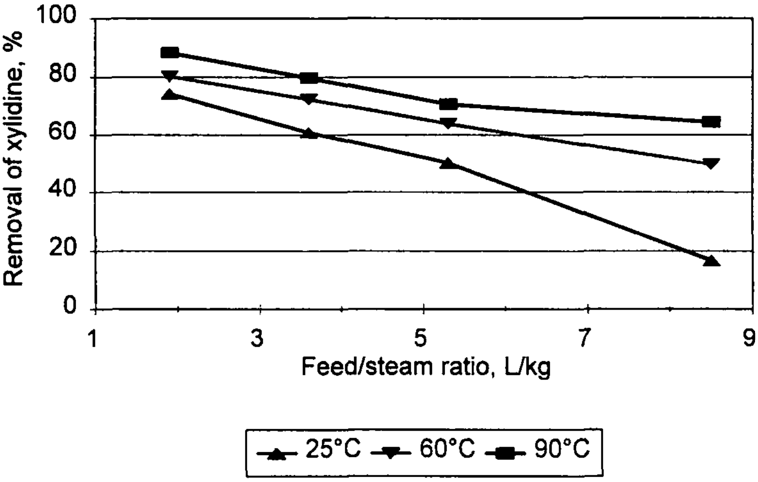


Figure 2 Removal efficiency of xylidine from contaminated water experiments (initial concentration - 245 ppm)

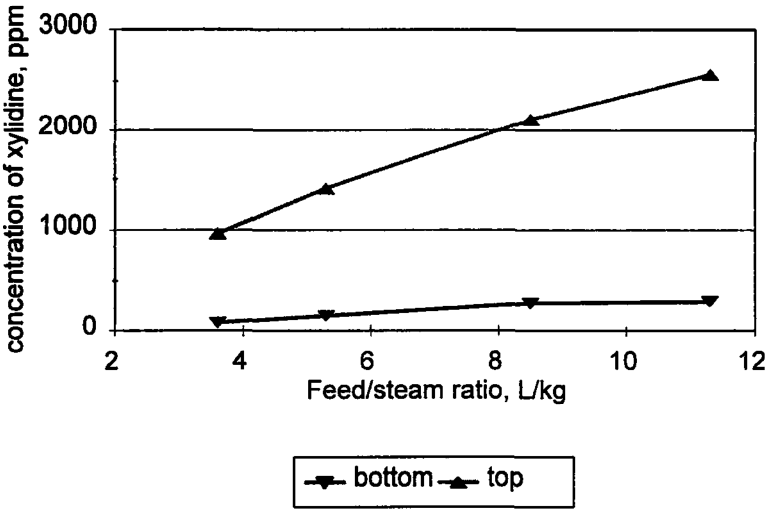


Figure 3 Concentrations of xylidine from contaminated water experiments (initial concentration - 978 ppm)

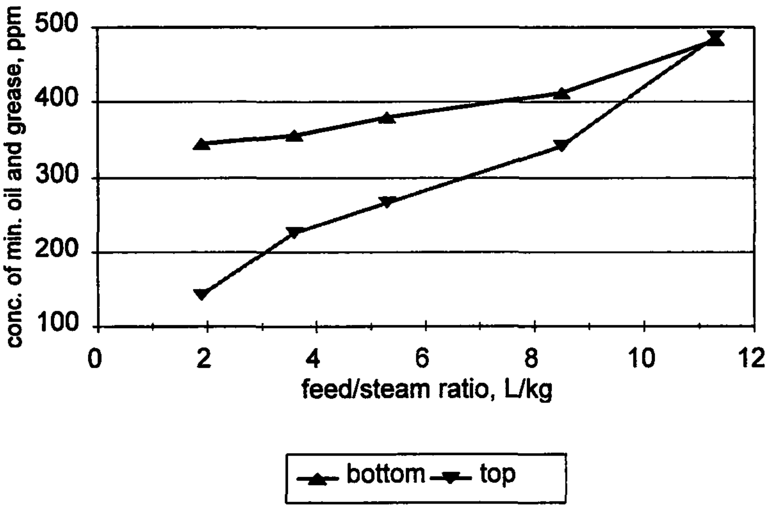


Figure 4 Concentration of mineral oil and grease from contaminated water experiments (initial concentration - 553 ppm)

Figures 3 and 4 show the results of experiments utilizing contaminated water from soil washing experiments for which the feed stream was preheated to 90 °C. Figure 3 shows that the effect of the feed/steam ratio on the concentration of xylidines recovered in the column tops stream is not as prominent as for the spiked samples. It is proposed that this is due to the carryover of mineral oil and grease (MOG) in the column tops stream which acts as a co-solvent for the xylidine, as shown in Figure 4.

Conclusions

Analysis of the research results indicates, that under optimum conditions, steam stripping is technically feasible and an effective method for removal and concentration of xylidine from contaminated water.

The separation process effectiveness can be increased by making use of a preheated feed stream and by maintaining the feed pH value above six.

References

Avotins, J., Kokars, V., Ouellette, L., Whittaker, H., 'Development of Treatment Trains for Remediation Demonstration Project at Former Missile Sites' , to be presented at 13th Technical Seminar on Chemical Spills, Calgary, Alberta, 1996.

Chemical Safety Data Sheets, Volume 4b: Toxic chemicals (m-z), Royal Society of Chemistry.

Ladanowski, C., Proceedings of the 10th Technical Seminar on Chemical Spills, St. John, N.B., 1993.

Punt, M., Whittaker, H., Proceedings of the Eighth Technical Seminar on Chemical Spills, Vancouver, B.C., 1991

Sundstrom, D.W., Klei, H.E., Wastewater Treatment, Prentice-Hall, 1979.
Traver, R.P., O'Brien, S., Clean-up of Contaminated Sites, Insight Press, Article VII, 1992.

Tchobanoglus, G., Schroeder, E.D., Water Quality, Addison-Wesley Publishing Company, 1987.

REEVALUATING TANKCAR COMMODITY TRANSFER FACILITY DESIGN AND SPILL CONTAINMENT PANS TO LOWER ENVIRONMENTAL RISKS AND DISPOSAL COSTS.

By Merrill Bishop, President,
Trans Environmental Systems, Inc
P O Box 40163
Cleveland, OH 44140

ABSTRACT

This presentation will review the standard railroad track spill containment methods currently in use at industrial facilities and then proceed to establish relative costs New site design ideas will be introduced that will greatly reduce initial capital costs for construction By minimizing the collection of rainwater, the plant operators can reduce the costs of disposal of contaminated rainwater and reduce the possibility of minor releases that will be washed into a major remediation expense

Many industrial plants use sheet type, open spill deflectors on their loading railroad spur tracks to guide any spills into collection moats where it is collected, tested, and disposed of These weather related deposits now end up in these pans The cost of this method of spill collection is developed using current construction methods and costs

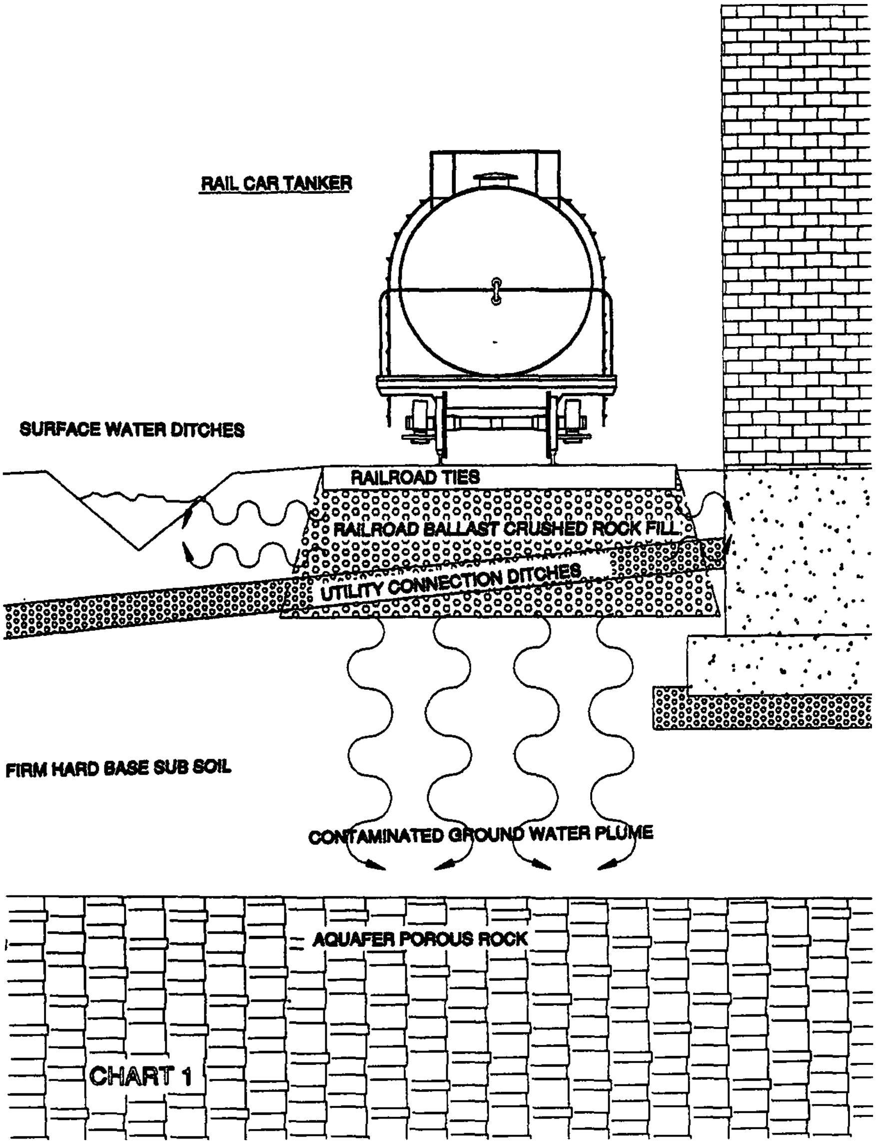
The cost of testing and disposal of the collected rainwater and the labor to clean out these moats and drainage systems rarely is weighed by the same person specifying the purchase of a spill pan system These follow-on operational costs and employee safety issues are discussed herein Innovative new designs are presented that overcome the traditional problems of rainwater, groundwater flows, and drainage piping systems By incorporating these innovations in new facilities, and in retrofitting of the present transloading sites, plant operators can lower their environmental liability

Millions of dollars have been spent on remediation of contaminated groundwater and soil at industrial plant sites. A few billion more words have been written justifying the clean-up methods to regulatory commissions and to company financial officials Most of this expenditure of effort could have been prevented with the investment of a few thousand dollars worth of spill prevention equipment. Often, with just minor changes in the manner that the unloading/ loading site was laid out, the impact of an accidental release could have been minimized. Consequently, the financial impact to the company could have been reduced and the company's reputation within the industrial community could have been better protected..

With more strict enforcement of the "Clean Waters Act" by the EPA and the "flame" of public awareness being fanned by active environmental groups, railroad transloading facilities may well become the target of increased surveillance and public criticism While the railroad industry has managed to avoid the public spotlight, excluding train derailments, they are becoming increasingly aware that in certain instances their switching yards and spur tracks are contaminated. **This residue of many years of spills and releases is usually caused by less than careful handling during the transfer of commodities** Environmental awareness should encourage the companies using railroad shipments to use proper spill containment on site, or to contract with transloading facilities that are properly equipped. <u>These concerns underscore the importance that transloading facilities are designed to insure that inadvertent releases do not get into the surface or sub-surface ground water to cause soil or water contamination</u>.

The costs related to soil and ground water remediation are well documented. The remediation industry has quickly grown into a multi-million dollar business that employs lawyers, hydrologists, geologist, chemists, civil engineers, and a large group of bureaucratic department administrators. It does not take long to figure who pays for this vast pool of specialists and administrators. A few years ago a large petro-chemical company acquired a new site that had been contaminated by many years of careless handling of hazardous materials. Upon digging the footings for a new building, **they paid $1,000 per cubic yard for the disposal of the removed soil.** This was not just the dump truck and backhoe costs. It included the lawyers fees, the permit filing preparation, the many trips to the EPA office to discuss the proposed plans and to obtain the clean-up permit, as well as the team of soil analysts and chemists that were required to confirm the soil conditions. A typical industrial plant's spur track, under just one tank car, may include 500 cubic yards of material that would be subject to spill contamination. **Very few industrial companies can afford $ 500,000 per tank car position to remediate.**

It is difficult for some industrial managers to visualize that a plant site is actually a maze of mini-aquifers. Using the standard practice of backfilling all piping ditches with "pea-sized" gravel to properly seat the pipes, you now have constructed a flow path around the outside of each buried utility conduit or pipe. This web of sub-surface flow is a "sleeping" situation that can quickly awaken and bite you in the billfold. One of the largest, longest and worst of these plant aquifers is your railroad spur track.


RAIL CAR TANKER
SURFACE WATER DITCHES
RAILROAD TIES
RAILROAD BALLAST CRUSHED ROCK FILL
UTILITY CONNECTION DITCHES
FIRM HARD BASE SUB SOIL
CONTAMINATED GROUND WATER PLUME
AQUAFER POROUS ROCK
CHART 1

To better understand how to limit your environmental liability, let us review a little basic civil engineering as applied to railroad track construction. The coarse crushed rock base under the railroad ties, called ballast, is placed there to provide a firm base and distribute the hundreds of tons of force that hammer on the rails with a passing train With firm subsoil, this layer of compacted ballast rock may be only two feet thick and fifteen feet wide (See Chart #1) More than likely this ballast goes to a depth of four to six feet and may spread to over twenty feet at the base. This channel of porous, crushed rock also allows rainwater to drain down and away from the ties. This draining away of surface water also limits the growth of trees and other vegetation near the tracks. These channels of porous rock may run endlessly for miles and usually are only broken by an occasional railroad bridge or culvert at a stream crossing. A railroad embankment is perceived as a dike but really is a creek filled with crushed rock with a slow moving, but constant downhill flow This basic civil engineering design has worked well for over a hundred years, but the scary downside of this rock filled aquifer is that it will quickly transmit a chemical spill down this channel and into the surface or sub-surface groundwater Each succeeding rain or spring thaw adds more water to irrigate this contamination further from the source.

Many railroads and transloading facilities have installed conventional spill diverting aprons under their tank car loading and unloading locations to divert any dribbles and inadvertent discharges into control trenches and into collection moats or sumps While this is a step in the right direction it also creates a number of other problems and recurring expenses for the transloading and terminal operations

These **conventional spill diverting aprons, whether of fiberglass or steel, do not actually hold any liquid but merely divert it into cross-under trenches** and then it is piped into collection moats. These diverting panels overlap like shingles and must be installed tightly under the head of the rails This often requires cutting notches for rail splice plates and other required track hardware Any liquid landing directly on top of the head of the rail will still flow down the sides and often pass through the gap between the pan and the neck of the rail. **The overlapping panels, even if they are caulked upon installation, will often leak** since the panels are subject to both thermal expansion and the continual flexing caused by a passing railroad car wheel These long bottom seams, or lap joints, interfere with liquid flow and are subject to differential forces when walked upon

Though advertised as spill pans, these overlapping sheets require extensive support construction Since the pans will collect everything that drops within their surface area, the supporting piping or trench system must be sized to handle the expected flow of the chemical spill, as well as the peak rain fall of that region. For example, in New Jersey with an average rainfall of 53 inches per year, **a typical tankcar-sized open spill pan will collect over 25,000 gallons of surface water per year that must be disposed of properly.** Depending upon the slope of the railroad bed at the location of these aprons, a cross-under trench is required every hundred feet to divert this collected flow into a piping system and into the collection pits The sizing of piping is a civil engineer's routine design consideration. In this case the piping may involve a series of eight inch feeder pipes emptying into larger and larger piping until reaching a collection pit or moat **During a**

heavy rain of only one inch, a single tank car position will create a flow of over 500 gallons of water down this system.

Often hundreds of feet of rainwater piping will be terminated into one large pit for processing. This pit has to be sized to handle the rainwater flow as well as the EPA specified amount of discharge from the tank cars If your local EPA enforcement official interprets that the commodity you are planning to transload meets certain governmental criteria, he could require that the pit be sized to contain the contents of a single tank car plus the heaviest rain in ten years plus a 10% safety factor A pit that will hold 25,000 gallons of rainwater as well as 27,000 gallons from a tankcar will be the size of two railroad tank cars or roughly fourteen feet wide, by ten feet deep, by fifty feet long Since these moats will be containing hazardous materials, in most cases under new EPA diking directives, these pits must be lined with an epoxy coating or other sealant **Concrete by itself is actually porous to many petro-chemicals over a period of time** and usually settling cracks or construction joints can open up and allow slow releases into the packed sand base under the concrete If pipes traverse this backfill sand reservoir, contamination can now enter the piping maze throughout the plant site.

Few companies using tankcars can afford to build large canopy shelters to limit accumulated rainwater in these collection systems, trenches or moats. Often they install oil-water separators to remove the major amounts of petro-chemicals in the collected water Unfortunately these separator units cannot be allowed to freeze so they require a heated shelter building near the collection moat A complex series of pumps will be needed to handle the contaminated water and any separated oils or commodities **With stricter enforcement of the "Clean Waters Act", municipal sewer plants are now reluctant to accept this pre-processed rainwater and will require outside laboratories to approve the collected water prior to its discharge into public sewers. This often costs $ 1,000 per sample, depending on the amount of analysis or intended disposal.** When using open spill diverting aprons, where all spills drain into the same moat, the contamination of this rainwater will be a variable "brew" of chemicals that will require more complex testing and processing This "brew" definitely should not be discharged into a septic field because the basic design of a septic field is a direct avenue into the sub-surface water system **In most states, the cost of hauling off this contaminated water will vary, often over $1.00 per gallon.** Even if your plant has its own wastewater pre-processing capability, there is a cost involved in handling this tainted rainwater. Some facilities have quoted around sixty cents per gallon. Incinerators do not want it since it requires thousands of BTUs of good burning fuel to evaporate the water. Advanced filtration systems like RO's (reverse osmosis) are usually too expensive for terminal operators to afford, and too complex to properly operate to insure output within the EPA guidelines. If plant operators cannot dispose of the contaminated rainwater within the plant they must pump it into trucks or tank cars, and pay the toll to ship and dispose of the "brew"

At most large chemical plants and refineries, the loading rack area has been covered with a canopy roof to reduce the amount of rain water collected and provide some basic weather protection These large canopy structures often will cover two or more tank cars with an elevated platform between the tracks to facilitate an operator opening the tank car hatches and monitoring the loading. With the railroad safety clearance of 23 feet above the top-of-rail, these structures must be high and braced to withstand the wind effect on a tunnel shaped building. In cold, snowy regions this structure must also withstand a heavy snow loading since there is no heat on the underside of the roof panels to melt the residual accumulation

In regions of adverse weather and high winds, side walls are usually added to these loading rack buildings to limit the blow-in of rain and snow. This added protection also creates additional construction and permitting problems. In most locations the local fire marshals require that these enclosed facilities be sprinkler system protected. This requires a complex, dry pipe system since the overhead sprinklers are not in a heated environment and must function at 20 degrees below zero This adds appreciably to the cost of enclosing a loading rack with a canopy and walls.

While the previous discussion has been focused on the construction of open-apron type spill pan systems, the day-to-day upkeep of these systems should be examined before deciding to purchase and install them at a transloading facility Open pans by their design collect anything that blows into them including snow, debris, dirt or sand. **The snow and ice problem is one of the most difficult to handle because it is a very labor intensive chore to chip and shovel out these pans. Often the task of unplugging the frozen drains and the cross-under trenches is done more than once, due to refreezing.** Conventional open-type spill aprons do not have a smooth bottom because of the overlapping connections. A yard worker picking the ice out of these trenches and sheets will often damage the joint seals which are brittle at these temperatures. During the sunny winter days, the snow on the surface of these conventional spill aprons may thaw and drain into the piping system only to refreeze because the ground around the drainage pipe is frozen.

Most large refineries that have deep, large moats to collect the composite spills and rainwater also have well trained and equipped maintenance staffs. **Under the OSHA Confined Space directive any personnel entering tanks or sump pits deeper than shoulder heighth must be trained and equipped with breathing apparatus and a second trained person must remain outside the moat ready to retrieve the first maintenance person.** This is not only an expensive situation for the small transloading terminal operator but due to the repulsive nature of this work, **the turnover rate of this type of maintenance personnel will necessitate continual training and certification.** If these pits are not maintained and are allowed to fill up with washed in dirt, sand, and debris from these open spill aprons, soon the pit will not meet the required containment volume. The spill collection moat condition is always on the EPA's checklist and your OSHA Confined Space training records need to be current and properly maintained.

Before turning to a timely solution to the previously discussed problems, let us summarize the approximate cost of using the open pan systems for just one tankcar position. Multiple tankcar positions would not necessarily double these costs, but would add to both initial costs and reoccurring expenses.

a.	Overlapping sheet type spill pans cost around \$100 to \$125 per linear foot, so use \$110 per foot for a 60 foot tank car for a total purchase price (not including shipping and taxes)..........	\$ 6,600 US
b.	Piping and cross-under trenching will vary for each site, but at around \$50 per foot for trenching and 8" PVC drain pipe, include 100 ft...	\$ 5,000 US
c.	Since the grating on these open aprons is a separate cost ,and so is the hardware ,leave this blank.	(It could be a few thousand US dollars)
d.	A concrete pit as described above (14' x 10' x 50') will cost approximately	\$ 80,000 US
e.	Applying an epoxy coating that will stand up to petro-chemical solvents	\$ 40,000 US
f.	Building a canopy roof over one position and adding side walls down to the 7 ft perlin with no insulation. Two side walls..	\$50,000 US
g.	Installing a dry pipe, pre-action type sprinkler systems (not including supply piping and pump) .	\$60,000 US
h.	Disposal of blown-in rainwater. Assume 45" of annual rainfall over an area of 11' by 60' and a cost of \$1.00 per gal. for 18500 gal....	\$18,500 US
I.	With maintenance men at \$10.00 per hour and a minimum of two men for four hours, twice a year and adding \$100 per man for equipment costs. .	\$ 560 US
j.	Administrative overhead, permit filing, inspection fees and laboratory sampling fee at \$1,000 per sample every month.	\$15,000 US

These approximate costs will usually not be seen by the same person in larger organizations so the purchasing agent for the construction engineer will usually not have to worry about the recurring costs that must be budgeted by the operations manager. The cost of administering the water testing and permit filing is often blurred into administrative overhead. The Plant managers and decision makers need to have all of these costs when submitting their budget requests

There are many design features that can be built into a transloading site to limit your surface and ground water problems.

a. Divert all pass-through surface water and roof downspout water away from the area where the possible spill would occur This will limit the floating effect that could quickly spread a spill through the railroad ballast and down to the stream.

b Build raincover canopies over the spill collection area or purchase containment pans that have raincovers

c. If the site does not yet have tracks on it, install a polyethylene membrane sheeting under the ballast area and building up the edges to form a basin (See drawing #2). By installing a minor open pumping area like a house basement sump drum, any water or contamination can be collected and removed. If water in this sample sump tests contaminated. it is a simpler task to clean the confined ballast or remove and replace it rather than have this area of contamination slowly migrate down gradient and pollute even more ballast

d. Most EPA officials advocate single point discharge of surface water from hazardous material sites With a single, quickly shut-off drainage or sluice gate, any overflow, spill contaminated water, or even water from a sprinkler system putting out a fire can be contained This is the most economical place to build in the capacity of the total tank car under U S EPA 40CFR 112 7(4)(ii) and the heaviest rain in ten years One major shortcoming of this system is that if it is not allowed to drain during snow and runoff season, it may fill up with ice and be ineffective The capacity and shut off design must be capable of all season operation as well as being operated quickly even under the situation of lost electrical power

e If tracks are already installed in the transloading area it will greatly slow the migration of spills if a bulkhead screen or polyethylene sheet could be installed vertically directly through the ballast area at given intervals and sample sump pits installed immediately up gradient from these screens or weirs These weirs would inhibit the sub-surface flow of water and force any lighter liquid contamination to the surface where it can be detected and removed through the sump pit pumping

f If specific tracks or collection pans are used for a given commodity, only tie these collections units together or to the same auxiliary concrete collection pit. Groundwater that is contaminated with only one commodity is much easier to handle than one that is a "brew" of many different compounds that could interact For instance, a spill of sodium hypochlorite

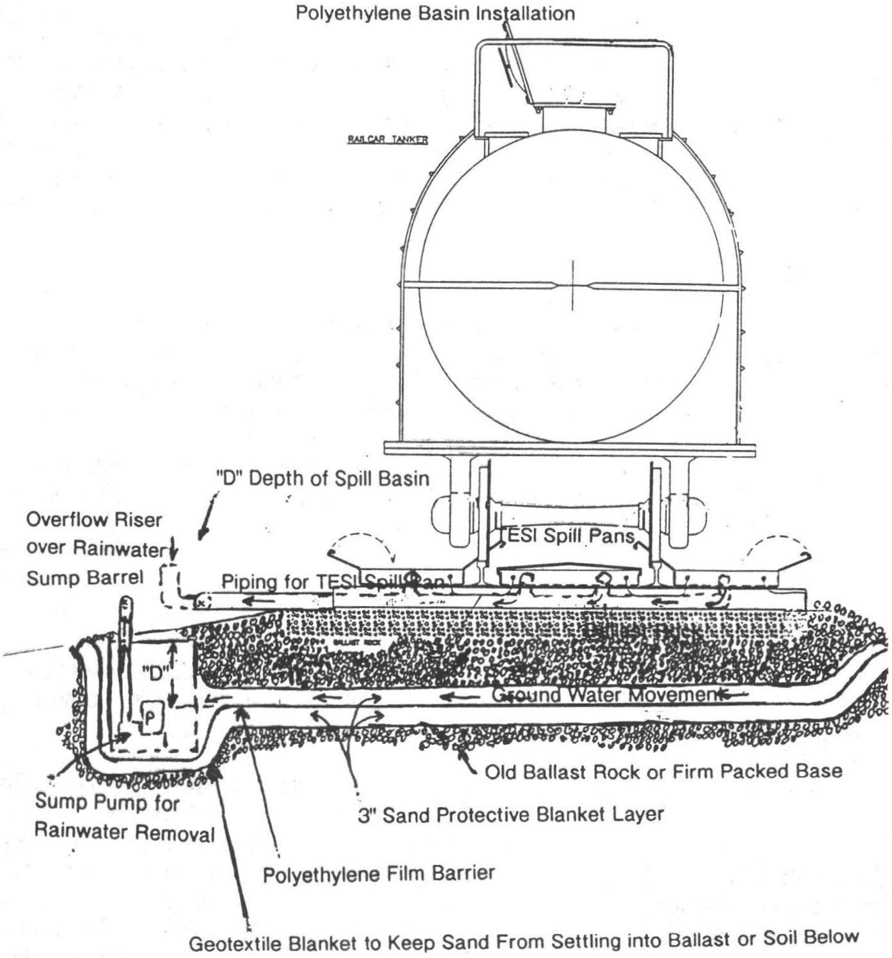

Polyethylene Basin Installation
RAILCAR TANKER
"D" Depth of Spill Basin
Overflow Riser
over Rainwater
Sump Barrel
TESI Spill Pans
Piping for TESI Spill Pan
"D"
P
BALLAST ROCK
Ballast Rock
Ground Water Movement
Old Ballast Rock or Firm Packed Base
Sump Pump for
Rainwater Removal
3" Sand Protective Blanket Layer
Polyethylene Film Barrier
Geotextile Blanket to Keep Sand From Settling into Ballast or Soil Below

CHART 2

would not be good going into a sump pit that is laced with ammonium hydroxide. The resulting chemical reaction could be deadly to operating personnel above the moat or pit

g. Use dry break hose fittings as much as possible and label specific hoses for given uses. These hoses should be racked so that if they do drain, the liquid will be contained. These small dribbles add up to big problems year after year in the same place. If self-contained spill pans with lids are used, leave the pan lid open under the bottom valve for at least overnight following loading to insure that this valve or the steam heat tubing is not leaking. Only after you are sure of the load would you install the safety caps on these outlets.

h. Install, properly maintain, and use high level shutoff devices or alarms. Always insure that you have some alarm device on the tank car or truck to warn of impending overflow Overweight filling that would require pumping off or draining a few gallons from a tank car or tanker truck exposes you to greater risk of spills.

i Develop training programs for all personnel on how to handle tank car equipment, pumps, and hoses The first excuse offered to an EPA investigator following a release will be that the worker or supervisor was not trained to handle the situation. Insure that the required emergency training is genuine and that all soak-up materials and personal safety equipment is available and that it works. This include emergency pumps to empty sump pits or a vacuum trailer and spare tanker trucks Even a facility with shortcomings in design can be improved by anticipating what most likely will go wrong and then positioning the correcting equipment nearby.

A recent innovation on the spill pan market is a self-contained, relocatable pan unit that has a rolling retractable raincover. This unit, manufactured by **Trans Environmental Systems, Inc. of Cleveland, overcomes many of the problems with open, apron type spill pans.** The TESI pan is installed by lag bolting it down to the spur track railroad ties and its rolling lid is lower than top-of-rail so it will not interfere with car movement The containment system also includes two outboard side pans that have flip-flap lids that swing out over the top of the rail head and divert any dribbles into the outboard pans. **These units, when piped together, will contain over 400 gallons of liquid without the need for an auxiliary sump pit.** These pans are equipped with NPT pipe couplings in the ends for piping to a sump pit if the user desires or regulatory officials deem that a greater holding capacity is needed. **Federal EPA statistics from the Emergency Response Notification System, ERNS, show that over 94 % of all petroleum and oils releases reported in 1995 were less than 500 gallons.** (See Chart #3) The use of either the ten or twenty foot long pan under each loading or unloading position allows for the isolation of any release of commodity. **Since the TESI design pans are closed during inclement weather or when not in use, they will not fill up with rainwater, snow or debris. This**

Emergency Response Notification System
Reports of Oil, Paint, and Coatings Releases, 1995[1]

Type of Reported Release	Total Reports	Reports less than or equal to 500 gallons[2]	Reports greater than 20,000 gallons
Total Non-Petroleum Oil	8,066	7,855	17
Rail-Related Non-Petroleum Oil	53	47	3
Total Petroleum Oil	10,804	9,874	50
Rail-Related Petroleum Oil	390	288	7
Total Paint or Coatings	336	334	0
Rail-Related Paint or Coatings	3	3	0

Type of Reported Release	Total Reports	Cause[3]						
		Dumping	Equipment Failure	Natural Phenomenon	Operator Error	Other Cause	Transportation Accident	Unknown
Total Non-Petroleum Oil	8,066	147	526	41	147	174	101	6,930
Rail-Related Non-Petroleum Oil	53	3	10	1	1	2	2	34
Total Petroleum Oil	10,804	304	983	65	285	333	165	8,669
Rail-Related Petroleum Oil	390	14	66	2	12	28	10	258
Total Paint or Coatings	336	9	41	6	10	11	6	253
Rail-Related Paint or Coatings	3	0	1	0	0	0	0	2

[1] This information is based on initial notification data and may be subject to change. This search was performed on January 22, 1996, and reflects data as of this date.

[2] This category includes records with unknown quantities. Many large releases have unknown quantities at the time of the report.

[3] A single report may have more than one cause associated with it.

CHART 3

source containment avoids the need for extensive piping, large pits, and eliminates processing thousands of gallons of contaminated rainwater. These complete pan sets sell for less than the annual cost of rainwater disposal using open apron type containment methods. Major railroad environmental managers and hazardous waste carriers have endorsed this new method.

Method for Estimating the Evaporation Rate and Downwind Dispersion from Spills of Hydrochloric Acid

Robert K. Jones and Roy Overstreet
National Oceanic and Atmospheric Administration
Seattle, Washington
USA

Abstract

Hydrochloric acid is one of the most common hazardous materials involved in chemical spills. Estimating the size of the toxic gas cloud associated with a major spill is complicated by the difficulties inherent in calculating the evaporation rate from an acid solution. The evaporation rate depends on the concentration, which can change significantly as the pool evaporates. This paper presents a simple method for estimating the time-dependent concentration of the pool, release rate and downwind dispersion of hydrogen chloride from the spill of an aqueous solution.

Introduction

Computer models are widely used during emergency response situations to estimate hazard zones associated with toxic gas clouds. Even though hydrochloric acid is one of the most common substances involved in injury-related spills, there have been few attempts to model the time-dependent evaporation and dispersion of the aqueous solution. Modeling the hazard zone associated with liquid mixtures can be complicated because the concentrations of the components change as the mixture evaporates. An additional complication arises when modeling aqueous solutions of very polar substances, like hydrogen chloride (HCl), due to the complicated nature of the relationship between evaporation rate and concentration. This paper describes a simple method for estimating the time-dependent evaporation rate and downwind dispersion of HCl from an aqueous solution.

Method

The method incorporates reasonable assumptions and approximations that allow us to express the peak ground-level concentration of HCl as an algebraic function of distance from the pool. A central premise of the method is that the partial pressure of HCl can be adequately approximated by a simple function of the mass of HCl remaining in solution without explicitly accounting for the evaporation of the water. We coupled the time-dependent evaporation rate to a Gaussian dispersion model using an approximation that is based on the recognition that very close to the pool the peak concentration depends predominately on the peak evaporation rate, while at long distances from the pool the concentration depends more on the time-integrated evaporation rate.

The rate at which a constituent of a mixture evaporates has been described by a rate law proposed by Stiver and Mackay (1984):

$$\frac{dm_i}{dt} = -\frac{K_i \cdot M_i \cdot S \cdot P_i}{R \cdot T}, \tag{1}$$

where K_i is the mass transfer coefficient and is a function of wind speed, Schmidt number, and pool dimensions, M_i is the molecular weight of the component, S is the surface area, R is the gas constant, and T is the temperature and considered constant in the scenarios which we model. The equilibrium partial pressure of a component in a mixture (P_i) can be a complicated function of the masses of all the components of the mixture.

A rigorous application of Eq. (1) to a hydrochloric acid solution must account for the evaporation of both the HCl and water. The partial pressure of HCl can be described well with an exponential function of its weight fraction and the partial pressure of water by a linear function of its weight fraction. By fitting these functional forms to the tabulated data (see Perry et al. 1984), a pair of coupled differential equations were written to describe the evaporation rates of HCl and water:

evaporation
Exponentie

$$\frac{dm_{HCl}}{dt} = -\frac{K_{HCl} \cdot M_{HCl} \cdot S}{R \cdot T} \cdot \left[A \cdot \exp\left(\frac{a \cdot m_{HCl}}{m_{HCl} + m_{water}} \right) \right], \tag{2}$$

Linear

$$\frac{dm_{water}}{dt} = -\frac{K_{water} \cdot M_{water} \cdot S}{R \cdot T} \cdot \left(B + \frac{b \cdot m_{water}}{m_{HCl} + m_{water}} \right), \tag{3}$$

where, A, a, B, and b are constants found from least squares fits to the tabulated partial pressure data. These coupled differential equations were solved using a fourth order Runge-Kutta formula. Figure 1 presents the predicted time dependence of the weight fraction of HCl in a pool, 20 meters (m) in diameter, initially containing 10000 kilograms (kg) of 36% hydrochloric acid, at a temperature of 25 degrees centigrade (°C), exposed to a 1 meter per second (m/s) wind.

Due to the non-linear relationship between concentration and partial pressure, the evaporation rate of HCl drops more quickly than the concentration. As the mass of the evaporating pool approaches zero, the ratio of the evaporation rate of HCl to water equals the mass ratio of HCl to water in solution. This defines the condition for which further evaporation will not affect the concentration of the solution. In the limit, the concentration approaches a terminal value which is close to the concentration of the constant boiling azeotrope. This terminal concentration depends weakly on the temperature, but does not depend on the initial concentration of the solution.

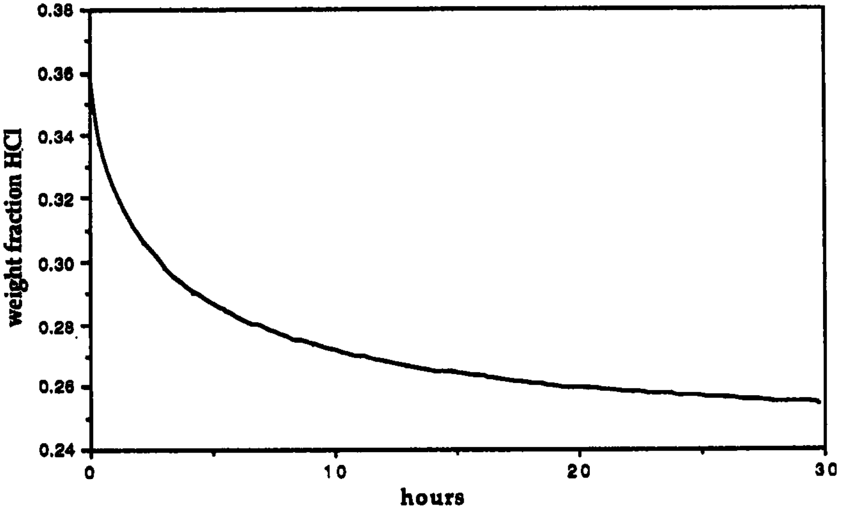


FIGURE 1. Weight fraction of HCl as a function of time.

This paper presents a method for approximating the evaporation rate of HCl without explicitly accounting for the evaporation of water. This approximation method is computationally simpler than the two-component model described above, since the rate law can be described with a single differential equation. For an isothermal evaporation process the partial pressure and, hence, the evaporation rate of HCl can be easily determined at two times: at the onset of evaporation (the concentration is at its initial value); and when the mass of HCl remaining in the pool approaches zero (the concentration approaches the terminal value). We propose that the evaporation rate can be approximated between these extremes by an exponential function of the mass of HCl remaining in the pool:

$$\frac{dm_{HCl}}{dt} = -\frac{K_{HCl} \cdot M_{HCl} \cdot S \cdot P_T}{R \cdot T} \cdot \exp\left[\left(\frac{m_{HCl}}{m_o}\right) \cdot \ln\frac{P_o}{P_T}\right], \qquad (4)$$

where, m_o = initial mass of HCl in the solution,
P_o = the initial partial pressure of HCl in solution,
P_T = the partial pressure of HCl at the terminal weight fraction.

The time dependence of the evaporation rate can be found by solving this rate equation and differentiating the resulting expression for mass with respect to time:

$$\frac{dm_{HCl}}{dt} = -Q_o \cdot \left[1 + \left(\frac{Q_o}{m_o} \cdot \ln\frac{P_o}{P_T}\right) \cdot t\right]^{-1}, \tag{5}$$

where, $$Q_o = \frac{K_{HCl} \cdot M_{HCl} \cdot S \cdot P_o}{R \cdot T}.$$

The partial pressure of HCl at the terminal concentration, P_T, can be found at the desired temperature in the following manner. The dependence of partial pressure on weight fraction can be found by fitting a function to tabulated partial pressure in the vicinity of the azeotrope (see Perry et al. 1984 for tabulated data).

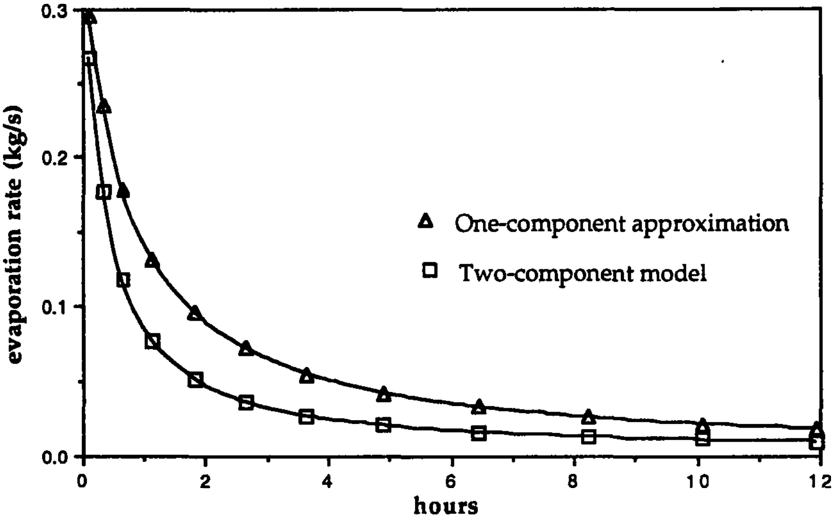


FIGURE 2. Comparison of evaporation rates using a two-component model and the proposed one-component approximation.

At the terminal concentration, the ratio of the evaporation rates equals the mass ratio in solution. The value of W_{HCl} that satisfies the following equation is equal to the terminal weight fraction W_T:

$$\frac{K_{HCl} \cdot M_{HCl} \cdot P_{HCl}}{K_{water} \cdot M_{water} \cdot P_{water}} = \frac{W_{HCl}}{1 - W_{HCl}}, \tag{6}$$

where P_{HCl} and P_{water} are explicit functions of the weight fraction. Once the terminal weight fraction is known, the terminal partial pressure can be found from the functional relationship between partial pressure and weight fraction.

Figure 2 compares of the evaporation rates predicted using Eq. (5) with those using the two-component model for a pool, 20 m in diameter, initially containing 10000 kg of 36% hydrochloric acid, at 25 °C, exposed to a 1 m/s wind. Evaporation rates computed using the one-component model are consistently higher but within a factor of two of those found using the more rigorous two-component model. This level of agreement generally holds for any hydrochloric acid solution with an initial concentration greater than the terminal concentration. However, for initial concentrations less than the terminal concentration Eq. (5) might predict evaporation rates much lower than the two-component model.

The downwind dispersion of evaporated HCl is estimated by the use of a Gaussian plume model with a time-dependent source. The source, given by Eq. (5), decreases as 1/t, which presents a difficulty in obtaining analytic solutions to the advection-diffusion equation. However, there is a well-known analytic solution for the centerline concentration for a Gaussian plume having an exponential source (Wilson 1981a, 1981b). Furthermore, such a model is easily extended to one that uses a series of exponential sources.

$$Q(t) = \sum_{i}^{n} \gamma_i \cdot e^{-k_i \cdot t} \tag{7}$$

The original 1/t source in Eq. (5) was replaced by Eq. (7) with two terms:

$$Q(t) = \frac{Q_o}{1+\mu}\left(\mu \cdot e^{-k_1 \cdot t} + e^{-k_2 \cdot t}\right), \tag{8}$$

where $k_1 = \frac{1}{\varphi - 1} \cdot \frac{Q_o}{m_o} \cdot \ln\left(\frac{P_o}{P_T}\right)$, $k_2 = \frac{k_1}{\mu^2}$, and $\mu = \frac{m_o}{Q_o} \cdot k_1$.

The constant φ is a dimensionless parameter chosen by eye to maximize the match between Eqs. (5) and (8).

The parameter μ and the rate constants k_1 and k_2 are specified functions of puddle mass and area, mass transfer coefficient, solution strength, and vapor pressure. Usually, $\mu >> 1$, so that the first term in parentheses of Eq. (8) governs the early part of the discharge, while the second term ensures that mass is conserved for long lived emissions, such as that from a slowly evaporating pool. The form of Eq. (8) was adapted from transient discharges from long gas pipes, where both short-term and long-term releases can be important (Wilson 1981a, 1981b). Also, Eq. (8) is easily simplified. If $\mu = 0$, the source is a single-term exponential. if $\mu = k_2 = 0$, the source is reduced to a steady source Q_o.

The general solution to the advection-diffusion equation can be written

$$C(t) = \sum_{i=1}^{2} \beta_i \cdot C_i(t). \tag{9}$$

The concentration $C_i(t)$ is found to be (van Genuchten and Alves, 1982 and Overcamp, 1988):

$$C_i(t) = \frac{Q_o \cdot e^{-k_i \cdot t}}{2 \cdot (\pi \cdot \sigma_y \cdot \sigma_z \cdot u)} \cdot e^{-\frac{1}{2}\left[\frac{x^2}{\sigma_x^2} - \left(\frac{\alpha_i \cdot \sigma_x}{u}\right)^2\right]} \cdot \left[1 + \mathrm{erf}\left(\frac{u \cdot t}{\sqrt{2} \cdot \sigma_x} - \frac{\alpha_i \cdot \sigma_x}{\sqrt{2} \cdot u}\right)\right], \tag{10}$$

where the coefficients are

$$\beta_1 = \frac{\mu}{1+\mu},$$

$$\beta_2 = \frac{1}{1+\mu}, \text{ and}$$

$$\alpha_i = \left(k_i + x\frac{u}{\sigma_x^2}\right).$$

Equation (10) uses Briggs' rural dispersion coefficients for σ_y and σ_z (Plate 1982). In recognition of the possible importance of longitudinal dispersion in transient releases, Beals' (1971) formulation for the coefficient σ_x has been used. The simple, analytic solution given by Eq. (10) assumes that the dispersion can be calculated locally, so that the σ's do not require integration with respect to downstream distance x. Wilson (1981a, 1981b) showed that for transient sources, the shape of the plume's centerline concentration was very similar to the shape of the source itself, giving rise to a so-called "frozen-source" approximation.

Figure 3 compares the 1/t evaporation rate given by Eq. (5) and the matching double-exponential given by Eq. (8).

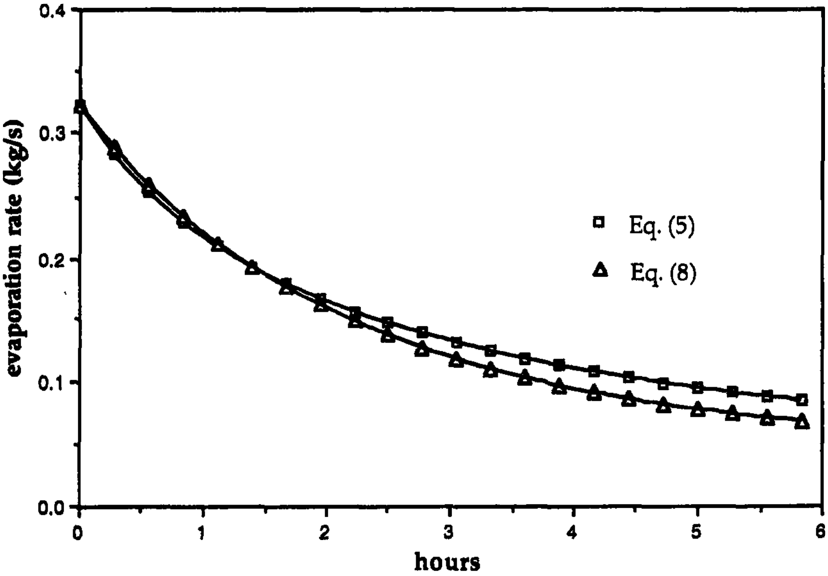


FIGURE 3. Comparison of evaporation rates as a function of time predicted using Eq. (5) and with Eq. (8).

Hazard zones are often determined by calculating downwind plume "footprints" from Gaussian models. In the case of transient releases, it is much easier to focus on the downwind history of the maximum, centerline concentration rather than a complete footprint. The location and magnitude (C_{max}) of the maximum in the concentration from Eqs. (9) and (10) can be found by a simple maximization routine. This paper presents a much simpler method of determining the location and value of the peak concentration that obviates the need to use Eqs. (9) and (10) altogether. This method is based on the similarity in formulation of the centerline concentration for a steady release and that for an exponential release averaged over the transit time to the receptor, which is essentially the distance to the receptor (x) divided by the wind speed (U). The peak concentration can then be calculated as a function of downstream distance from the source with the following approach.

The average discharge rate is defined as follows:

$$Q_{ave} = \frac{1}{2} \cdot \frac{m_R}{t_{ave}}, \tag{11}$$

where m_R is the amount of material released into the atmosphere during the nominal travel time, x/U, and t_{ave} is the discharge-weighted average travel time.

The mass released until x/U is

$$m_R = \int_0^{\frac{x}{u}} Q(t)\cdot dt, \qquad (12)$$

and the discharge-weighted, average travel is given by

$$t_{ave} = \frac{\int_0^{\frac{x}{u}} Q(t)\cdot t\cdot dt}{\int_0^{\frac{x}{u}} Q(t)\cdot dt}\,. \qquad (13)$$

A receptor located at x experiences, at time x/U, a peak concentration

$$C_{peak} = \frac{Q_{ave}}{\pi\cdot\sigma_y\cdot\sigma_z\cdot U}\,. \qquad (14)$$

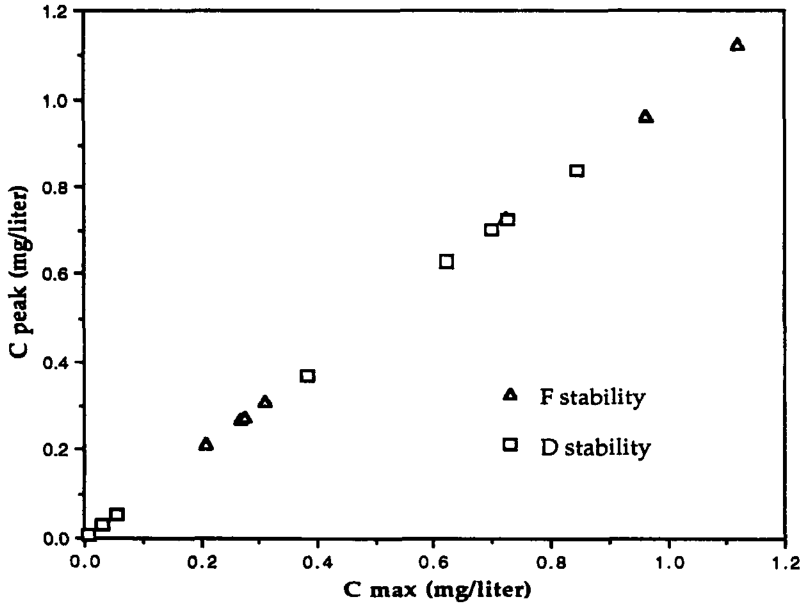


FIGURE 4. Comparison of predicted peak concentrations from the maximization of Eqs. (9) and (10), C_{max}, and from Eq. (14), C_{peak}.

The predicted peak concentrations for a range of wind speeds, pool sizes, and distances from the source using the simplified method described by Eq. (14) were compared with those predicted using the Gaussian dispersion method described by Eqs. (9) and (10). Figure 4 clearly shows that for D and F stability the simple form described by Eq. (14) gives almost exactly the same result as that obtained from maximization of Eqs. (9) and (10).

The simplified method for obtaining peak concentrations can be easily combined with the release rate approximation described by Eq. (5). The integrals in Eqs. (12) and (13) can be solved analytically, and the expression for the average release rate given by Eq. (11) can then be written as an algebraic function of distance downwind:

$$Q_{ave} = \frac{Q_o}{2}\left\{ \frac{\left[\ln\left(1 + \frac{Q_o \cdot x}{m_o \cdot U} \ln \frac{P_o}{P_T}\right)\right]^2}{\left(\frac{Q_o \cdot x}{m_o \cdot U} \ln \frac{P_o}{P_T}\right) - \left[\ln\left(1 + \frac{Q_o \cdot x}{m_o \cdot U} \ln \frac{P_o}{P_T}\right)\right]} \right\} \qquad (15)$$

Sample Calculation

The computational steps needed to calculate the concentration downwind from a spill are outlined here and a specific example is given involving a 10000 kg circular pool of 36% hydrochloric acid with a surface area of 314 m^2. The temperature is considered constant at 25 °C , wind speed is 1 m/s, and the stability class is F.

The mass transfer coefficient for water can be computed using a formula proposed by Mackay and Matsugu (1973),

$$K = \frac{0.0048 \cdot U^{7/9}}{Z^{1/9} \cdot Sc^{2/3}}, \qquad (16)$$

where, K = mass transfer coefficient in m/s,
U = wind speed at 10 m in m/s, and
Z = diameter of pool in the direction of the wind in m.

The Schmidt number (Sc) is the ratio of the kinematic viscosity of air to the molecular diffusivity of the evaporating substance. At 25 °C the kinematic viscosity of air is 0.156 cm^2/s, and the molecular diffusivity of water vapor is 0.27 cm^2/s (Evans, 1993). The molecular diffusivity of HCl can be derived from that of water vapor using Graham's law (Thibodeaux, 1979)

$$D_{HCl} = D_{water}\sqrt{\frac{M_{water}}{M_{HCl}}}\ . \tag{17}$$

Calculated values for the Schmidt numbers for water and HCl at 25 °C are 0.58 and 0.84 respectively. The mass transfer coefficients for water and HCl are 0.0050 m/s and 0.0039 m/s respectively.

The functional dependence between partial pressure of HCl and weight fraction of HCl in solution in the vicinity of the azeotropic mixture is found by fitting an exponential function to the tabulated data at 25 °C (Perry et al. 1984),

$$P_{HCl} = 0.01817 \cdot \exp(38.71 \cdot W_{HCl}). \tag{18}$$

A linear function fits the partial pressure data for water,

$$P_{water} = 3629 - 8833 \cdot W_{HCl}. \tag{19}$$

These functions are combined with Eq. (6) and the terminal weight fraction (W_T) is found by using a numerical technique to solve the following equation,

$$\frac{K_{HCl} \cdot M_{HCl} \cdot (0.01817 \cdot \exp(38.71 \cdot W_T))}{K_{water} \cdot M_{water} \cdot (3629 - 8833 \cdot W_T)} = \frac{W_T}{1 - W_T}. \tag{20}$$

At 25 °C, the terminal weight fraction is 0.251.

The terminal partial pressure of HCl (P_T) is found by substituting the value for the terminal weight fraction into Eq. (18); the result is 301.3 pascals (Pa). The initial partial pressure of HCl (P_o) in a 36% solution at 25 °C is reported in tables to be 18,900 Pa (Perry et al, 1984). Dispersion coefficients for F stability can be expressed as simple functions of the distance from the source (in meters):

$$\sigma_y = \frac{0.04 \cdot x}{\sqrt{1 + 0.0001 \cdot x}}, \tag{21}$$

$$\sigma_z = \frac{0.016 \cdot x}{1 + 0.0003 \cdot x}. \tag{22}$$

Using these formulas for the dispersion coefficients and Eq. (15) for the average release rate, the peak concentration, in kg m^{-3}, can be calculated using Eq. (14):

$$C_{peak} \approx 84 \cdot \left\{ \frac{(1+0.0001\cdot x)^{1/2} \cdot (1+0.0003\cdot x) \cdot \left[\ln(1+0.00039\cdot x)\right]^2}{x^2 \cdot \left[(0.00039\cdot x) - (\ln(1+0.00039\cdot x))\right]} \right\}. \qquad (23)$$

Figure 5 is a graphical representation of Eq. (23).

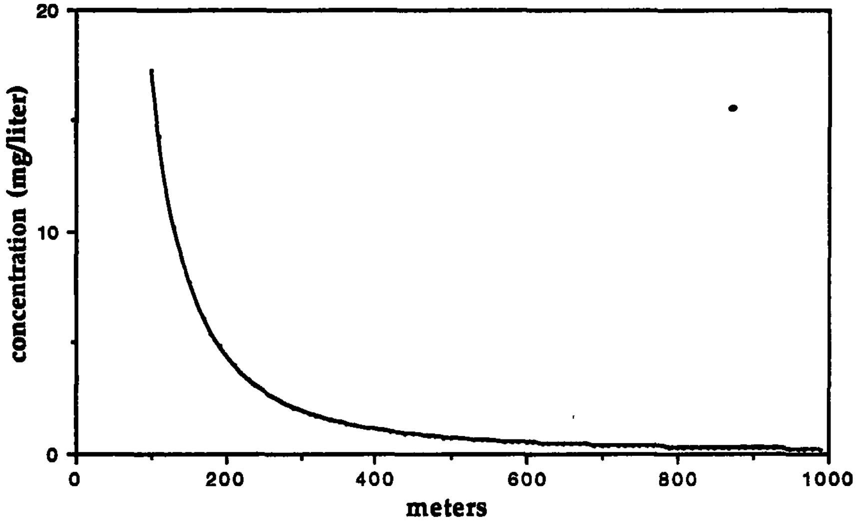


FIGURE 5. Peak concentration versus the distance from the source to the receptor.

Conclusions

We have demonstrated that the proposed method provides reasonable approximations for the evaporation rate from spills of hydrochloric acid. The simplified method for predicting the peak concentration as a function of distance to the receptor was shown to be a good approximation under D and F stability conditions. This computationally simple method can be executed with nothing more than a hand-held calculator and is appropriate for quick hazards analysis during a spill or as means of making initial estimates for contingency plans.

References

Beals, G. A., *Guide to local diffusion of air pollutants* , Technical Report No. 214, Scott Air Force Base, IL. U. S. Air Force, Air Weather Service, 1971.

Evans, M., *Modeling Hydrochloric Acid Evaporation in ALOHA,* Hazmat Report No. 93-3, National Oceanic and Atmospheric Administration, Seattle, 1993.

Mackay, D. and R. S. Matsugu, "Evaporation rates of liquid hydrocarbon spills on land and water", *Can. J. Chem. Eng.* 51: 434-439 (1973).

Overcamp, T. J., "Simple diffusion models for short term releases", Proceedings of the 81st Annual Meeting of ACPA, Dallas, TX, 1988.

Plate, E. J., *Engineering Meteorology* , Elsevier Scientific Publishing Company, New York, NY, 1982.

Perry, R. H., D. W. Green, and J. O. Maloney, *Perry's Chemical Engineers' Handbook, Sixth Edition,* McGraw-Hill Inc., New York, 1984.

Stiver, W. and D. Mackay, "Evaporation rate of spills of hydrocarbons and petroleum mixtures." *Environmental Science and Technology,* 18: 834-840 (1984).

Thibodeaux, L. G., *Chemodynamics: Environmental Movement of Chemicals in Air, Water, and Soil,* John Wiley and Sons, New York, 1979.

van Genuchten, M. Th. and W. J. Alves, *Analytic solutions of the one-dimensional convective-dispersive solute transport equation.* Technical Bulletin No. 1661, U. S. Dept. of Agriculture, 1982.

Wilson, D. J., "Along-Wind Diffusion of Source Transients", *Atmospheric Environment* 15: 489-495 (1981a).

Wilson, D. J., *Expansion and plume rise of gas jets from high pressure pipeline ruptures* , Contract No. 810786, Department of Mechanical Engineering, University of Alberta, Edmonton, Alberta, 1981b.

Notation

The following notation is used in this paper:
A = coefficient used in fitting partial pressure data (Pa);
a = coefficient used in fitting partial pressure data;
B = coefficient used in fitting partial pressure data (Pa);
b = coefficient used in fitting partial pressure data (Pa) ;
$C(t)$ = gas phase concentration of HCl as a function of time (kg/m^3);
$C_i(t)$ = partial concentration of HCl as a function of time (kg/m^3);
C_{max} = peak concentration from maximization of Eq. (9) (kg/m^3);
C_{peak} = peak concentration of HCl (kg/m^3);
K_i = mass transfer coefficient of component i (m/s);
K_{HCl} = mass transfer coefficient for HCl (m/s);
K_{water} = mass transfer coefficient for water (m/s);
M_i = molecular weight of component i (kg/mole);
M_{HCl} = molecular weight of HCl (kg/mole);
M_{water} = molecular weight of water (kg/mole);
m_{HCl} = mass of HCl remaining in solution (kg);
m_o = mass of HCl in solution initially (kg);
m_R = mass of HCl released into the atmosphere (kg);
m_{water} = mass of water remaining in solution (kg);
P_i = partial pressure of component i (Pa);
P_{HCl} = partial pressure of HCl as a function of weight fraction (Pa);
P_o = partial pressure of HCl initially (Pa);
P_T = partial pressure of HCl at the terminal weight fraction (Pa);
P_{water} = partial pressure of water as a function of weight fraction (Pa);
$Q(t)$ = evaporation rate of HCl as a function of time (kg/s);
Q_{ave} = average evaporation rate of HCl (kg/s);
Q_o = initial evaporation rate of HCl (kg/s);
R = gas constant = 8.3144 (J/K, mole);
S = surface area of the spill (m^2);
T = temperature of the solution (K);
t = time (s);
U = wind speed at 10 meters (m/s);
W_{HCl} = weight fraction of HCl in solution;
W_T = terminal weight fraction of HCl;
x = downwind distance from the center of the spill (m);
Z = dimension of the pool along the axis of the wind (m);
γ_i = weighting factor;
σ_y = dispersion coefficient in the horizontal plane;
σ_z = dispersion coefficient in the vertical plane.

→ décide de s'orienter vers
le "*life cycle*" of a product
from production to uses.

→ ?

Chlorine Gas Releases: Some Recent Prevention, Preparedness and Response Activities of Public Health Agencies in Quebec.

Philippe Guerrier, M.Sc.(Env.), M.ATDR
Marc Rhainds, MD, M.Sc., FRCPC
Henri Prud'homme, MD
Pierre Auger, MD, M.Sc., FRCPC
Renaud Leroux, MD, ccmf (M.U.), Adm. A.

Environmental Health Emergencies Unit
Environmental Health Service
Public Health Department - Quebec City Region
2400 d'Estimauville
Beauport (Québec) G1E 7G9

Abstract

Spectacular accidents involving chlorine have contributed to making the public and governments aware of the potential health, environmental and financial impacts of chlorine gas releases. Such releases may occur at any stage of this product life-cycle, i.e. production, transportation, handling and use. Chlorine is a widely used product and an acutely toxic chemical. Therefore, public health officials must undertake prevention, preparedness and response activities in order to reduce the risks for the public associated with this chemical. In Quebec, although chlorine producers and transporters are now strongly regulated and involved in various voluntary programs, accidents still do occur. However, these accidents may now take place at the user level where lack of training and financial constraints tend to facilitate in certain cases the occurrence of such events. The main users are aluminum, pulp and paper or water purification plants. Serious chlorine releases may also occur when bleaching agents, i.e. sodium hypochlorite, are mixed with other chemicals such as acids.

Introduction

In 1979, a freight train derailed on a November holiday weekend in Mississauga (Ontario). This train carried hazardous chemicals, among them a chlorine tank car and a propane tank car. Some cars began to leak and others exploded. Some responders were exposed but there were no victims. The police decided to evacuate 217 000 people, representing 75 % of the population of this city [1,2]. Ten years later, in December 1989, another train carrying four chlorine tank cars derailed in St-Léonard-d'Aston (Québec): as a preventive measure, 1000 persons were evacuated during four days [3].

Spectacular accidents involving chlorine such as the Mississauga and St-Léonard-d'Aston train derailments have contributed, in the last two decades, to public and government awareness of the possible health, environmental and financial impacts of chlorine gas releases. In many private and public organizations, this awareness was to be followed by numerous practical activities.

In Quebec, emergency planning related to health matters in the 16 administrative regions has been transfered to the Regional Health and Social Services Boards (RRSSSs). These boards are mandated to plan and co-ordinate action with respect to three main activities: "public health", "physical health (EMS)" and "psychosocial support (stress counselling services)". Public health activities must be undertaken by public health agencies called Directions régionales de santé publique (DRSPs) that are branches of these boards. In most regions, among them the Quebec City Region, chemical spills have been identified as events for which DRSPs have to undertake prevention, preparedness and response activities.

1. Prevention and Preparedness Activities for Public Health Agencies related to Chlorine Releases

1.1. Background

In risk assessment terms, DRSPs must identify the major hazards in their respective regions, estimate the risks to public health that may result in the event of an accident, ensure active monitoring of the main health risks and inform the public about these health risks.

Frequently, these activities require the collaboration of other organizations such as municipalities and industries at the local level, and of other governmental agencies at the provincial and federal levels.

Between 1990 and 1992, some prevention activities had been set out by the DRSP-Quebec City region in the Quebec City metropolitan area. The activities involved several users of hazardous materials, in particular a major pulp and paper company and a liquid storage company. The collaboration produced detailed databases of these industries' hazardous chemicals.

These inventories contained information on the hazardous chemicals location, storage conditions, etc. Such efforts made all the stakeholders, particularly the first responders, more aware of the major hazardous installations and spill hazards, as well as of their partners in terms of roles, resources and concerns. The data were managed using a Decision Support System based on a Geographic Information System and a Relational Database Management System (RDBMS) (Figure 1)[4].

For various reasons, among them the fact that information could not be shared between all the stakeholders through a computerized network, the database ended up being managed only by the Quebec City Emergency Operations Centre. This centre was able to maintain and update the content of the database that concerned "physical health", "public health" and "psychosocial support", but did not have sufficient human and financial resources to manage information concerning hazardous materials in the Quebec City metropolitan area, let alone the whole Quebec City region.

Therefore, the Environmental Health Emergencies Unit of the Public Health Department decided to adopt a more comprehensive approach that would take into account not only the users but also producers, transporters and businesses which supply, handle or sell chemicals in the Quebec City region.

In this approach, only the information concerning the most dangerous chemicals would be gathered and managed in the database.

1.2 The Life-Cycle Method and the Spill Priority List.

In 1986, a multi-stakeholder group chaired by Environment Canada released a report entitled From Cradle to Grave: A Management Approach to Chemicals[5]. The task force proposed a comprehensive framework in which careful attention is paid to all stages in the life-cycle of chemicals. Seven life-cycle stages were identified. An initial "Research and Development" phase covers the development of all new substances and processes. "Introduction to the Marketplace" addresses all preparations for commercialization as well as test marketing. The "Manufacturing" stage represents actual commercial production. "Transportation" is the physical movement of chemicals by rail, ship, truck, pipeline or aircraft. Those 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 with consumer use as secondary consideration. Finally, "Disposal" is the dispersion of the chemical or by-products into the environment once the substance loses its commercial or chemical value[6].

This management process was selected by the Public Health Department to improve its prevention, preparedness and response activities to accidental releases of hazardous substances. This approach facilitates a more comprehensive information management by public health agencies.

In 1991, a Chemical Spill Priority List was established by Environment Canada. This list was developed by a simple ranking of reported spill frequency, supply volumes, historical spill volumes, toxicity data, stabililty and persistence. In this list, Ammonia (UN 1005) came first and Chlorine came second [7,8]. These two chemicals are also identified in other documents such as the US EPA Comprehensive Reference Guide on Extremely Hazardous Substances in 1988 and the MIACC List 1 of Priority Hazardous Substances in 1994 [9,10].

1.3 Results

The DRSP - Quebec City region selected chlorine to undertake its first comprehensive study of a hazardous chemical in the region.

The decision was based on the following facts :

- there have been several accidents in the past involving chlorine users in the Quebec City region, some of which have required an important response effort, in particular from Quebec City firefighters;
- chlorine releases into the environment may occur during the main life-cycle stages of this hazardous material, i.e. production, transportation, handling and use;
- there are major producers of chlorine in Quebec;
- chlorine is transported by road and rail into and through the Quebec City region;
- there are several important users of this product in this region;
- chlorine was selected for a full-scale simulation exercise in 1994;
- a report of a canadian workshop called CLAP (Chlorine Life-Cycle Accident Prevention Workshop) was available.

This workshop, held in Edmonton, Alberta, brought together manufacturers, transporters, distributors, end users (both industrial and municipal), and government. This workshop dealt with the management of chlorine from its production through the transportation and distribution phases to the end uses, including disposal[11]. Using this life-cycle approach, it was possible to identify more precisely the producers, transporters as well as the users of chlorine.

Manufacturing of chlorine in Quebec.

The Chemical Referral Centre of the Canadian Chemical Producers' Association (CCPA) was the first organization to be contacted. This organization gave precise information about the producers. In Quebec, chlorine is manufactured by the electrolysis of chloride salts in two chemical plants, one (ICI Canada Inc.) near Trois-Rivières in Becancour, the largest industrial park in Canada and one (PPG Canada Inc.) in Beauharnois, near Montréal.

These plants are committed to the Responsable Care program initiated by the CCPA. They have their own chemical emergency response teams and participate in the CHLOREP and TEAP (Transportation Emergency Assistance Plan) emergency plans. CHLOREP is administered and coordinated by the Chlorine Institute located in Washington, D.C. TEAP is developed by CCPA.

Contacts with producers was positive in two ways. On the one hand, it allowed the producers to gain knowledge of the contingency plans of the Health and Social Services Boards (RRSSSs) in Quebec. On the other hand, it lead to their participation in various activities developed by RRSSSs, among them a training workshop on chlorine designed especially for public health responders.

Transportation and use of chlorine in Quebec.

In North America, the major consumer of chlorine is the chemical industry. The largest end use of chlorine is in the production of ethylene dichloride (UN 1184) for the manufacture of vinyl chloride monomer[12]. In the USA, 28% is used to manufacture plastics, 35% to manufacture other chemicals, including drugs and silicon for electronic chips or epoxy resins, 18% to produce solvents, 14% for pulp and paper bleaching and 5% for drinking water purification. In Canada, industry produced 1.17 million tonnes of chlorine in 1993, a 14% reduction compared to 1992 levels[13].

In Quebec, the major uses of chlorine are found in the pulp and paper industry, the aluminum sector and the purification of drinking water. Liquid chlorine is shipped to aluminum plants in bulk in railroad tank cars (50 and 82 tonnes). For municipal water purification plants and pulp and paper companies, chlorine is usually transported by trucks in cylinders (68 kg) and short ton containers (902 kg). The trucks may transport up to 11 tons (cylinders) or 20 tons (ton containers).

In the international classification system, chlorine belongs to Class 2 (gases) in the subdivision 2.3 (poisonous gas). Its 4-digit PIN (Product Identification Number) is UN 1017. It may be shown on the diamond-shaped placard or on the adjacent orange panel displayed on the ends and sides of a rail car or tank[14].

In many pulp and paper companies, the pulp is bleached. The purpose of the bleaching process is to increase the whiteness of the pulp by removing or decoloring the remaining lignin and other colored degradation products in the pulp. In the past, one of the more common practices was to bleach the pulp with chlorine and more recently with chlorine dioxide.

As chloroorganic compounds may be formed when chlorine is used in the bleaching, it has been partially replaced in this process by other chemicals, such as peroxides, oxygen, ozone, complex binders, enzymes, and peracetic acid [15,16]. Nevertheless, in the Quebec City region, chlorine is still used in smaller quantities to purify raw water used in the process. An large aluminum plant also uses chlorine in its processing to purify aluminum and manufacture special products.

In the Quebec City region, chlorine may be stored in large quantities in municipal water purification plants (up to 22 tons). Apart from emergency prevention and preparedness activities, public health officials collaborate with municipalities since addition of chlorine to raw water that contains humic substances may result in several products such as trihalomethanes[17].

Contact with a major transporter allowed to develop a full-scale exercice called "Yellow Alert". The spill scenario involved the collision of a truck, provided by the transporter and carrying 21 one-ton containers, with a school bus: a fire in the bus gas tank would have caused the release of chlorine from a one-ton cylinder as the fusible plug would have melted due to the heat[18]. The company provided its expertise to develop a realistic scenario. Information found in the Environment Canada's Enviroguide on Chlorine was also valuable[19].

The ALOHA™ program was one of the computerized tools selected to help develop the scenario. The ALOHA™ program (Areal Locations of Hazardous Atmospheres) is a model for estimating the movement and dispersion of gases. ALOHA™ contains two separate dispersion models: a Gaussian and an heavy gas model.

Figure 2 presents how data were entered using this model when the user specifies the type of source (in this case, a one-ton container). ALOHA™ needs to know what the tank looks like, how big it is, how much of a chemical, either liquid or gas, could be stored in the tank, and the storage temperature and/or pressure. A horizontal cylinder is chosen as tank type and orientation. ALOHA™ requests that two of the following three values be entered: diameter, length, or volume[20].

Figure 3 presents the output obtained with ALOHA™. Output options are dispersion footprint, concentration as a function of time at a given point, source strength as a function of time and text summary.

2. Response Activities for Public Health Agencies related to Chlorine Releases

2.1. Background

When a chemical spill occurs, the activities of Quebec public health agencies (DRSPs) consist in assessing the health risks for workers, responders and the public in general and recommending proper protection measures. Afterwards, the public health agencies must evaluate the response, undertake an epidemiological follow-up and study the short and long-term effects of the incident on the people who have been exposed.

Between January 1992 and September 1995, in the Quebec City Region, 76 response activities were carried out by the Environmental Health Emergencies Unit of the Public Health Department, among them the full-scale simulation exercise involving chlorine, described previously. After this simulation exercise, the only two responses concerning chlorine gas were relatively minor exposure episodes in a residential and a commercial environment. The two episodes were not caused by chlorine gas containers but involved the mixture of bleach (sodium hypochlorite - UN 1791) and acids.

2.2 Chlorine release in a swimming pool

In September 1995, an important accident occurred inside a swimming pool building in the Quebec City region. A 12% sodium hypochlorite solution (UN 1791) was used to purify the swimming pool water, whereas an hydrochloric acid solution (UN 1789) was used for pH control. There was a leak in the pipe carrying the sodium hypochlorite solution. This chemical reached and reacted with the hydrochloric acid solution stored in a container.

When sodium hypochlorite and an acid are mixed, chlorine gas and water are released[21, 22].

$$H^+Cl^- + Na^+OCl^- \rightarrow HClO + Na^+ + Cl^-$$

$$HClO + H^+Cl^- \rightarrow Cl_2 + H_2O$$

Chlorine gas reacts with water to form hydrochloric and hypochlorous acids. Hydrochloric acid also causes inflammation that may, along with nascent oxygen release, be one of the mechanisms of tissue damage by chlorine.

Chlorine gas began to fill the utility room where these chemicals were stored. A member of the swimming pool staff opened the door and as a result, chlorine gas reached the dressing room and the staff office, mainly through the ventilation system. Following the firefighter and EMS response, more than 100 persons were directed to a hospital for evaluation. Two of them were admitted to the intensive care unit.

Chlorine gas may cause a variety of symptoms which depend on the severity of exposure. Several guidelines have been developed to assist in the control of health hazards.

The Threshold Limit Values (TLVs™) are intended for use in the practice of industrial hygiene. The IDLHs (Immediately Dangerous to Life and Health Concentrations) have been established to ensure that a worker could escape without injury or irreversible health effects from an IDLH exposure in the event of the failure of respiratory protection equipment. ERPGs (Emergency Response Planning Guidelines) 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[23].

TLV™, IDLH and ERPGs values for chlorine [24,25,26]	
TLV-TWA: 0.5 ppm	**(ACGIH, 1996)**
IDLH: 10 ppm	**(NIOSH,1994)**
ERPG-1: 1 ppm	**(AIHA, 1988)**
ERPG-2: 3 ppm	**(AIHA, 1988)**
ERPG-3: 20 ppm	**(AIHA, 1988)**

In this case, the municipal firefighters did not have the proper tools to estimate the chlorine concentration in the swimming pool building. Nevertheless, the public health response team was concerned with the possibility and consequences of exposure to high doses of chlorine.

Chlorine is an acutely toxic chemical that can cause adverse effects on the eyes, upper and lower respiratory systems, kidneys, liver, and the nervous system at high exposure levels. It may be fatal at concentrations in excess of 60 ppm[27]. Exposure to high concentrations of respiratory irritants such as chlorine 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)[28,29]. 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.

Other researchers had previously described a similar syndrome after toxic inhalation to products other than chlorine such as ammonia (UN 1005), sulfur dioxyde (UN 1079) and acid fumes[30]. Many questions related to acute exposure to chlorine remain unanswered. 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[31].

In this case, the public health agency - Quebec City region has evaluated the response. A follow-up is currently in progress to study acute and chronic effects (medical and psychological aspects) of the incident on the persons who were exposed.

Concluding remarks

In Quebec, the public health agencies'staff has received the basic training to ensure its own safety and protect the health of the people involved in chemical spills. Now, some public health agencies undertake prevention, preparedness and response activities that focus on the chemicals which are the most commonly spilled and which may present serious health risks for the population. Chlorine should be considered as one of these priority chemicals.

Chlorine is presently at the centre of an environmental debate which is extremely complex considering, on the one hand the benefits of chlorine for activities such as water purification and, on the other hand, the unwanted by-products and breakdown products[32]. Nevertheless, as long as chlorine is produced, transported and used, it is essential for public health responders to have good knowledge of this hazardous chemical through its entire life-cycle, and manage and share information in this perspective.

In Quebec, chlorine producers and transporters have taken important measures to bring more security in the first stages of this product life-cycle. Nevertheless, the quantities involved in these stages require public health officials to continue to collaborate with these companies in prevention and preparedness activities in order to respond effectively, if ever an accident occurs. Accidents may also take place at the user level in aluminum, pulp and paper or water purification plants. Lack of training and financial constraints tend to facilitate in certain cases the occurrence of such events. Another concern, supported by a recent major accident, are chlorine releases due to the mixture of bleaching agents, i.e. sodium hypochlorite, with other chemicals such as acids.

As stated in the MIACC Chlorine Workshop, the priorities in terms of emergency response should include protective equipment, evacuation versus sheltering, control and containment of chlorine, media access to information, decontamination and stress counselling services.

Public health responders have an important role to play in training chlorine users and first responders to increase their awareness of the health risks due to chlorine such as RADS, in order that these users and responders do not become the first casualties in case of a real chlorine release. If an accident should occur, public health officials will be able to focus on their main concern which is the protection of the population and the follow-up of the people exposed. Close collaboration with producers, transporters and users can be very beneficial: these stakeholders can be informed about the emergency plan of the Quebec Health and Social Services Boards and in counter part, they can input their expertise in various prevention and preparedness activities such as training, full-scale and table-top exercises.

Acknowledgment

The authors would like to thank Yvon J. Thiffault, Ing., ICI Canada Inc, Marc Germain, Ing., STANCHEM Inc. and Alain Beaulieu, PPG Canada Inc, and the Environmental Health Emergencies Unit staff (DRSP-Quebec City Region). Special thanks also to Daniel Houle for his valuable suggestions concerning the English 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.

---

[1] Scanlon, Joseph, *Toxic Chemical and Emergency Management: The Evacuation of Mississauga, Ontario*, in :Urien, Rosenthal, Charles, Michael T., Hart, Paul T., (eds.), Coping with Crises. The Management of Disasters, Riots and Terrorism, Charles C. Thomas Publish., Springfield, Illinois, pp. 309-322.

[2] Amyot, Denis, *The Mississauga Saga*, Emergency Preparedness Digest, Ottawa, Ont., pp. 5-12, January-March 1980.

[3] Denis, Hélène, *Gérer les catastrophes, L'incertitude à apprivoiser*, Les Presses de l'Université de Montréal, Montréal, Québec, 1993, p.236.

[4] Guerrier,P., Sérodes,J., *Chemical Spills: Prevention and Preparedness Activities of Public Health Agencies in Quebec.*, Proceedings of the 12th Technical Seminar on Chemical Spills, Environment Canada, 1995, pp. 99-111.

[5] Environment Canada, *From Cradle to Grave: A Management Approach to Chemicals*, Ottawa, Ontario, September 1986.

[6] 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.

[7] 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, 1991.

[8] Lawuyi, R., Fingas, M., *Environmental Impact of Polychlorinated Biphenyls (PCBs) Spills and Fires*, Proceedings of the Twelfth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, 1995, p. 67.

[9] U.S. Environmental Protection Agency, *Extremely Hazardous Substances : Superfund Chemical Profiles*, volume 1, Noyes Data Corporation, 1988.

[10] Major Industrial Accidents Council of Canada, *MIACC Lists of Hazardous Substances, MIACC List 1, Priority Hazardous Substances*, Ottawa, 1994.

[11] Major Industrial Accidents Council of Canada, *Chlorine Life-Cycle Accident Prevention Workshop Report*, CCAIM-MIACC, Ottawa, Ont., November 1993.

[12] Lawuyi, R., *The Impact of Chlorine on the Environment*, Proceedings of the Ninth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, 1992, p. 159.

[13] Isaacs, Colin, *Chlorine: Is it blurring our vision?*, Hazardous Materials Management, August 1994, pp. 26-27.

[14] CANUTEC, *Initial Emergency Response Guide*, Transport Canada, 1992.

[15] Lawuyi, R., *The Impact of Chlorine on the Environment*, Proceedings of the Ninth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, 1992.

---

[16] Torén, Kjell, Hagberg, Stig, Westberg, Håkan, *Health Effects of Working in Pulp and Paper Mills : Exposure, Obstructive Airways Disease, Hypersensitivity Reactions, and Cardiovascular Diseases*, American Journal of Industrial Medecine 29:111-122 (1996).

[17] Lawuyi, R., *The Impact of Chlorine on the Environment*, Proceedings of the Ninth Technical Seminar on Chemical Spills, Environment Canada, Ottawa, 1992.

[18] Guerrier, P., Sérodes, J., *Chemical Spills: Prevention and Preparedness Activities of Public Health Agencies in Quebec.*, Proceedings of the Twelfth Technical Seminar on Chemical Spills, Environment Canada, 1995, pp. 99-111.

[19] Environnement Canada, *Le chlore*, collection Enviroguide, Ottawa, juillet 1984.

[20] NOAA, US-EPA, *ALOHA™ 5.0 (Areal Locations of Hazardous Atmospheres) for the Apple® Macintosh™ Computer*, Distributed by the National Safety Council, Washington, D.C., December 1990.

[21] Hattis, R.P., Greer, J.R., Dietrich, S., Olafsson, S., McAndrew, K.R., *Chlorine Gas Toxicity from Mixture of Bleach with Other Cleaning Products - California*, Epidemiological Notes and Reports, MMWR, vol. 40, n°36, September 13th, 1991, p. 627.

[22] Barbeau, C., Ph.D., Université Laval, personnal communication, 95-10-27.

[23] 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.

[24] American Conference of Governmental Industrial Hygienists, *Threshold Limit Values (TLVs™) for Chemical Substances and Physical Agents and Biological Exposure Indices (BEIs™)*, ACGIH, 1996.

[25] NIOSH, *NIOSH Pocket Guide to Chemical Hazards*, National Institute for Occupational Safety and Health, June 1994.

[26] American Industrial Hygiene Association, *Emergency Response Planning Guidelines*, AIHA, Akron, OH, 1988.

[27] Dungan, A.E., *Characteristics of Chlorine and an Application to Life-Cycle Management*, Chlorine Life-Cycle Accident Prevention Workshop Report, CCAIM-MIACC, Ottawa, Ontario, November 1993.

[28] Brooks, S.M., Weiss, M.A., Berstein, I.L., *Reactive Airways Dysfunction Syndrome (RADS). Persistent Asthma Syndrome after High Level Irritant Exposures.* Chest 1985, 88:376-84.

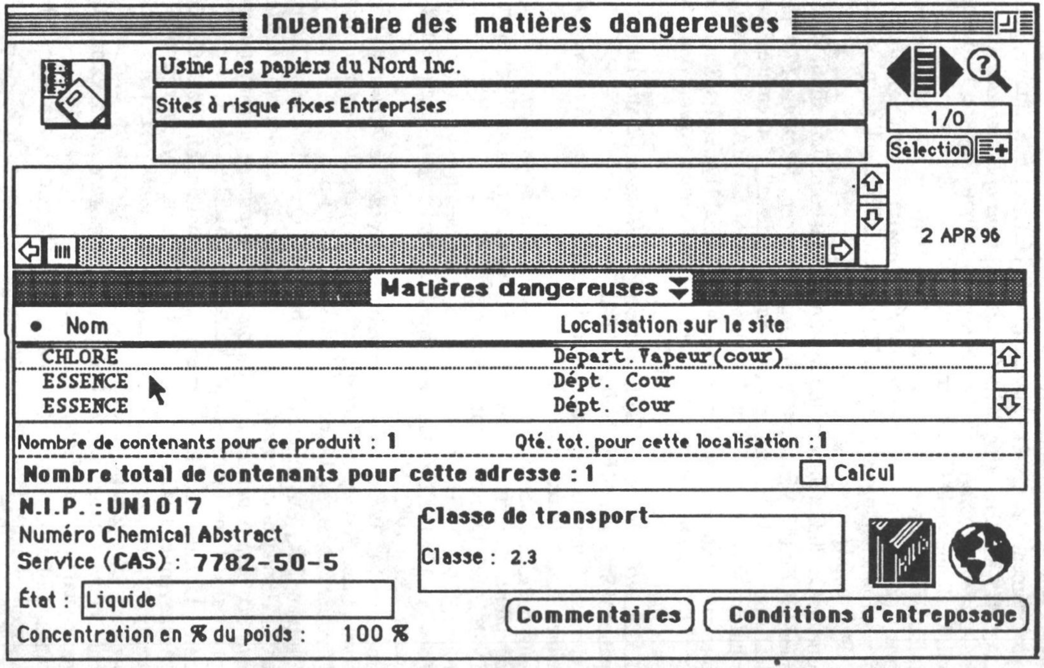
[29] Brooks, S.M., Weiss, M.A., Berstein, I.L., *Reactive Airways Dysfunction Syndrome. Case Reports of Persistent Airways Hyperreactivity Following High-Level Irritant Exposures*, J. Occup Med 1985, 27:473-6.

[30] Courteau, J.P., Cushman, R., Bouchard, F., Quévillon, M., Chartrand, A., Bhérer, L., *Survey of construction workers repeatedly exposed to chlorine over a three to six month period in a pulpmill: I. exposure and symptomatology*, Occupational and Environmental Medecine 1994, 51:219-224.

[31] 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 1994, 51:225-228.

[32] Isaacs, Colin, Chlorine: Is it blurring our vision?, Hazardous Materials Management, August 1994, pp. 26-27.

Figure 1: Managing the Chemical Inventory of a Pulp and Paper Company with SOS IGLOU™ (the RDBMS module is based on Omnis™ 7.).



Inventaire des matières dangereuses

Usine Les papiers du Nord Inc.

Sites à risque fixes Entreprises

1/0

2 APR 96

Matières dangereuses

● Nom	Localisation sur le site
CHLORE	Départ.Vapeur(cour)
ESSENCE	Dépt. Cour
ESSENCE	Dépt. Cour

Nombre de contenants pour ce produit : 1

Qté. tot. pour cette localisation : 1

Nombre total de contenants pour cette adresse : 1

☐ Calcul

N.I.P. : UN1017

Numéro Chemical Abstract Service (CAS) : 7782-50-5

État : Liquide

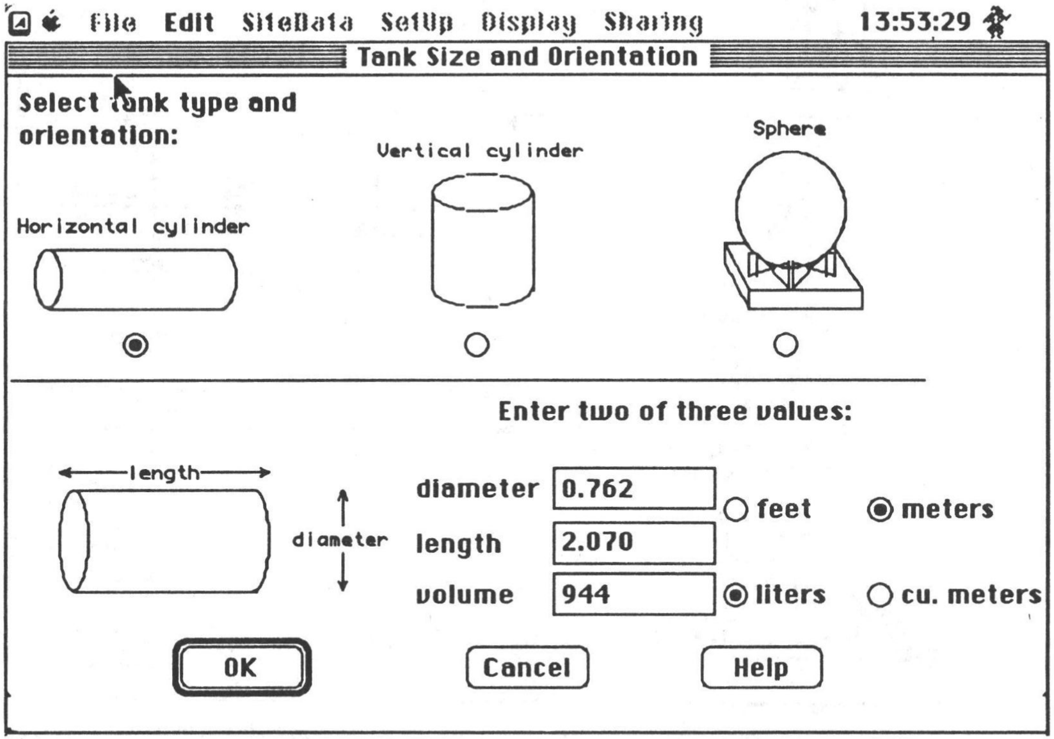
Concentration en % du poids : 100 %

Classe de transport

Classe : 2.3

© Synergie Information Systems. SOS IGLOU™ is now available in version 3.0.

Figure 2 : Using ALOHA™ 5.0 (for the Apple® Macintosh™) to develop the chlorine spill scenario.



Select tank type and orientation:

● Horizontal cylinder ○ Vertical cylinder ○ Sphere

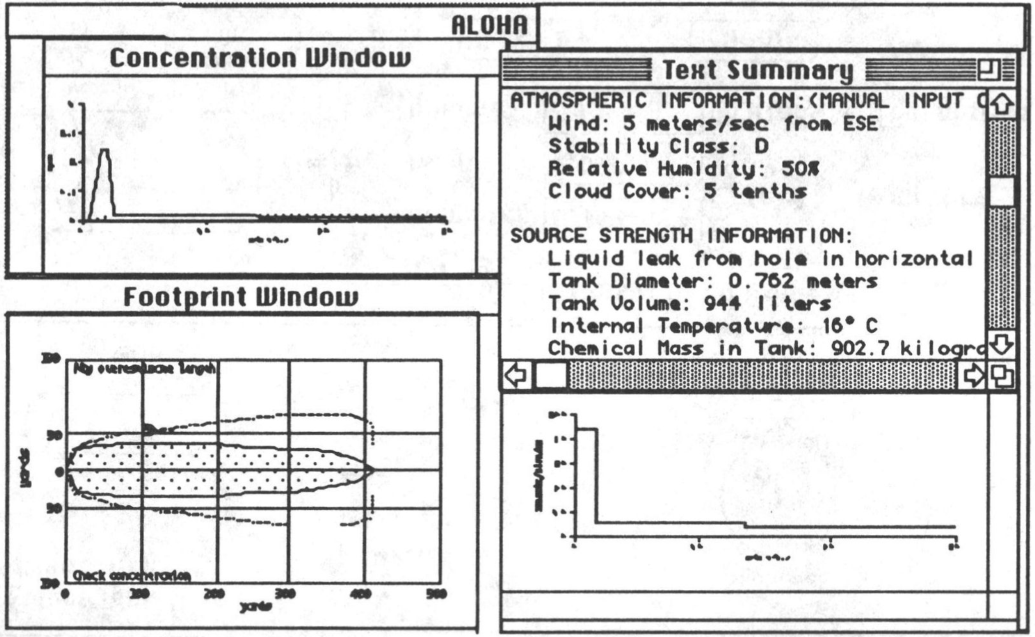
Enter two of three values:

diameter 0.762 ○ feet ● meters

length 2.070

volume 944 ● liters ○ cu. meters

Figure 3 : Output obtained with ALOHA™ 5.0. ALOHA™ is now available in version 5.2.



```
ATMOSPHERIC INFORMATION:(MANUAL INPUT O
   Wind: 5 meters/sec from ESE
   Stability Class: D
   Relative Humidity: 50%
   Cloud Cover: 5 tenths

SOURCE STRENGTH INFORMATION:
   Liquid leak from hole in horizontal
   Tank Diameter: 0.762 meters
   Tank Volume: 944 liters
   Internal Temperature: 16° C
   Chemical Mass in Tank: 902.7 kilogra
```

Merv & R. overstreet
Things → this is common knowledge

VALIDATION OF THE EUROSPILL CHEMICAL SPILL MODEL.

J. Rusin, T. Lunel and L. Davies.

AEA Technology plc., National Environmental Technology Centre, Culham, Abingdon, Oxfordshire, UK.

ABSTRACT:

The chemical spill component of EUROSPILL has been developed by AEA Technology (formerly Warren Spring Laboratory) over the past six years in order to provide information on the position, size and distribution of a chemical spill. The model will also estimate the partitioning of the chemical between atmosphere, sea surface, water column and seabed. In addition it provides information on the chemical hazards to man and the marine environment.

Development has followed an iterative approach of laboratory studies and small scale sea trials. Thus empirically derived mass transfer coefficients have been calibrated with small experimental releases at sea. However fundamental to the development of the model is the stringent testing of model integrity through larger scaled releases simulating real spill conditions.

In this study we carried out 10m^3 releases of styrene and styrene/divinylbenzene (mixed at 9:1) and monitored chemical fate of the surface slick through remote IR sensing and discrete sampling. Water column concentrations were monitored at depths between 0.5-5m using in situ fluorometry and discrete water sampling.

Comparison of EUROSPILL predictions with sea trial data shows close agreement in the overall fate of the chemical slicks in terms of trajectory, surface area and the relative partitioning styrene and divinylbenzene from the surface slick. EUROSPILL was observed to overestimate the maximum water concentration of a dissolved chemical by 6-9 fold. However, because the overall relative partitioning between the chemicals was very close to that measured, and because of the risks associated with under predicting the dissolved concentration of toxic chemicals, we do not recommend at this stage that EUROSPILL is modified. This validation exercise has shown that EUROSPILL can be used with some confidence to predict the slick position, surface area, persistence, partitioning and hazards to the marine environment.

1. INTRODUCTION:

The chemical component of the spill model EUROSPILL has been developed by AEA Technology plc. (formerly Warren Spring Laboratory) for the Coastguard Agency's Marine Pollution Control Unit over the past six years. The model has principally been designed to provide the responder with a spill response management tool from which the following information can be obtained in order to guide response operations in the event of a spill:

1. Position of slick
2. Size and distribution of chemical slick
3. Partitioning of chemical between atmosphere, floating on the sea surface, dissolving or dispersing in the water column and sinking to the sea bed.
4. Chemical hazards to the marine environment.

Development of the model is an iterative process where the following data gathering and experimental approaches have been used to derive and calibrate the model algorithms and their different coefficients:

1. Laboratory work to give an initial insight into the relevant processes and using empirical values of physical/chemical properties to synthesise a basic model.
2. Small scale trials at sea to compare model predictions with observations at sea
3. Specific experiments at sea designed to understand specific physical processes taking place at sea in order to derive the empirical constants to apply to the different algorithms.

These stages have been carried out and reported (Lunel, 1991, and Hurford and Wallace. 1991) . However it is considered that the development process should ideally incorporate a fourth and final experimental stage. This should involve larger scale releases at sea in order to validate the algorithms against a realistically scaled spill simulation.
The principal aim of this work was to provide a data set against which the predictions of the EUROSPILL chemical module can be validated. If necessary, these data can then be used to improve the existing algorithms by refinement of the mass transfer coefficients for solution and evaporation used in the model.

2. BACKGROUND WORK ON EUROSPILL:

The development of EUROSPILL as an aid to the responder in decision making and management of a chemical spill is highly dependent on model testing through field validation studies. Through model design, EUROSPILL takes a more realistic approach to the prediction of chemical partitioning by assessing physical and chemical properties on a chemical by chemical basis as opposed to using broad categorisation into classes such as floaters, floater-evaporators, dissolvers, sinkers etc. (Cormack 1982). Although categorisation provides responders with an immediate picture of the way in which the chemical is likely to behave on the sea surface, when considering the hazard posed by a spill it is necessary to consider the possible partitioning of the chemical more carefully. Many chemicals have the potential to cause a major hazard even at low concentrations (of the order of parts per million, ppm). For example under Cormack's classification (1982) styrene is classified as a floater, and has a finite vapour pressure (0.00725 atm) and solubility (0.3 kgm^{-3}) and thus may pose a hazard both in the air and the water phases.

Therefore, to accurately predict different partitioning, it is important that the model takes account of the interaction between the processes of evaporation, dissolution, spreading and dispersion calculated using specific chemical property data. Eurospill has different algorithms which independently assess these partitioning processes.

The physical properties of the chemical can be obtained from data tables and are contained in the Eurospill chemical data base. The mass transfer coefficients (k_S and k_E) which describe the way in which the rates of solution and evaporation are affected by environmental conditions, are obtained from experimental work at sea.
AEA Technology carried out a number of small scale sea trials involving continuous releases of acetates of varying solubilities and vapour pressures (Lunel, 1991) to test the validity of the mass transfer coefficients of solution and evaporation. These trials represented the first attempt to determine the mass transfer rates for evaporation and solution using releases of chemicals at sea. The trials indicated that the relationship formulated by Mackay and Yeun (1983) or the mass transfer rate for evaporation agrees closely with the field data. However, the measured data showed that the relationships for mass transfer for solution (Mackay and Yeun, 1983 and Liss and Merlivat 1983) over estimate the mass transfer rate at wind speeds above $5ms^{-1}$. This has important implications for calculating the rate of solution of floating slicks and the rate of evaporation of chemicals dissolved in the water column - reducing the rates of both processes. So, while mass transfer rates for a floater-evaporator appear to be in good agreement with the relationship predicted by Mackay and Yeun (1983), it appeared that, for dissolvers or dissolver/evaporators, the literature over estimated the mass transfer rates for their dissipation.
While the EUROSPILL model can process all chemical categories in much the same way, the model is perhaps most appropriately validated through study of chemicals with a tendency to float and with low solubility and high boiling point, i.e. those chemicals that are more likely to persist in higher concentration without readily dispersing and diluting, thus posing a lower environmental risk. The major route for the disappearance of surface chemical slicks is through evaporation and dissolution. Since these processes are critical in the behaviour of most chemicals spilt at sea, a large amount of the effort involved in the sea trial work for EUROSPILL development was directed at obtaining the coefficients for dissolution and evaporation.
Unlike the algorithms describing the fate of oil used in EUROSPILL and OSIS, the chemical model has not been tested against larger spills of chemicals. It is considered that larger scale releases, of the order of 10 tonnes, of chemicals should be carried out to test the predictive capabilities of EUROSPILL, and provide validation data for the algorithms employed.

3. EXPERIMENTAL PROCEDURES:

All procedures described had been the subject of a HAZOP study which was reported in a formal safety case. Pre-trial modelling to assess the worst case concentrations of chemicals in the water column and in the atmosphere formed the basis of the safety case. The safety case including the hazard assessment and control procedures was then subjected to independent peer review before commencing with the experimental programme.

In order to validate the model we carried out one experimental release of styrene, one of styrene/divinylbenzene at a ratio of 9:1, and one of Gullfaks crude oil.

The styrene release was used to validate the spill model using a chemical which is routinely transported in bulk at sea. Styrene has a relatively low but measurable vapour pressure and solubility and so can be used to test the model algorithms for evaporation and solution.

The styrene /divinylbenzene release was used to validate the ratio of mass transfer coefficients for evaporation and solution used in the model since different physical properties of the two chemicals mean they will partition differently over time.

The Gullfaks crude oil release was used as a reference slick to gauge the relative persistence of oil and chemical slicks. The slick can also be used to validate the spreading and dispersion algorithms of the model. Thus, any discrepancies between model and reality due to spreading and dispersion can be accounted for when validating the chemical model.

All these slicks were monitored by fluorometry, phase doppler particle analyzer (PDPA), remote sensing and surface sampling.

3.1. Chemical Release and Sampling Protocol:

The procedures used in the chemical release and sampling procedures followed all the management controls identified in the HAZOP study and peer reviewed safety case. Prior to any of the releases taking place a VHF Sécurite message was broadcast from the co-ordinating vessel the MV Lowland Cavalier (Figure 1), warning other shipping of the operations and to maintain a 2km distance The French Naval ship ELAN held position at the edge of the exclusion zone in order to warn any vessels that had not received the Sécurite message.

Three discrete 10 tonne slicks (one oil, two chemical) were discharged directly from the ship under gravity to a floating chemically resistant hose trailing downwind from the ship summarised below:

Table 1. Experimental releases.

Experimental Release	Amount Released	Time of Release
Gullfaks Crude	10 tonnes	08:30
Styrene	10 tonnes	10:54
Styrene / Divinylbenzene mix (9:1)	10 tonnes	16:54

Following the pre-sea trial atmospheric modelling, it was vital that the wind conditions did not deviate from 8-12 knot wind speeds during the releases and slick monitoring in order to ensure proper functioning of the respiratory and personal protective equipment being used. The weather conditions and sea states for each experimental release are summarised below:

Table 2. Meteorological conditions during experimental releases.

Experimental Release.	Wind speed (knots)	Wind Direction	Wave Period	Wave Height	Sea Temp.	Air Temp
Gullfaks Crude	10	ENE	4 seconds	0.9 metres	18	18
Styrene	11	ENE	4 seconds	0.9 metres	18	18
Styrene Divinyl benzene mix (9:1)	10	NE	4 seconds	0.9 metres	18	18

Two sampling boats (Figures 2 and 4) were deployed for each release. Each was equipped with differential global positioning system (DGPS) from which range and location of sample position could be logged.

The first sampling boat (Figure 2) carried out the sub-surface plume profiling using up to five fluorometers, at depths between 0.5-5 metres. The water column particle size distribution was also measured using the PDPA operated from this boat. In addition the extent and concentration of the vapour above surface slick was measured using the UVIC's photo-ionisation detectors. Discrete water samples were also taken from this boat for analysis by fluorometry and instrument calibration.

The second sampling boat (Figure 4) was responsible for taking pad samples for GLC analysis.

3.2. Monitoring Techniques:

All sampling was carried out working with the following well proven experimental techniques and equipment for monitoring the surface slick and dispersed/dissolved chemicals:

3.2.1. Surface slick monitoring:

Aerial remote sensing for area of slick.:

All remote sensing operations were co-ordinated by Air Atlantique.

- The IR camera was operated in "black hot" throughout the trial
- After the first few runs of each day the IR camera was run on a fixed gain and offset throughout the day. The gain was set so as to maximise contrast between the slick and the sea without introducing noise (a grainy appearance) to the image.
- For each 10 tonnes release the imagery was mostly carried out from 1000ft at a minimum frequency of once every 15 minutes.

Surface sampling:

Surface pad samples to estimate slick thickness, mass on surface and the relative partitioning when a mixture of chemicals was released were taken as described below:

1. Note position relative to ship/slick by DGPS and the time and slick ID. Complete the sample identification form.
2. Place 30cm x 15cm 3M absorbent pad on the surface of the chemical slick for 30 seconds. Turn the absorbent pad upside down on the same area of the sea surface for a further 30 seconds.
3. Place the absorbent pad into wide necked fluorinated polypropylene container containing 100ml Chloroform to extract the Styrene/Divinylbenzene into the organic phase.

Pad samples were taken from the two chemical slicks and later analysed by GLC to quantify the amounts of chemical adsorbed. Samples were injected onto a 12'x1/8" column packed with 10% SP2100 100-120 Mesh packed column on temperature programme from 100°C-200°C (4°C/min). Integrated peak areas were quantified against standard stock solutions.

3.2.2. Dispersed/dissolved chemical monitoring:

The following measurements were made as described below:

- *In-situ* Fluorometry for total concentration in the water column using Turner fluorometers with flow through cells sampling from 0.5-5 metre depths. Each instrument was pre-calibrated prior to the experimental releases (Hurford & Buchanan (1987).
- Discrete 1 litre water samples were taken directly into 50ml chloroform. The organic phase was later separated, the aqueous phase re-extracted with 50ml chloroform. The two chloroform extracts were combined and analysed by fluorometry. Quantification of the chemical present was made against standard curves of styrene or styrene/divinylbenzene (9:1) depending on the chemical release. Comparison of the quantified concentration with the logged fluorometer readings enabled calibration response factors for each fluorometer to be determined. These were used to calibrate all the fluorometry data.
- Droplet size of dispersed oil/chemical droplets was monitored using PDPA (Lunel 1993).

3.2.3. Meteorological and Oceanographical monitoring:

Prior to the experimental releases, a Waverider buoy was deployed to give wave height and period and air and sea temperatures at hourly intervals. A meteorological buoy was also deployed to measure wind speed and direction, these measurements were additionally made from the ship Lowland Cavalier.

3.2.4. Vapour Concentration monitoring:

Portable photo-ionisation (UVIC) gas detectors were used to monitor atmospheric concentrations of the chemicals principally to ensure that they did not exceed the safe working levels of all PPE employed. These detectors were calibrated with a toluene span gas both before chemical release and after to check that there had been no significant baseline drift.

4. DISCUSSION OF RESULTS

All the above procedures were successfully completed and samples/data collected. This project was not intended to provide data to validate a vapour dispersion model as EUROSPILL at present does not incorporate a gas cloud model. However, it is worth comparing the vapour concentrations measured with the conservative estimates derived in the pre sea trial modelling. Here the gas dispersion model DRIFT determined a realistic maximum vapour concentration of approximately 1000ppm. Due to model assumptions in DRIFT (i.e. continuous vapour release from an inexhaustible pool) these estimates were assumed to still be reasonably conservative. The maximum atmospheric concentration measured was approx. 200 ppm during both chemical releases where clearly defined peaks were detected as the sampling boat passed through the slick (Figures 5 and 6). These levels were maximal during the release and dropped steadily thereafter, reaching near background concentrations within approximately 1 hour (Figure 7).

EUROSPILL was run to simulate the release of styrene under the meteorological/ oceanographic conditions measured during the spill. This was repeated for both styrene and divinylbenzene under the conditions summarised in table 2.
Figures 8 and 9 show the predicted mass balances for styrene for the two releases. These form the basis of all the model comparisons with the sea trial data. The most notable differences between the two releases are the relative mass of styrene on the surface and the rate of evaporation. These differences are mainly attributable to the different release conditions. The styrene only slick was released in approximately one third of the time (22 mins) taken to release the styrene/ divinylbenzene slick. As a consequence the slick was released over a smaller area leading to a slightly reduced evaporation rate .
The aim of the validation experiments was to test the following predictions of the EUROSPILL model;

- Position of the slick -Trajectory.
- Size and persistence of the slicks - Remote sensing / surface sampling.
- Partitioning of the chemicals - Surface sampling.
- Hazards to the marine environment - Water column monitoring.

The following discussion examines each of these in turn and critically reviews the performance of the model in accurately predicting each of these parameters.

4.1. Position of the Slick - Trajectory:

Using the remote sensing information and the pad sampling positions, comparisons can be made between observed and EUROSPILL predicted Trajectory with time. These are shown in Figures 10-12.

The trajectories of the Gullfaks oil and chemical releases predicted by EUROSPILL show close agreement with those estimated from the recorded positions during the sea trials. This supports the findings of previous sea trials where the model has been compared with experimental release.

4.2. Surface area and persistence of the slicks - Remote sensing data and surface sampling:

Air Atlantique operating from Cessna 404 collected all the remote sensing information. All the IR imagery collected at 1000ft has been analysed by AEA Technology. using standard image analysis techniques to measure the surface area of each slick. Previous work (Lunel, 1991) had demonstrated that Styrene is detected by IR to give good strong dark imagery which can thus be easily quantified in terms of slick surface area. This was also the case during these experimental releases as shown in Figure 13.

The Gullfaks release was made to assess the rates of spreading with an oil that has a natural tendency not to form stable emulsions (Lunel 1995). Figure 14 shows the surface area of the Gullfaks slick with time from release compared to the two chemical slicks. Although the slicks were all $10m^3$ the Gullfaks slick covers a considerably larger area because the surface area of the chemical slicks is rapidly reduced by evaporation and dissolution processes.

Assuming equal spreading rates between the chemicals and Gullfaks oil, the remote sensing data alone (Figure 14) would suggest a loss 90% of the surface chemical slick (predominantly styrene) from the surface during the first 40-60 minutes for both slicks. Figures 15 and 16 show detail plots of the surface area of the two chemical slicks against time compared to the model prediction. The surface area term displayed in the results table of EUROSPILL represents a prediction of the maximum surface area affected over the whole water column. This TOTAL surface area is seen to continuously increase as particles representing the chemical are spreading (the dominant process in the initial spill) and partitioning throughout the water column with time (Figure. 15). This total area term does not represent the surface area of floating chemical, this can only be estimated, as described in the EUROSPILL user manual (Leech et al., 1993), by carrying out contour analysis for the top 0.1m of the water column. This contour plot analysis (Figure 17) shows total chemical (i.e. floating and dissolved). However it is interesting to note that for the styrene/divinylbenzene spill, the contour analysis follows very closely the remote sensing area for the first 50 minutes during the actual release when spreading will have the main influence in the total surface area affected (Figure 16).

The styrene only release was achieved in approximately one third the time during which contour analysis of surface area gives a reasonable agreement with the remote sensing data . (Figure 15).

The persistence of the surface slicks is also best estimated using the same contour analysis to assess the residence time of chemical on the surface. Remote sensing data (Figures 15 and 16) show that the chemical slicks were detectable for approximately

120-150 minutes. The contour analysis of each slick (Figures 15 and 16) suggest that there is still chemical present in the top 0.1m for greater than 120 minutes. In fact contour analysis predicts that there is still chemical present for many hours after the release although the predicted concentrations become very low and are unlikely to be detected with IR cameras. It is therefore also important to note the EUROSPILL predicted concentration (and its significance) in the contour grid when assessing the persistence of the surface slick.

To summarise, the most appropriate way to estimate surface area and persistence of the floating slick with EUROSPILL is to use contour analysis for the top 0.1m. This will include both floating and dissolved phase chemical. Prediction of the surface area and persistence of the chemical slicks based on this analysis was in reasonable agreement with the remote sensing data, especially during the initial release period.

Assuming homogeneous thickness of the chemical slick, and that all samples are taken within the slick, it is the possible to estimate the observed mass of chemical remaining on the surface at any time. This is then compared with the EUROSPILL predicted values as shown Figure 18.

Thus assuming that each sampling pad (length 300mm, width 150mm) has both sides placed on the sea surface (the standard protocol) a total area of 900cm^3 is sampled. The amount of chemical adsorbed and quantified by GLC can be then be related to the slick area (from remote sensing data at time sample is taken) to provide an estimated measure of the amount remaining on the surface.

Figure 18 shows that for the styrene release the predicted mass on the surface only very roughly approximates the measured estimates. This could largely be explained by the fact that that the assumptions regarding the absorption and the surface area being sampled are not in practice entirely true. For instance it is likely that the amount of chemical absorbing to the sampling pads is from a larger surface area than that of the pad itself thus leading to an over-estimated surface mass. However, the most significant factor is likely attributed to the fact that the distribution of the surface slick was not homogeneous (as assumed in the estimation of actual surface mass) particularly with increased time following release, where the formation of small slicks and patches of variable thickness was noted.

4.3. Partitioning of the chemicals - Surface sampling.

It is only possible to assess the hazard posed by a chemical spill by considering the partitioning of the chemical between the air, the water surface, the water column and the sediment in detail. Many chemicals transported in bulk have a relatively high solubility and vapour pressure. In addition, unlike an oil spill, a chemical spill does not form a stable emulsion on the sea surface. Consequently the processes of evaporation and dissolution processes are critical in determining the partitioning and thus ultimate fate of a chemical. Therefore previous sea trial work for MPCU concentrated heavily on determining the mass transfer coefficients for evaporation and dissolution (Lunel, 1991). This work concluded that the mass transfer coefficient for evaporation, k_E, is of the order of $1x10^{-5}$ ms^{-1} and is given by (Mackay and Yeun 1983):

$$k_E = 46.2 \times 10^{-3}\ U^*\, Sc_G^{-0.67}$$

where: U^* = Friction velocity (ms^{-1})
Sc_G = Gas phase Schmidt number.

The mass transfer coefficient for dissolution, k_S is of the order of 1×10^{-5} ms^{-1} and is given by (Lunel, 1991):

$$k_S = 16 \times 10^{-4}\, U^* Sc_L$$

where: U^* = Friction velocity (ms^{-1})
Sc_G = Liquid phase Schmidt number.

These mass transfer coefficients k_E and k_S are the rate constants used to determine the mass transfer rates (dM/dt). These rates are dependent on physical properties of the chemical such as its solubility, S; vapour pressure, P; and relative molecular mass, M as well as the universal gas constant, R, temperature, T, and the surface area of the slick, A. The mass transfer rates for evaporation and solution are given by Equations 1 and 2 respectively:

Fommun equation

$$1. \quad \frac{dM_E}{dt} = \frac{k_E MPA}{RT}$$

$$2. \quad \frac{dM_S}{dt} = k_S SA$$

In summary the previous work involved experimental work concentrating on two issues. Firstly, chemicals which evaporated at a significantly faster rate than they dissolved were used in order to establish the mass transfer coefficient for evaporation. Secondly, chemicals which dissolved at a significantly faster rate than they evaporated were used in order to establish the mass transfer for dissolution. This large scale experiment by contrast, was designed to investigate the relative partitioning into the atmosphere and the water column of chemicals which both dissolved and evaporated. Styrene dissolves and evaporates whereas divinylbenzene only evaporates as shown by their vapour pressures and solubilities below:

Chemical	Vapour Pressure (atm)	Solubility(kgm^{-3})
Styrene	**0.00725**	**0.3**
Divinylbenzene	**0.00062**	**0.0**

The styrene and divinylbenzene will be lost from the surface slick at different rates because of their different physical properties. Styrene will be lost more rapidly because it has a higher vapour pressure and solubility, and is lost by both evaporation and dissolution whereas divinylbenzene is lost only by evaporation. The EUROSPILL predicted relative rates of loss for styrene and divinylbenzene will only match the observed values if the experimentally derived k_E / k_S ratio is correct.

The pad samples taken during the release of styrene and divinylbenzene enable comparison of the differential loss between the two compounds to be compared with similar estimates from EUROSPILL. In order to compare the loss of both chemicals from the surface, the Styrene : Divinylbenzene ratio has been plotted with time from release for both the sea trial results and the Eurospill results for the corresponding release. These ratio plots are shown in Figure 20. The ratio with time will be dependant on a number on all the mass transfer processes as well as factors including spreading. Furthermore the chemicals will to some extent be in a dynamic flux between the surface and dissolution before evaporation. Styrene has an overall faster rate of evaporation and greater dissolution (as expected from its higher vapour pressure and solubility) compared with divinylbenzene. Further, the comparison of the EUROSPILL derived chemical ratio with the actual measured chemical ratio shows a remarkably similar trend with time (Figure 20). This plot provides confidence that EUROSPILL can not only accurately predict the rate of loss of a chemical which evaporates, or a chemical which dissolves, but also a chemical which partitions significantly from the water surface into the atmosphere and the water column.
Model scenarios were run to investigate the effects of different wind speeds on the rates of partitioning for the different components.
Figures 21, 22 and 23 show the model predicted mass balances for the styrene release at wind speeds of 5,10 and 15 knots respectively. The most notable difference is seen from the plots of mass evaporated and mass on surface where the higher wind speeds drive a faster evaporation rate and thus faster removal of mass on the surface. A similar picture can be seen (Figures 24 and 25) for the styrene/divinylbenzene release although in this case the change in evaporation rate with wind speed is less marked as a result of the slower release rate and the resulting greater surface area. Therefore, EUROSPILL is shown to be sensitive to changes in wind speed since this has a direct affect on the rate of evaporation which is the main mass transfer process for these chemicals.

The principal aim of this study was to assess whether the partitioning rates predicted by EUROSPILL are realistic and to assess whether the model accurately predicts the differential partitioning between two closely related chemicals. When compared with the surface sampling results, EUROSPILL gives a remarkably good estimate of both the relative partitioning and the rate of loss from the floating surface slick of the two chemicals.

4.4 Hazards to the marine environment - Water column monitoring.

Throughout the releases the Phase Doppler Particle Analyser (PDPA) was used to monitor droplet size at a depth of 0.5m in the water column in order to assess the dispersion processes (Lunel 1993). For all slicks it was concluded that there was insufficient wave energy, as no significant change in particle volume or particle size distribution was observed when compared with background particle levels at sea. It was therefore concluded that dispersion was not a significant process affecting partitioning under these conditions.
Figure 26 shows the measured concentration at each depth as the sampling boat passes through the slick. Using this data digital ground modelling (using linear interpolation between data points) allows us to produce a vertical distribution contour plot of water

column concentration for each transect across the slick. Figure 27 shows the contour plot corresponding to the slick transect in Figure 26.

The maximum predicted concentration in EUROSPILL is the average concentration within the most impacted grid cell (EUROSPILL divides the total impacted area into a 15x15 grid with dimensions set automatically to cover the dimensions of the slick). Therefore it is likely that within this grid the concentrations in the most impacted boxes may be greater than the maximum predicted, especially if there is a patchy distribution within a large box. The maximum concentrations from EUROSPILL for each chemical slick are shown in Figures 28 and 29. The apparent 3 fold difference between the maximum predicted concentration of styrene for the two releases is most likely a result of the lower release rates with the styrene/divinylbenzene mixture and a resulting faster evaporation rate of the surface pool in that slick.

The maximum concentrations predicted by the model are summarised in Figure 30 and compared with those measured during the experimental releases. These data suggest that the EUROSPILL model is over estimating the maximum water concentration by 6-9 fold. This overestimate is despite previous work (Lunel 1991) which lowered the mass transfer coefficient for dissolution from those in the literature (Mackay and Yeun 1983). Thus EUROSPILL provides a closer estimate to the observed data than other models based on the values of Mackay and Yeun (1983) and Liss and Merlivat (1986). However the mass transfer rates of dissolution for dissolver/evaporators are still overestimated or the rates of dilution are under predicted.

An important model function of the predicted maximum concentration is to assess the likely risks posed to marine life through comparison with the GESAMP toxicity classification published for each chemical. In this case it is advantageous to overestimate the concentration and therefore assess the maximum risk to the marine organisms. Since the relative partitioning between styrene and divinylbenzene was predicted accurately we do not recommend at this stage modifying the mass transfer coefficient for dissolution. Rather we suggest that MPCU note that the predicted values are likely to be a conservative estimate of the concentrations in the water column.

5. CONCLUSIONS:

The laboratory and early sea trial experiments have established the credibility for the scientific basis of the EUROSPILL chemical model. However the hazards posed to responders and the environment in the event of a chemical spill meant that a large scale validation experiment was required by MPCU. The validation experiments have shown:

Position of the slick - EUROSPILL accurately predicts the trajectory of a chemical spill. This should provide MPCU with confidence in using the model to predict the movements of a chemical slick even though chemical slicks can be considerably more difficult to track than oil spills as many are colourless compounds.

Surface area and persistence of the slick - Contour analysis using EUROSPILL provides a good estimate of the surface area of the Styrene/ Divinylbenzene slick and a reasonable estimate for the Styrene release. Importantly in terms of potential response to the spill EUROSPILL can provide an estimate of the persistence of the surface slick providing that the user also assess that the predicted contour grid concentration is significant.

Partitioning of the chemical- Accurate prediction of the partitioning of the chemical between sea surface, atmosphere and water column is critical in determining the response to a chemical spill . It is the partitioning of the chemical which determines the hazards posed to the responders, the public and the marine environment. This validation experiment showed very close correlation between the relative rates of loss of styrene and divinylbenzene predicted by EUROSPILL and those observed in the field. This result in combination with previous field trials conducted for MPCU provides considerable confidence in EUROSPILL's prediction of the relative partitioning of chemicals at sea.

Hazard to the marine environment - Comparison of the maximum predicted concentration with those observed show that EUROSPILL over estimates the dissolved concentration of styrene 6-9 fold. Since the relative partitioning predicted by EUROSPILL was very close to observed, and because of the potential risks associated with under predicting the dissolved concentration of toxic chemicals, we do not recommend that EUROSPILL should be modified. MPCU should, however, note that EUROSPILL predictions may over estimate the maximum concentration of dissolved chemical by up to an order of magnitude.

In conclusion, this large scale validation of EUROSPILL has shown that the model can be used with some confidence in the event of a spill to predict the slick position, surface area, persistence, partitioning and hazards to the marine environment.

6. ACKNOWLEDGEMENT:

The authors thank MPCU of the UK Department of Transport's Coastguard Agency, for funding the work described; the styrene was kindly donated by the CEFIC (European Chemical Industry Council) Styrene Sector Group. We would also like to thank the following personnel for their significant contribution to the sea trials: R Dunn, N Bailey, M Sommerville, C Halliwell, A Dobie, C Sopp (AEA), D Thomas (Steptech) and F Merlin, G Le Nouy and all others aboard The Elan from CEDRE and the French Navy.

7. REFERENCES:

Cormack, D. "Response measures for chemical spillage". *Marichem* 1982 - Amsterdam. Ed: Singleton, Marichem Secretariat, Rickmansworth, UK. (1982)

Hurford, N., Buchanan, I., Law, R.J., and Hudson, P.M., "Comparison of two fluorometers for measuring oil concentrations in the sea", *Oil and Chemical Pollution*, 5:379-389 (1989).

Hurford, N., & Wallace, D., " Development of an oil and chemical spill simulation model for the North West European continental shelf and the Western Mediterranean /

Adriatic seas - interim report for the European Commission". *Warren Spring Report LR 809* (MP / BM). ISBN 0 85624 667 0. (1991).

Leech, M.V., Lunel, T., and Walker, M.I. "EUROSPILL 2: model user guide". *Warren Spring Report LR 987* ISBN 0 85624 847 9. (1993).

Liss,P.S. and Merlivat, L., "Air-sea gas exchange rates: Introduction and synthesis". pp 113-127. in *The Role of Air-Sea Exchange in Geochemical Cycling* Ed. P Buat-Menard., Reidel . Dordrecht, (1983).

Lunel, T. "Dispersant effectiveness at sea" *Proceedings 1995 oil spill conference*. pp 147-155. (1985).

Lunel, T. "Dispersion. Oil droplet size measurements at sea".. *Proceedings 16th Arctic and Marine Oil Spill Technical Seminar.* Environment Canada, pp 1023- 1056, (1993).

Lunel T. Eurospill: "Chemical spill model based on modelling turbulent mixing at sea".. *Proceedings of the Eighth Technical Seminar on Chemical Spills*. pp 47-60 (1991).

Mackay D., & Yeun A.T.K. "Mass transfer correlations for volatilisation of organic solutes from water" *Environ. Sci. Technol.* **17**, 211-17, (1983) .

Figure 1. MV Lowland Cavalier showing chemical storage tanks.

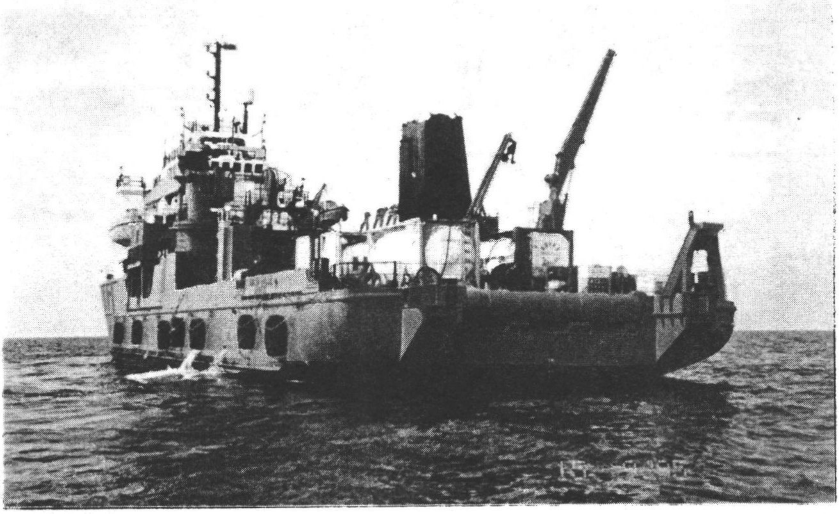


Figure 2. Sampling boat carrying out water column monitoring.

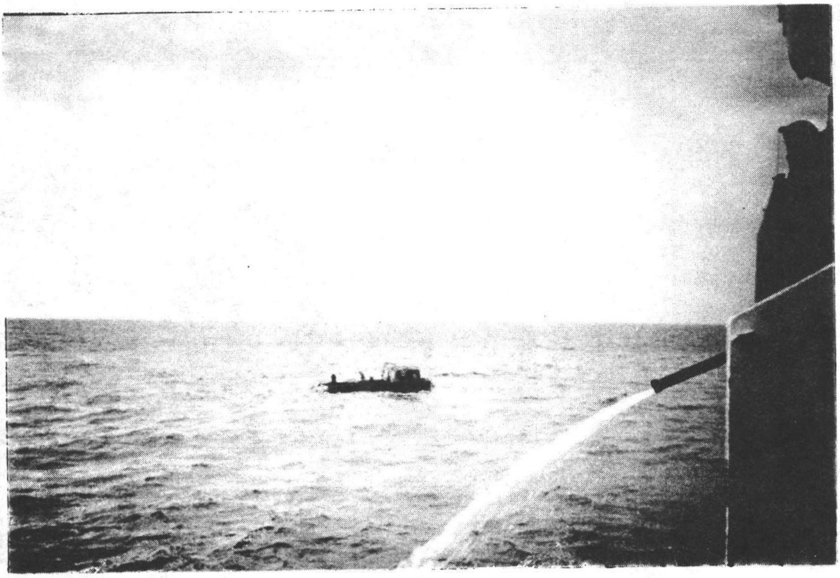


Figure 3. Monitoring in respiratory protective equipment.

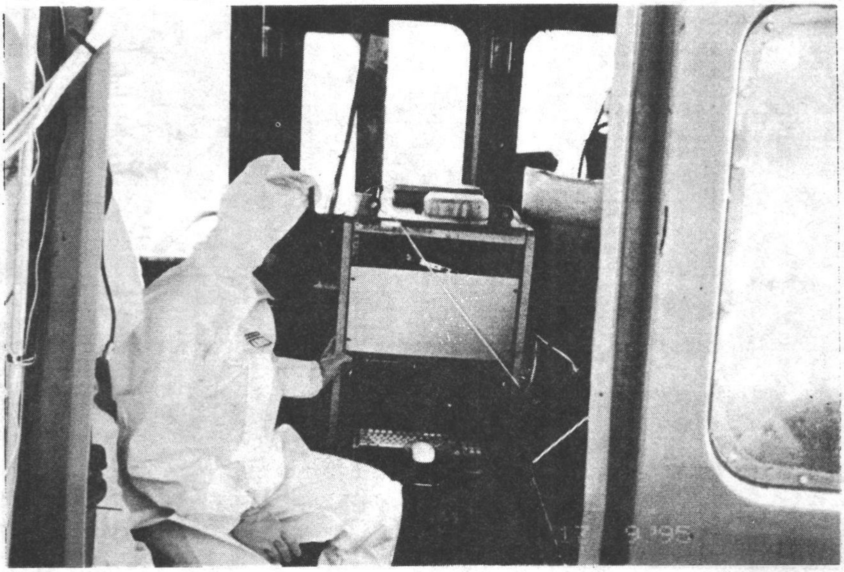


Figure 4. Surface-pad sampling in small boat.

Figure 5. Chemical vapour concetration measured by PID (UVIC) - During Release.

Vapour Name: TOLUENE

Sample Rate: 0.25 S

Total Number of Data Points: 1152

Total Logging Duration: 288.00 S

UVIC Log Time: 12:40

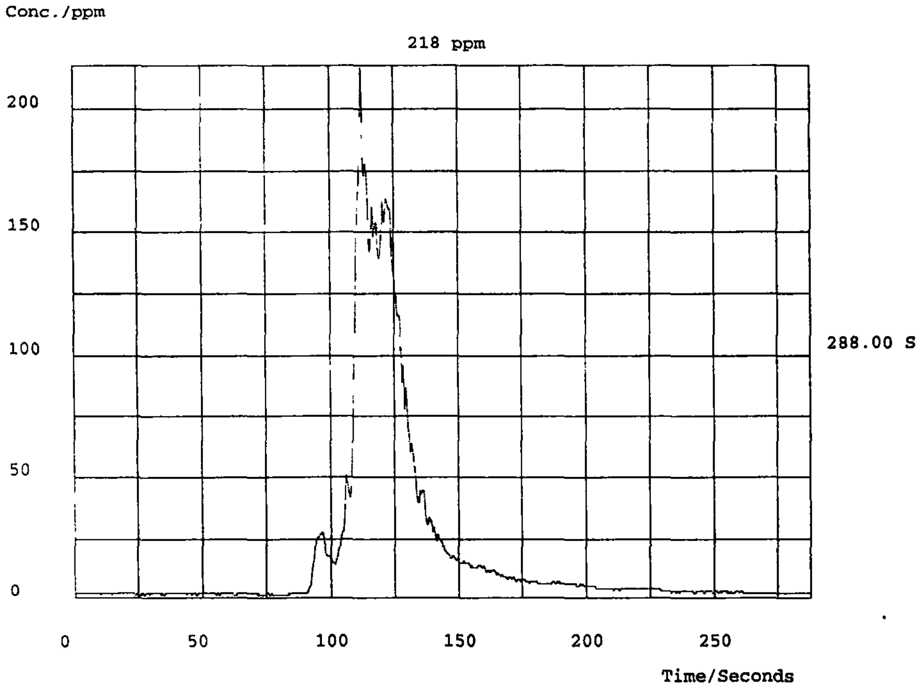
UVIC Log Date: 16/09/95

Data Block No.: 3

Data Point Measuring Units: ppm

Maximum Data Point Reading: 218

Minimum Data Point Reading: 0



Print Time & Date: 11:14 Friday, September 22, 1995

Figure 6. Chemical vapour concetration measured by PID (UVIC) - 0.5 hour after Release.

Vapour Name: TOLUENE

Sample Rate: 0.25 S

Total Number of Data Points: 4309

Total Logging Duration: 1077.25 S

UVIC Log Time: 13:07

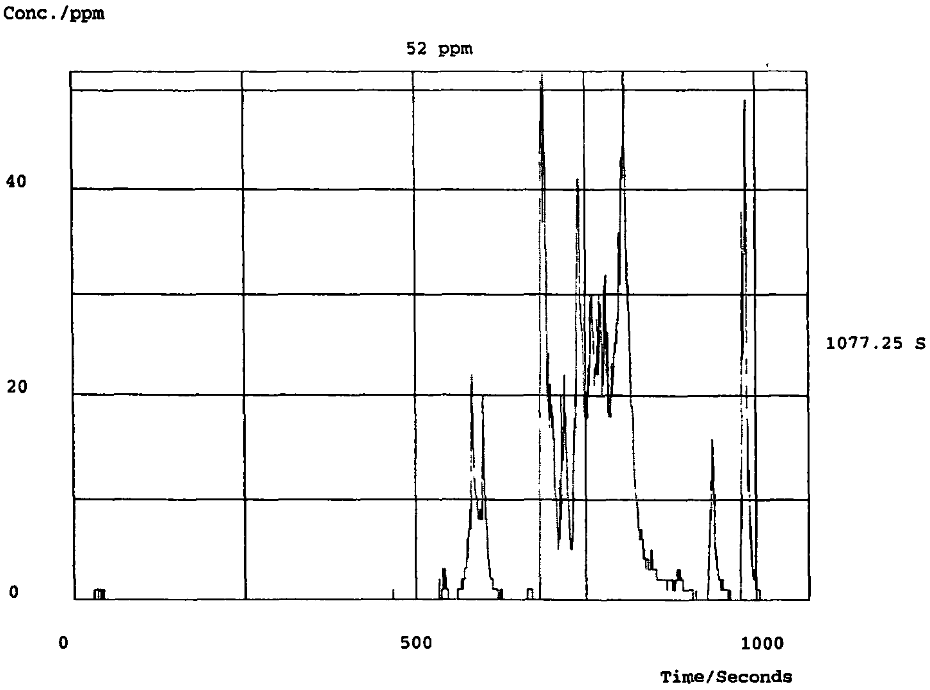
UVIC Log Date: 16/09/95

Data Block No.: 6

Data Point Measuring Units: ppm

Maximum Data Point Reading: 52

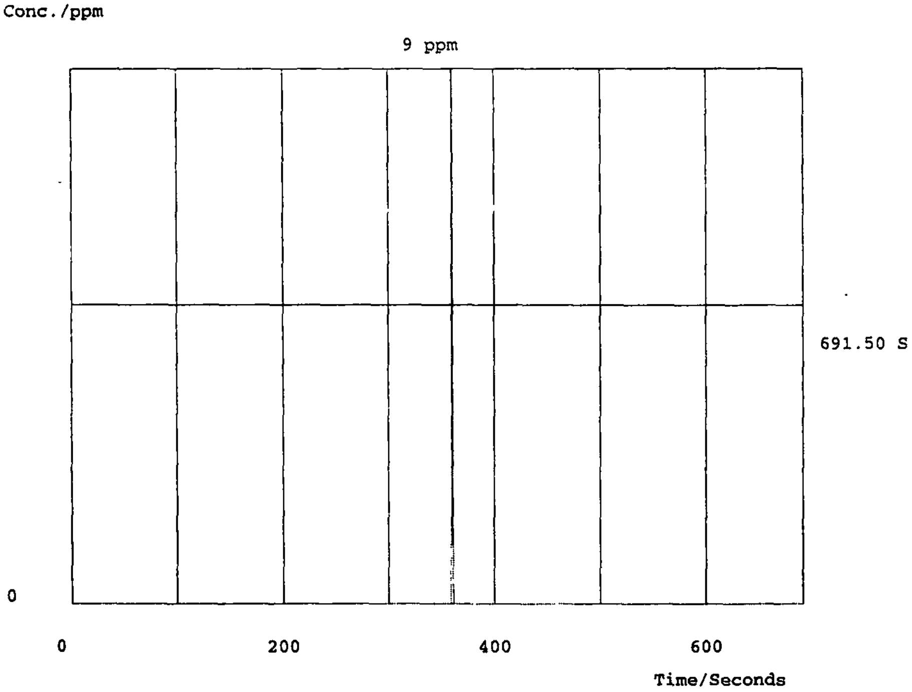
Minimum Data Point Reading: 0



Print Time & Date: 11:15 Friday, September 22, 1995

Figure 7. Chemical vapour concetration measured by PID (UVIC) - 1 hour after Release.

```
Vapour Name:       TOLUENE                              UVIC Log Time:       13:47

Sample Rate:       0.25 S                               UVIC Log Date:       16/09/95

Total Number of Data Points:      2766                  Data Block No.:      8

Total Logging Duration:           691.50 S


Data Point Measuring Units:       ppm

Maximum Data Point Reading:       9

Minimum Data Point Reading:       0
```



Print Time & Date: 11:16 Friday, September 22, 1995

Figure 8. Mass Balance of Styrene Slick

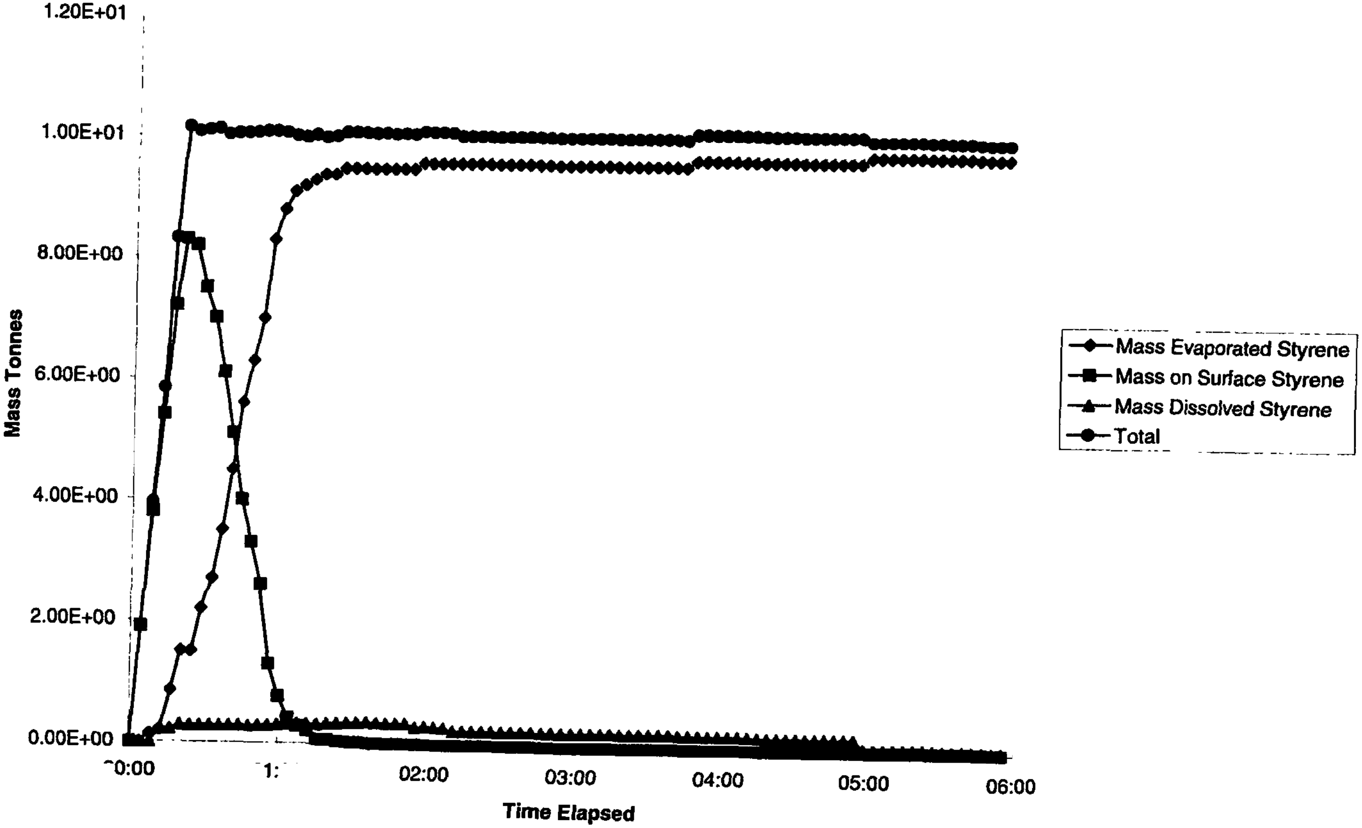


Figure 9. Styrene Mass Balance for Styrene / Divinylbenzene Slick

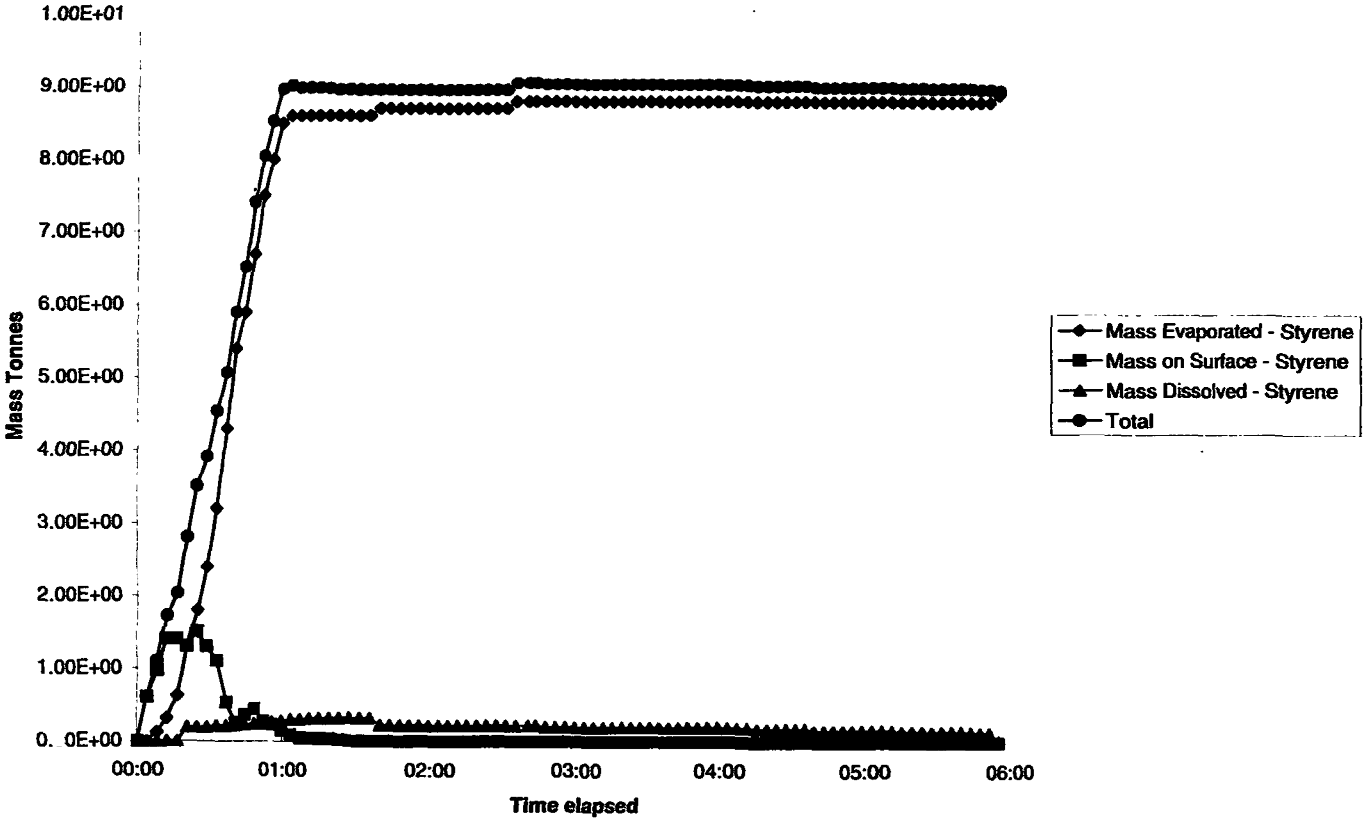


Figure 10. Gullfaks trajectory form EUROSPILL, IR remote sensing and pad sample positions.

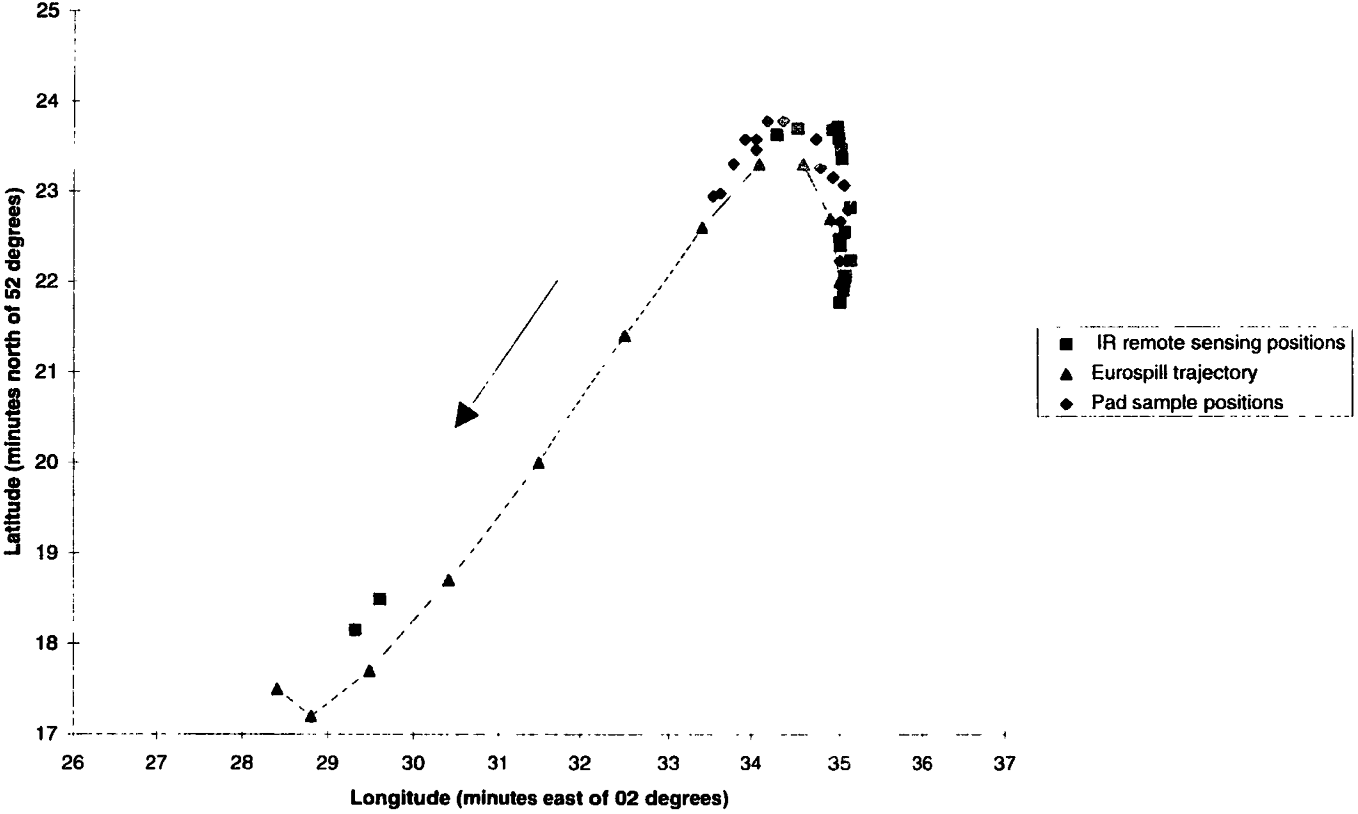


Figure 11. Styrene slick position from Eurospill model, IR remote sensing and pad sample positions.

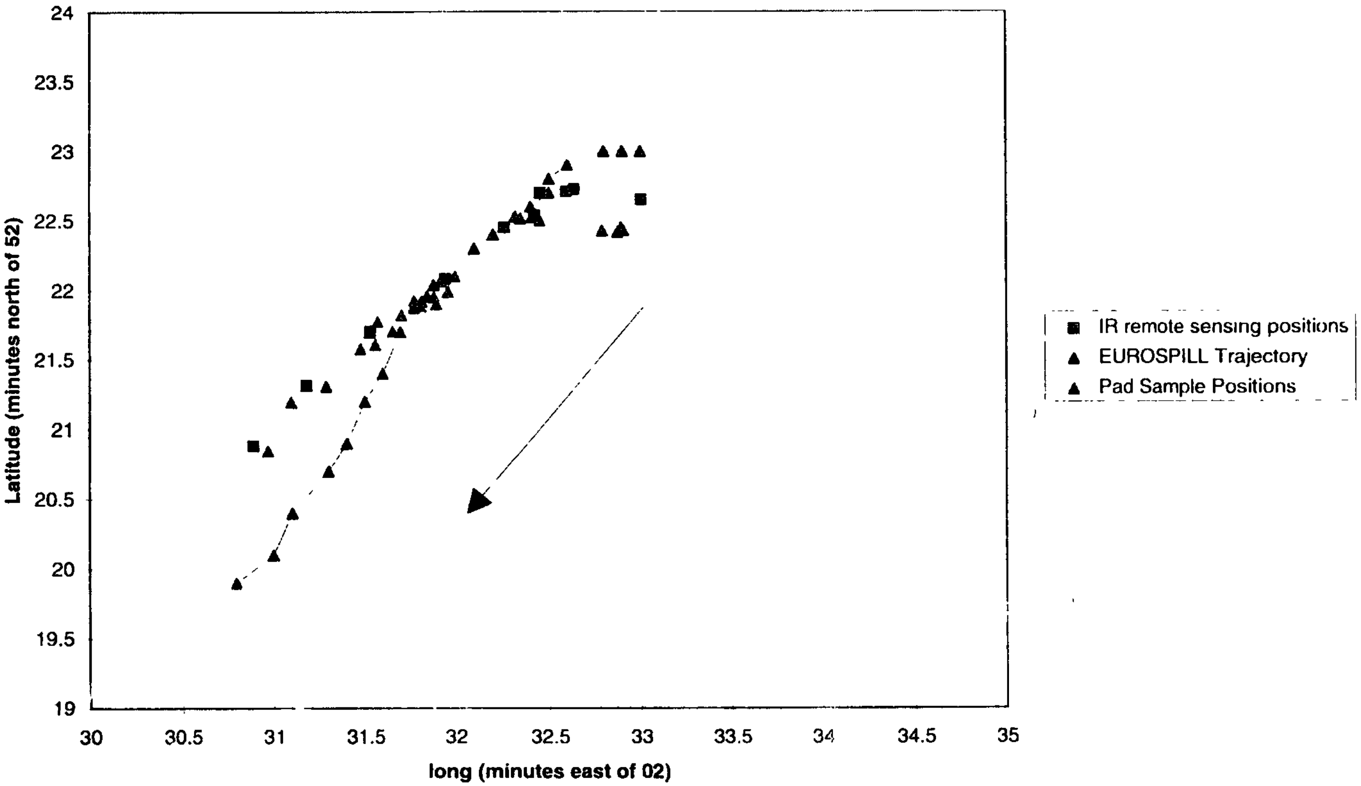


Figure 12. Styrene/Divinylbenzene slick trajectory from EUROSPILL, IR remote sensing and pad sampling positions.

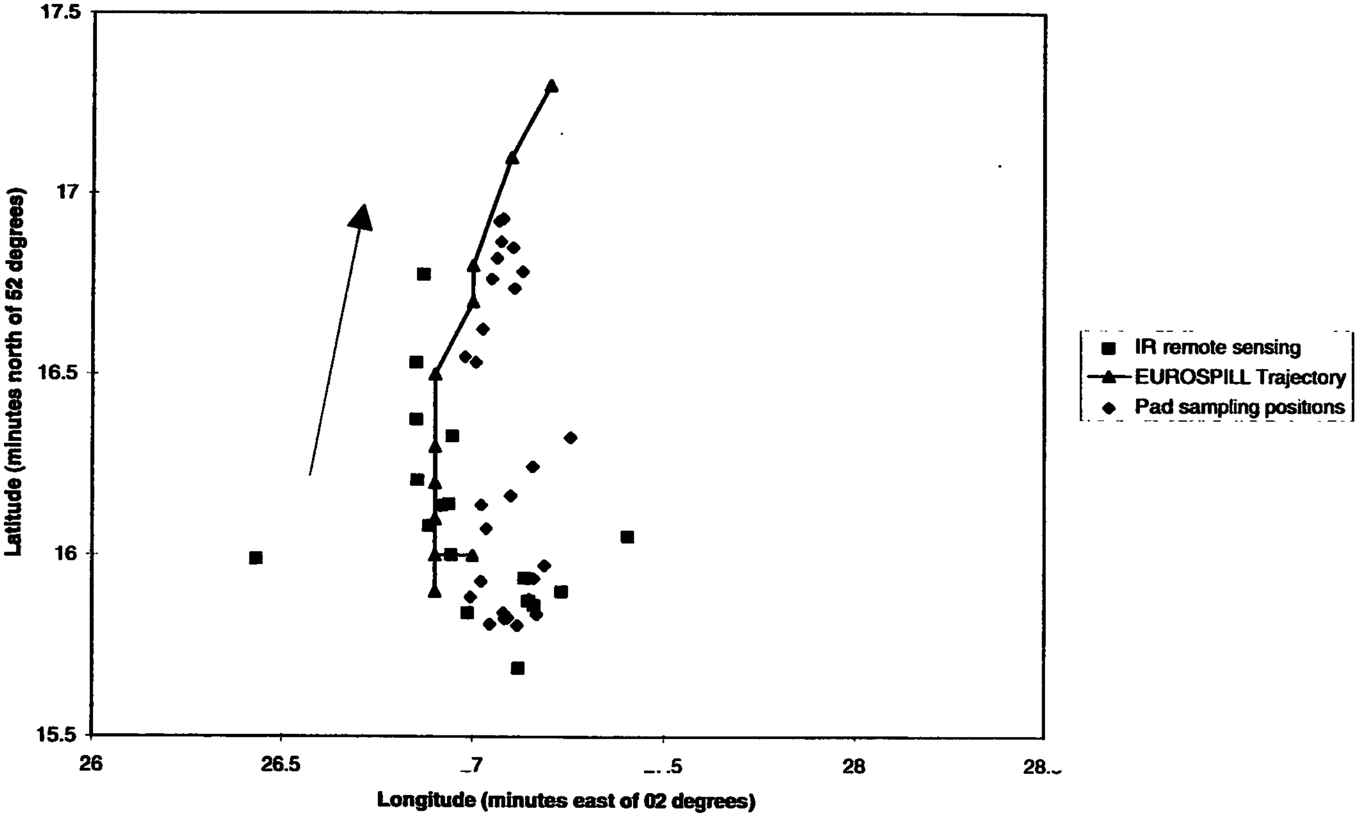
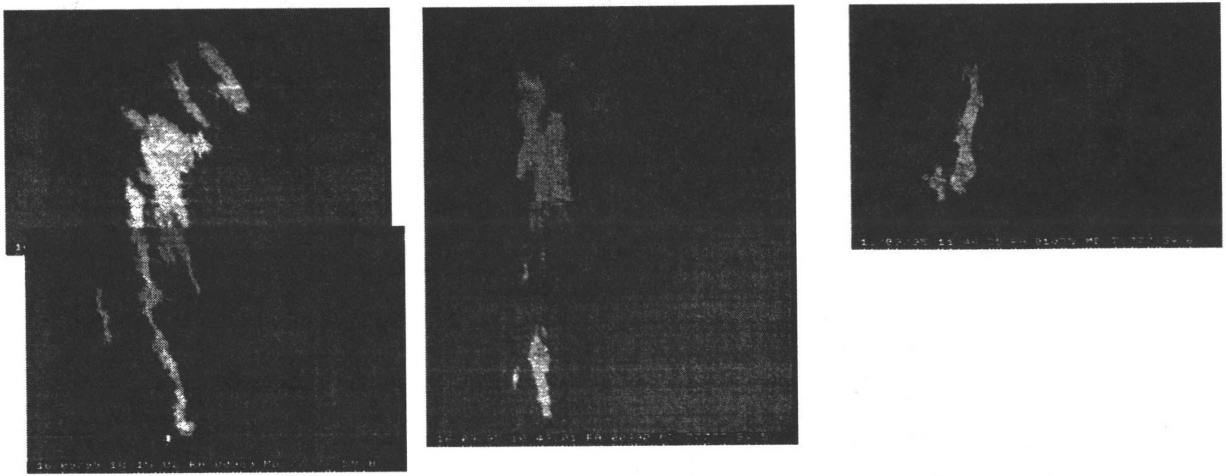


Figure 13. IR remote sensing imagery (1000 ft) of the styrene slick showing surface area and persistence.



Time from
start of release: 20 mins 60 mins 90 mins

Figure 14. Remote Sensing Area Data (m2)

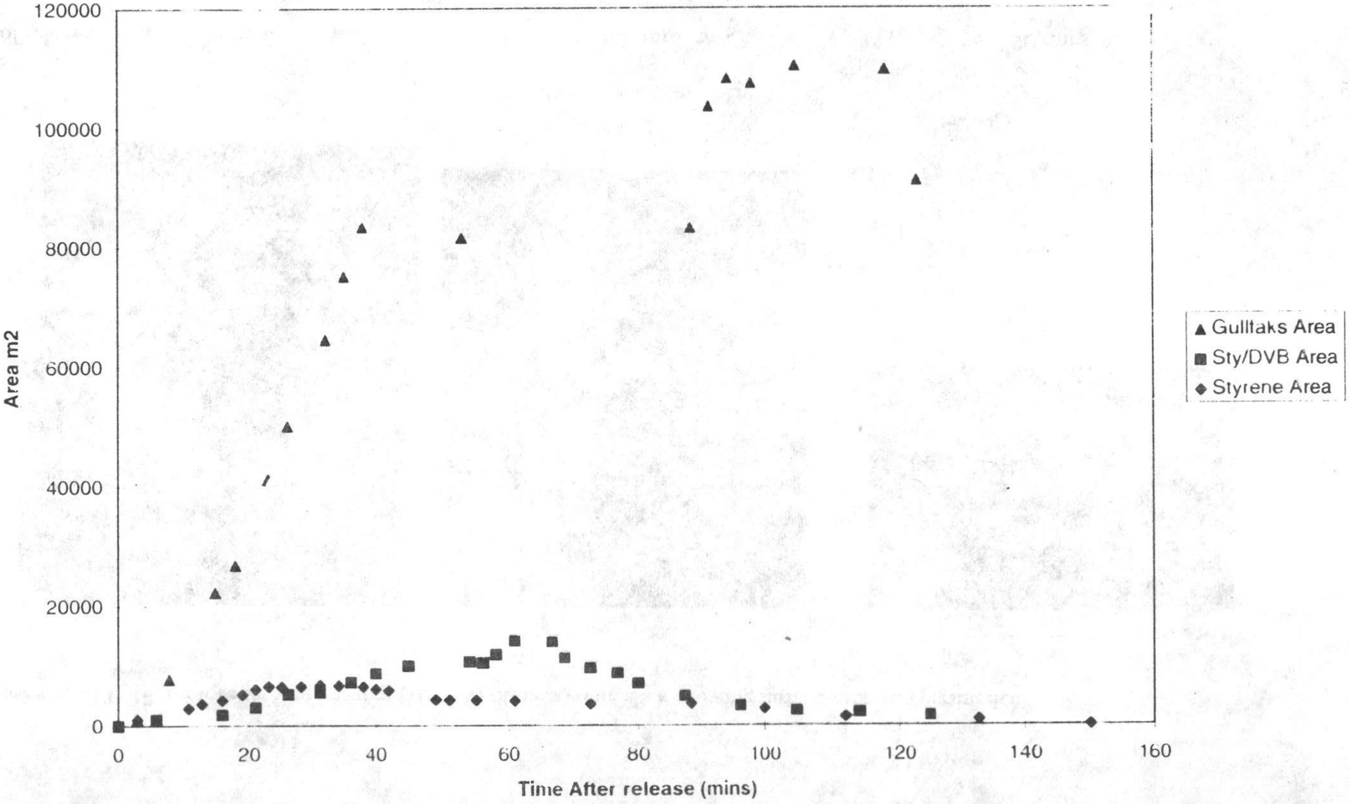


Figure 15. Surface area of Styrene Slick from remote sensing data and EUROSPILL prediction.

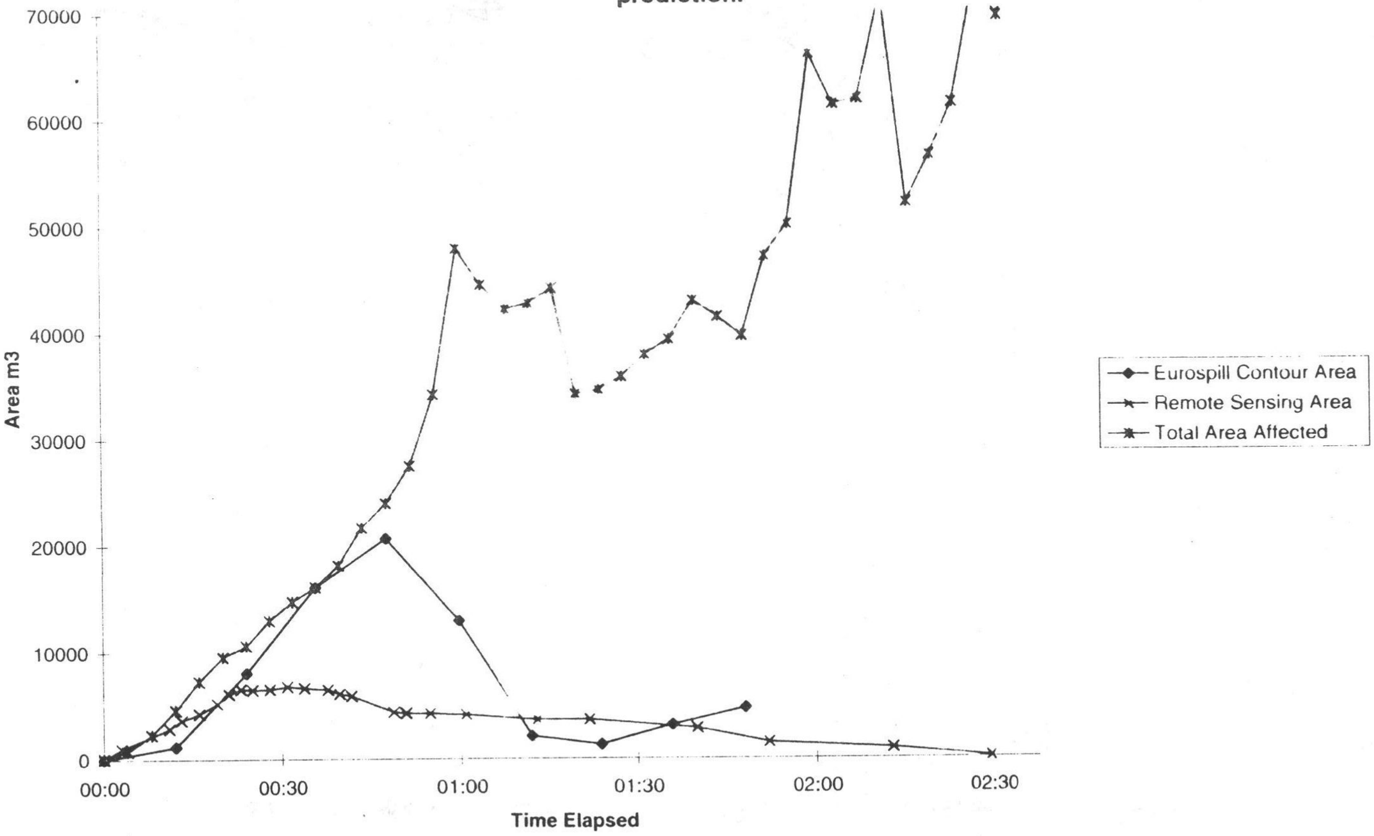


Figure 16. Divinylbenzene slick surface area - comparison of EUROSPILL predicted vs. observed

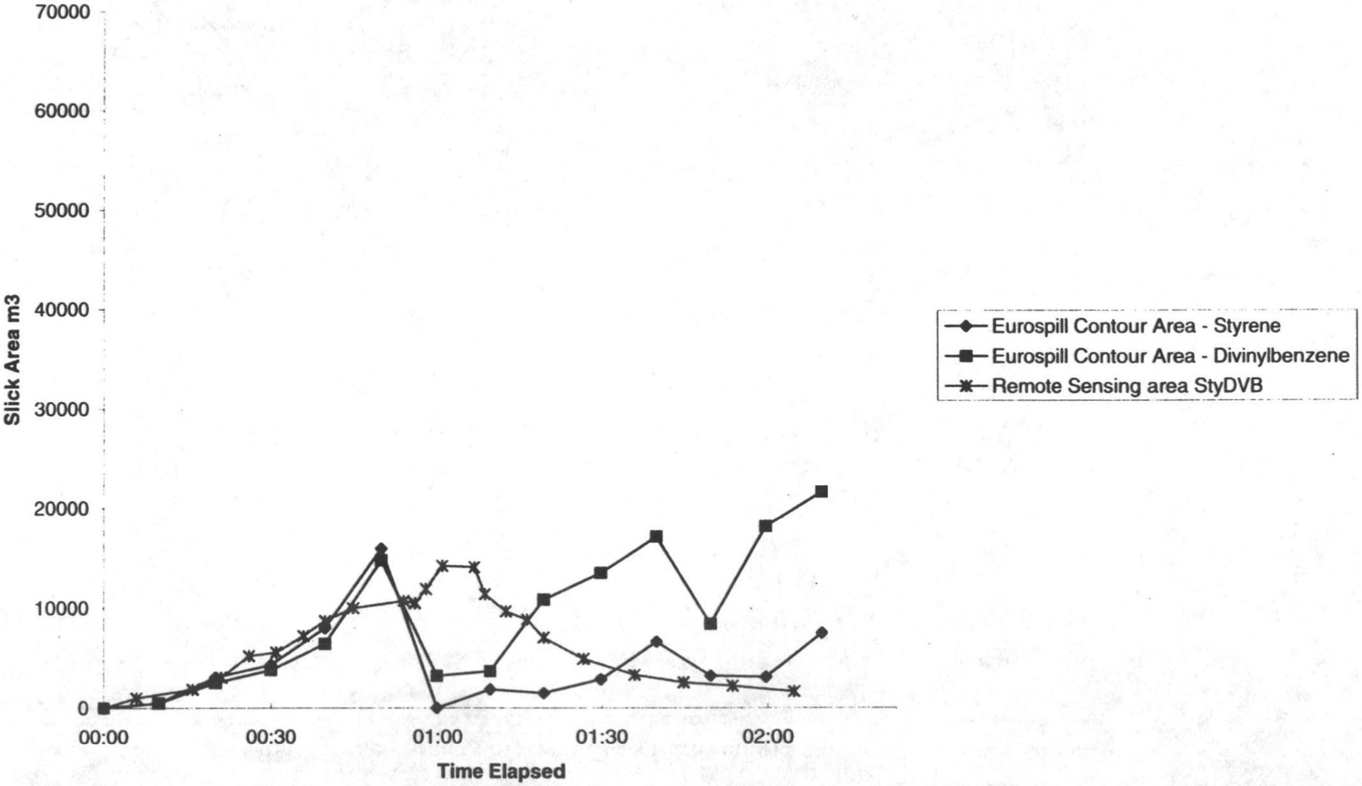


Figure 17. EUROSPILL output of maximum concentration in contour grid cells for the top 0.1m: a) During and b) 1 Hour after release.

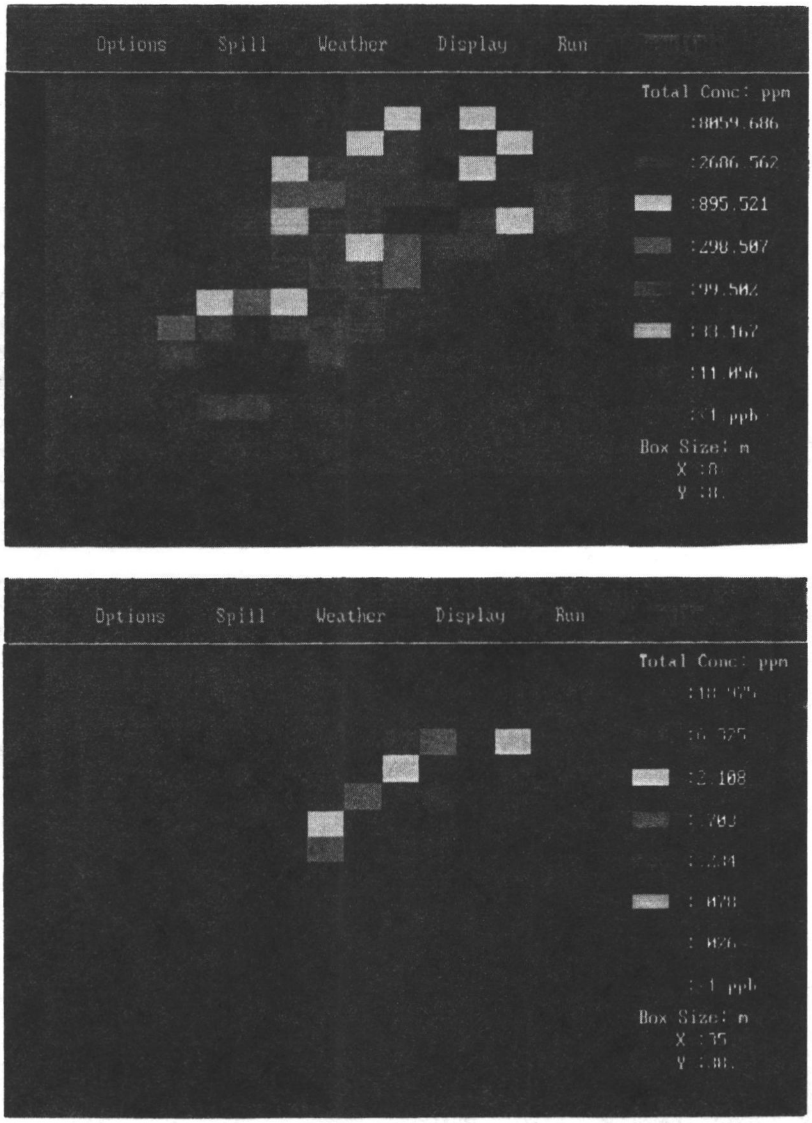


Figure 18. Surface Mass of Styrene (Tonnes) - Comparison of EUROSPILL prediction with sea trial estimate.

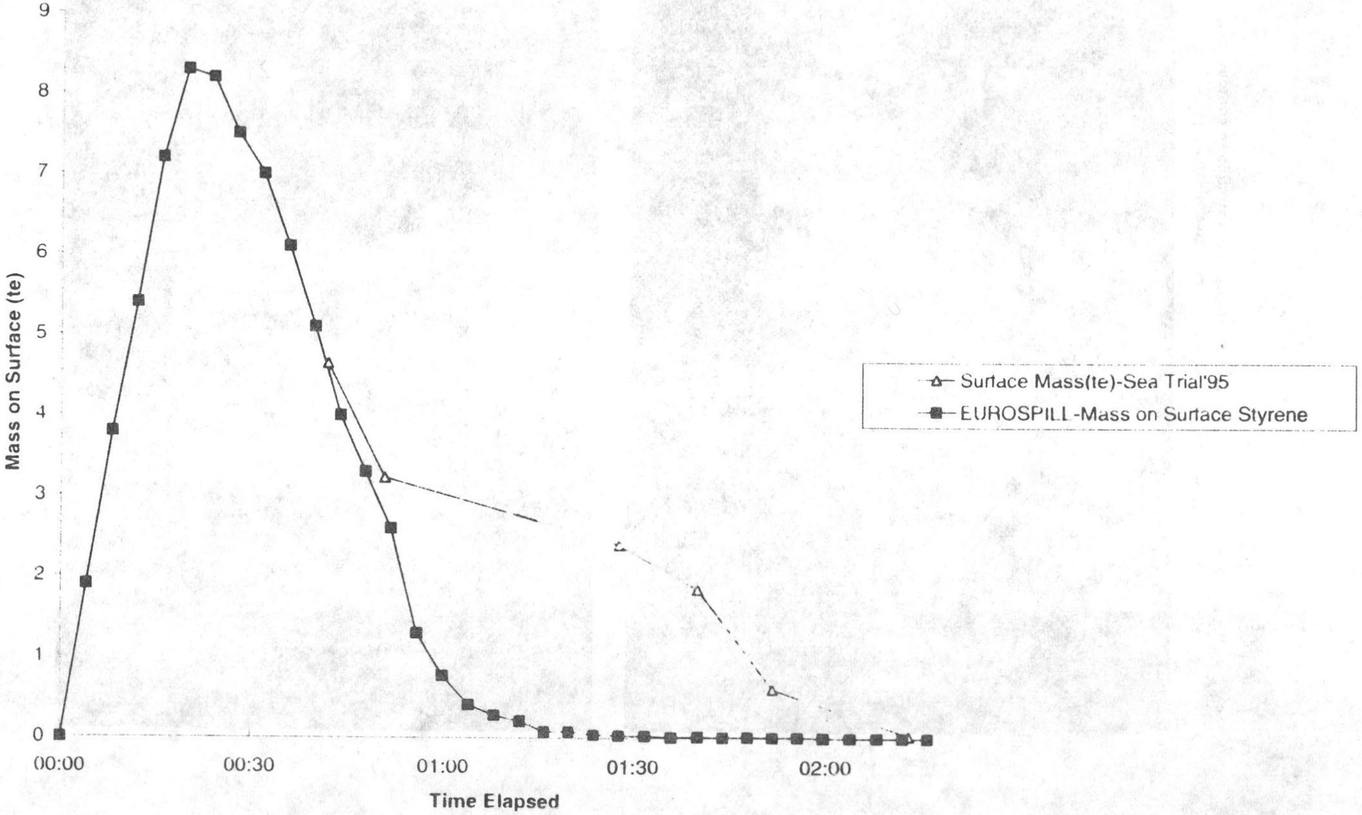


Figure 20. Styrene/Divinylbenzene Ratio. Comparison of Eurospill Predicted with Sea Trial Data.

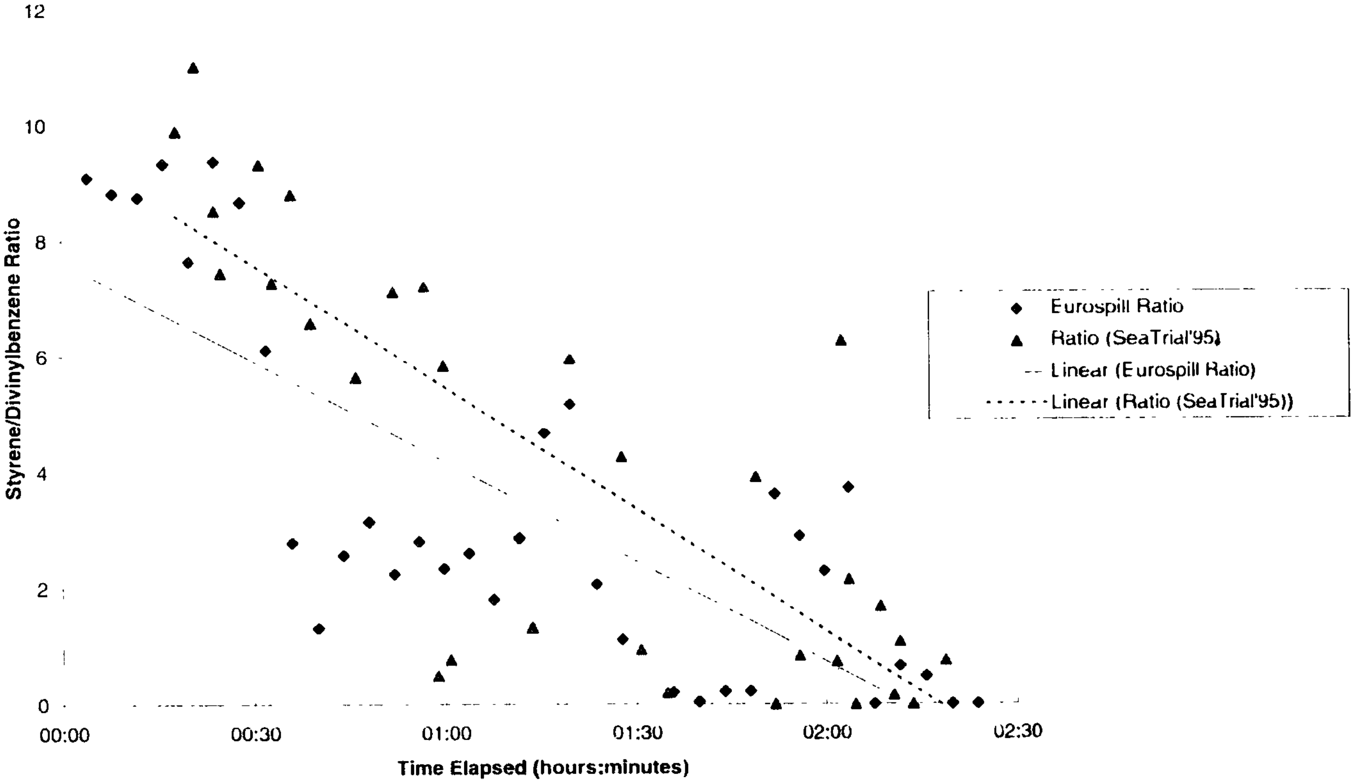


Figure 21. Mass Balance of styrene release, windspeed 5kt

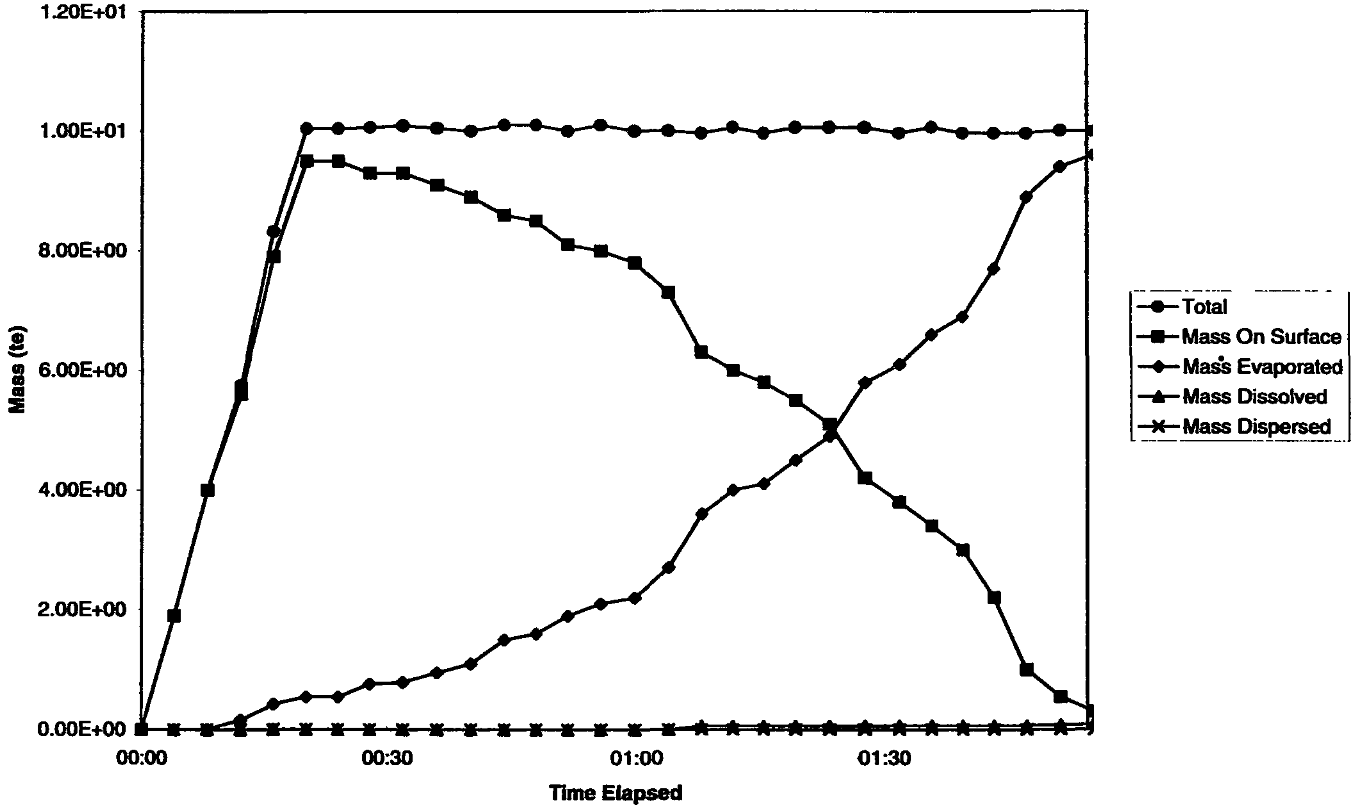


Figure 22. Mass Balance of Styrene only release, windspeed 10kt

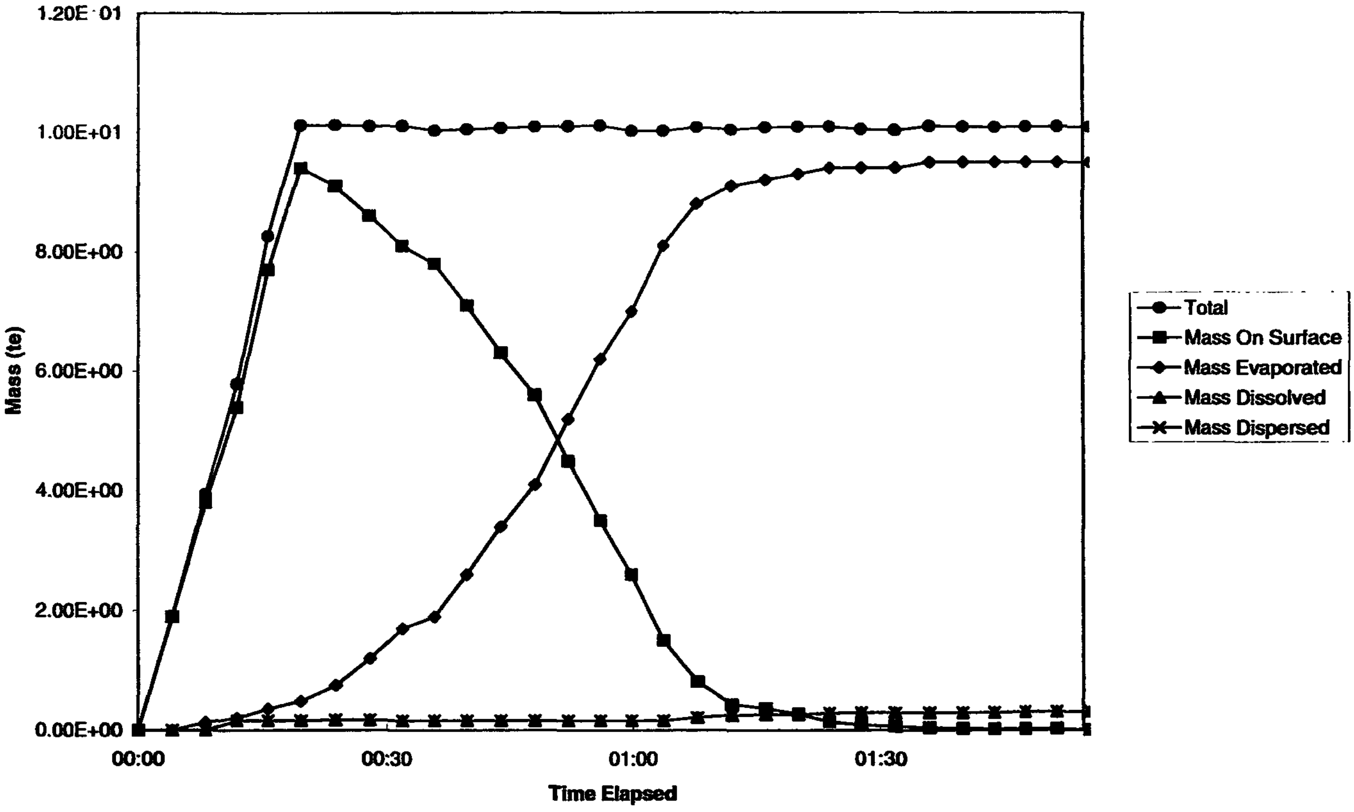


Figure 23. Mass Balance of styrene only release, windspeed 15kt

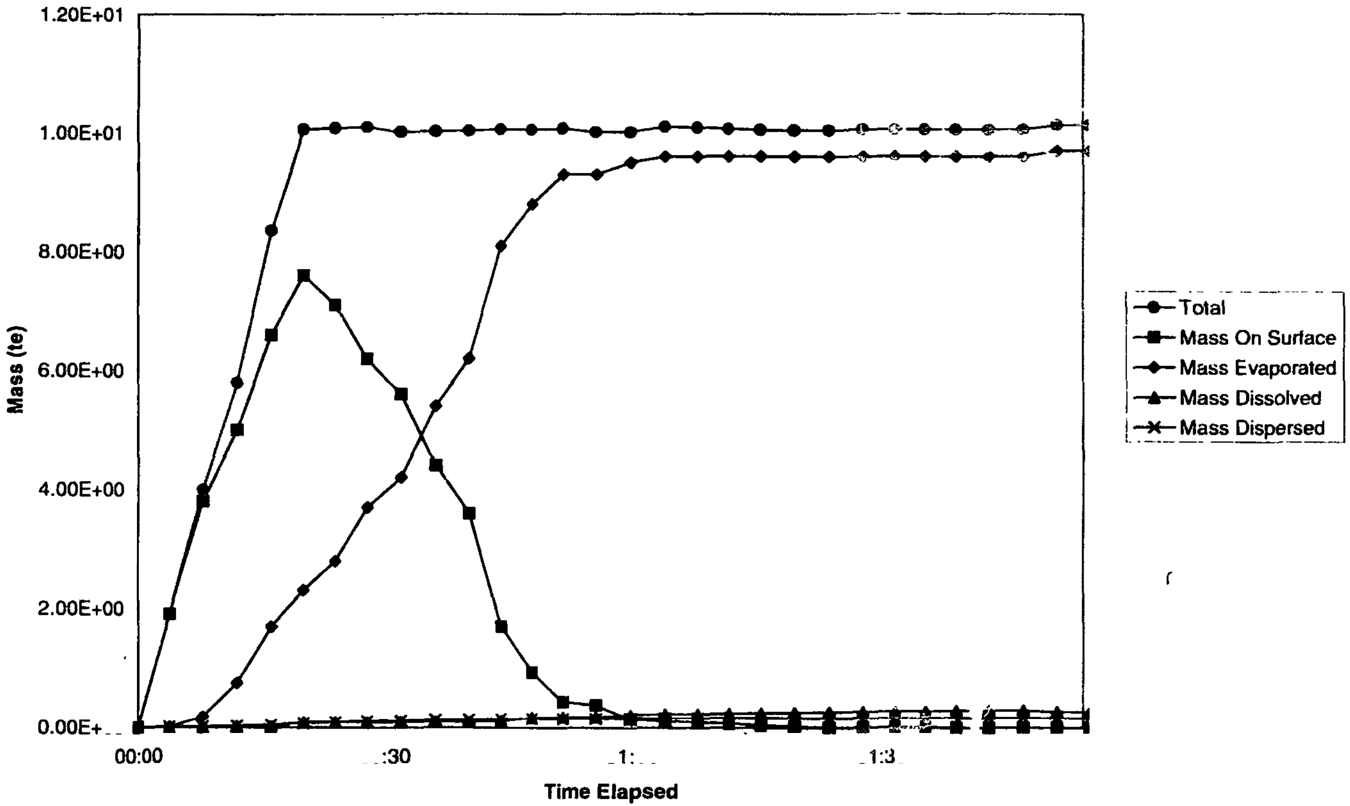


Figure 24. Mass Balance of Styrene from the STY/DVB mix release, windspeed 8kt

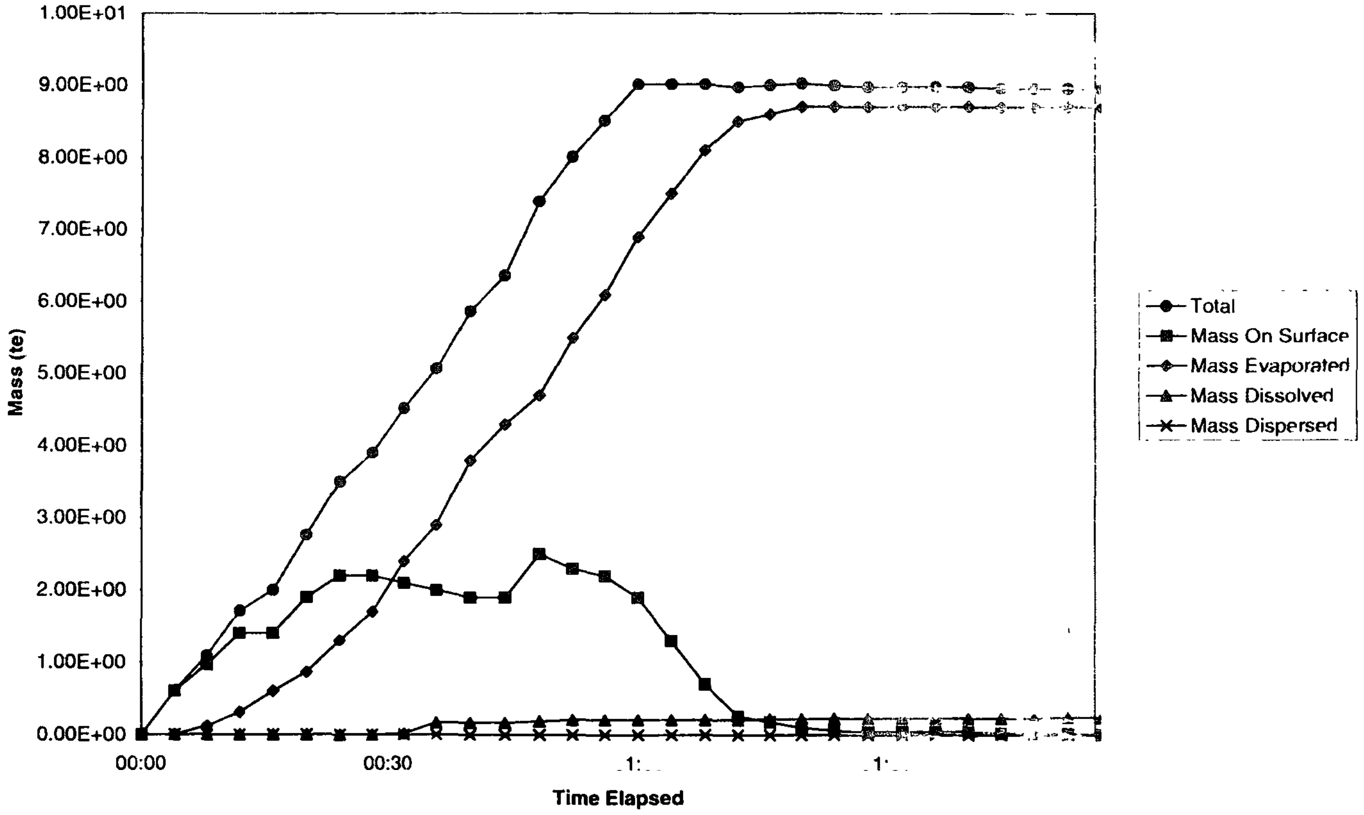


Figure 25. Mass Balance of Styrene form the STY/DVB Mix release, windspeed 12kt

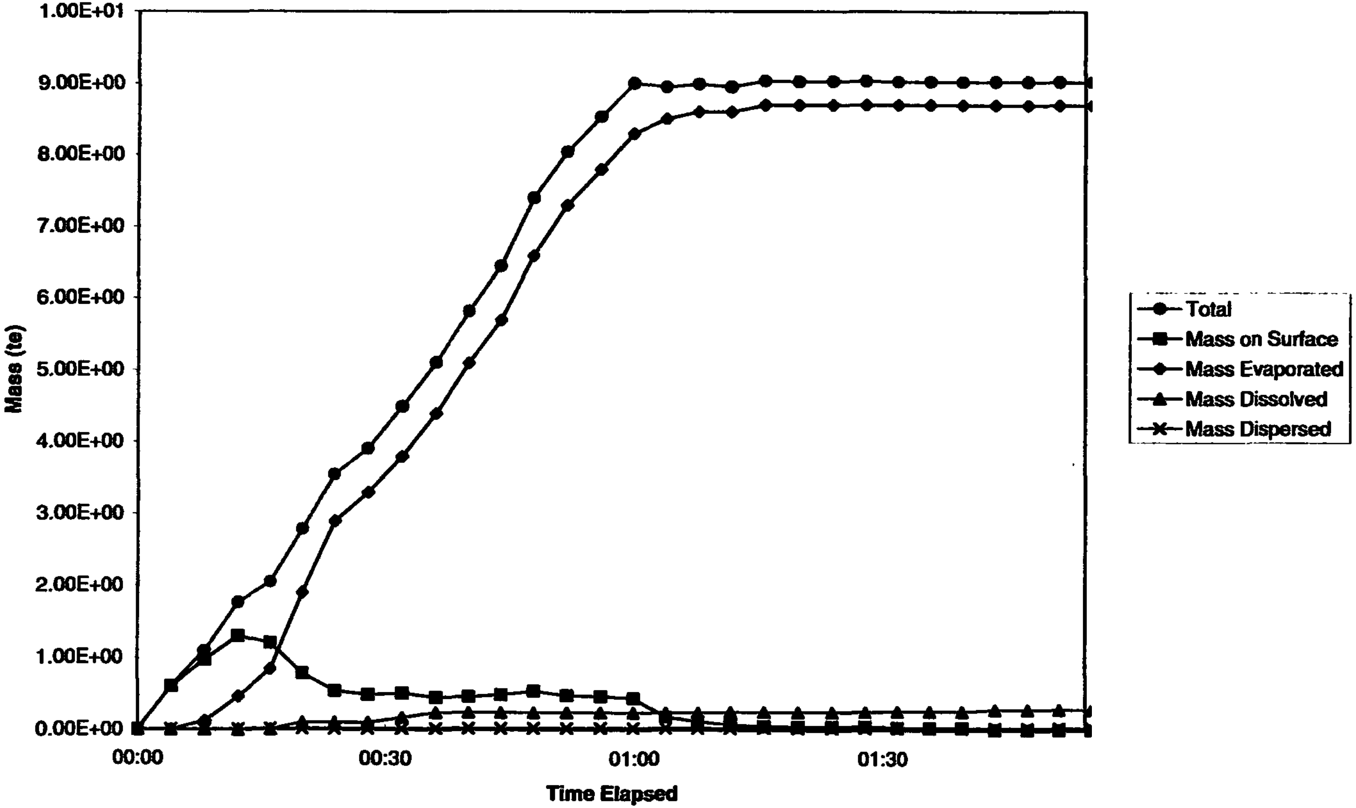


Figure 26. Chemical concentration against distance for a transect across the slick.

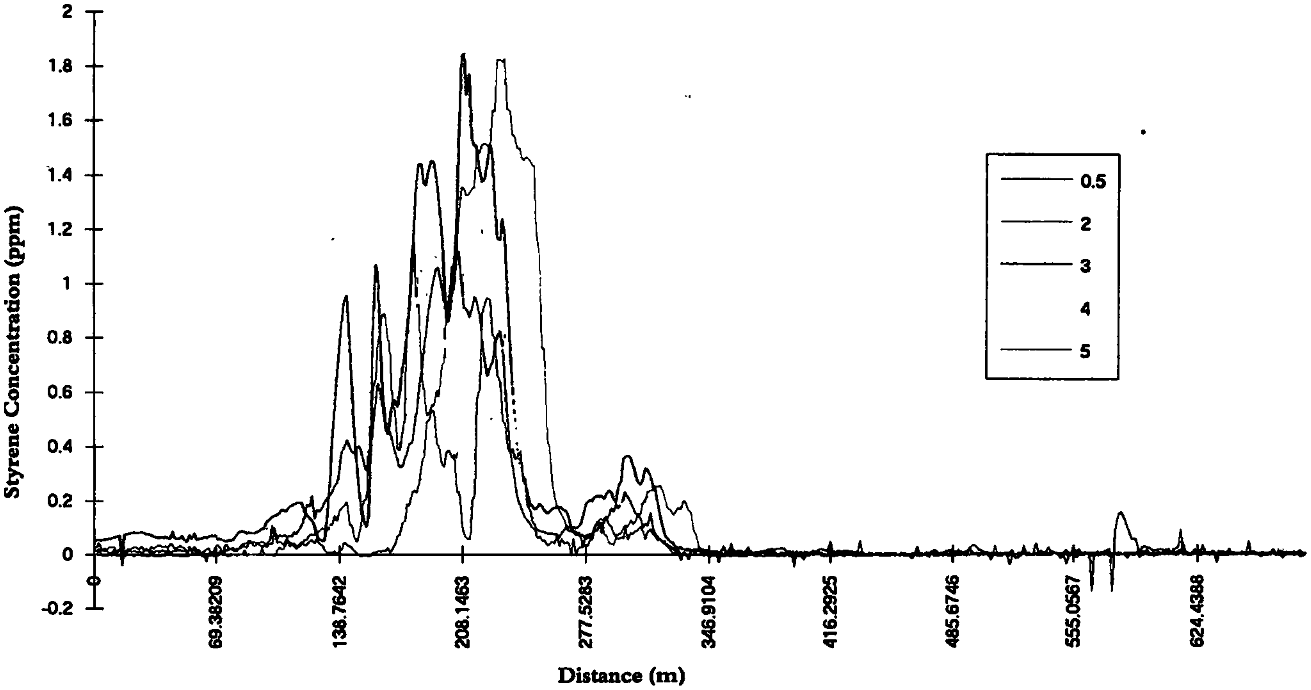
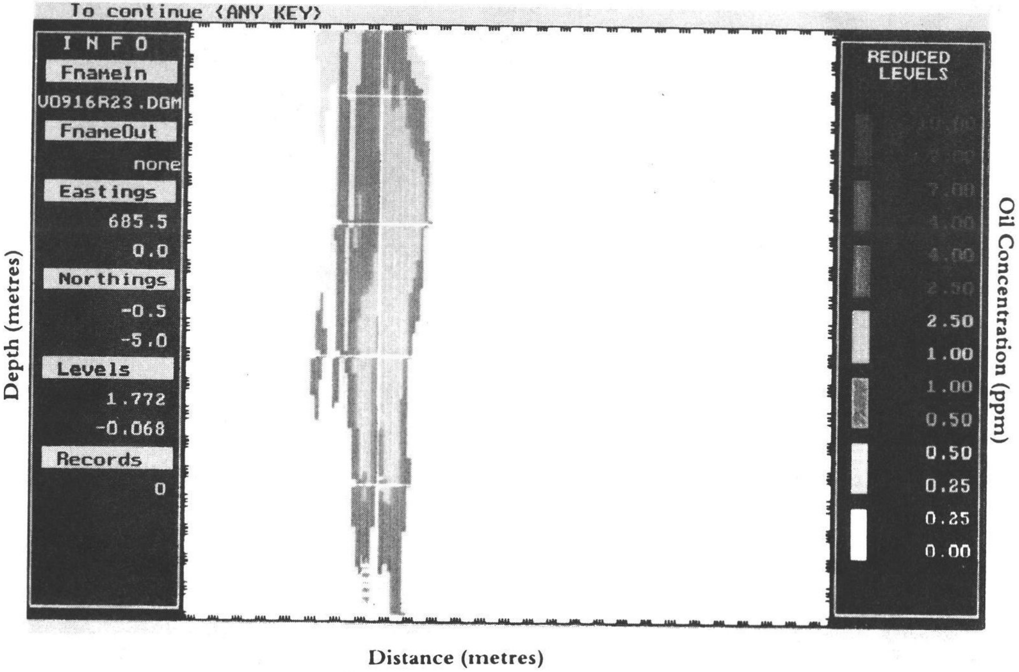


Figure 27. Contour plot of chemical concentrations (represented by colour bands) for across the slick. (derived from Figure 26).



To continue <ANY KEY>

INFO

FnameIn
V0916R23.DGM

FnameOut
none

Eastings
685.5
0.0

Northings
-0.5
-5.0

Levels
1.772
-0.068

Records
0

Figure 28. Maximum Water Concentration of Styrene (ppm) predicted by EUROSPILL for Styrene Slick.

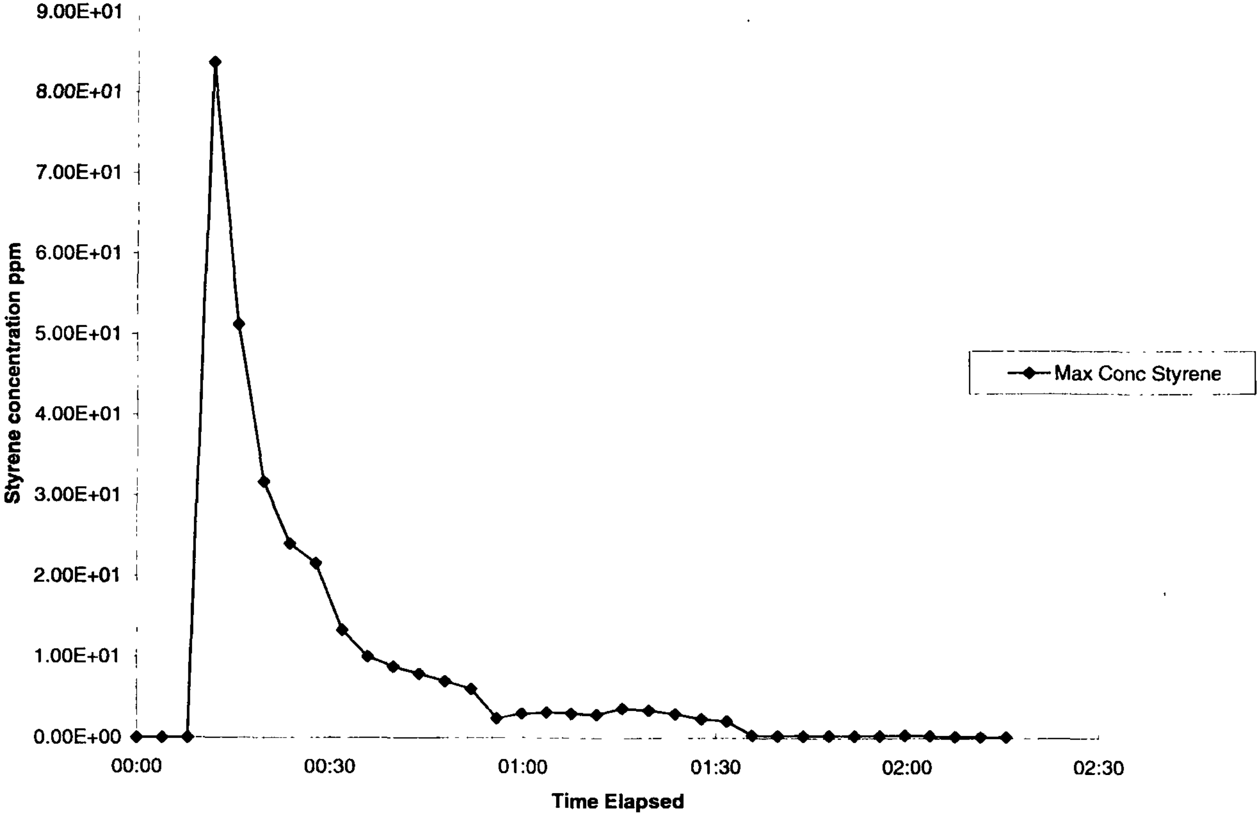


Figure 29. Maximum Water Column Concentrations (ppm) predicted by EUROSPILL for the Styrene/Divinylbenzene release.

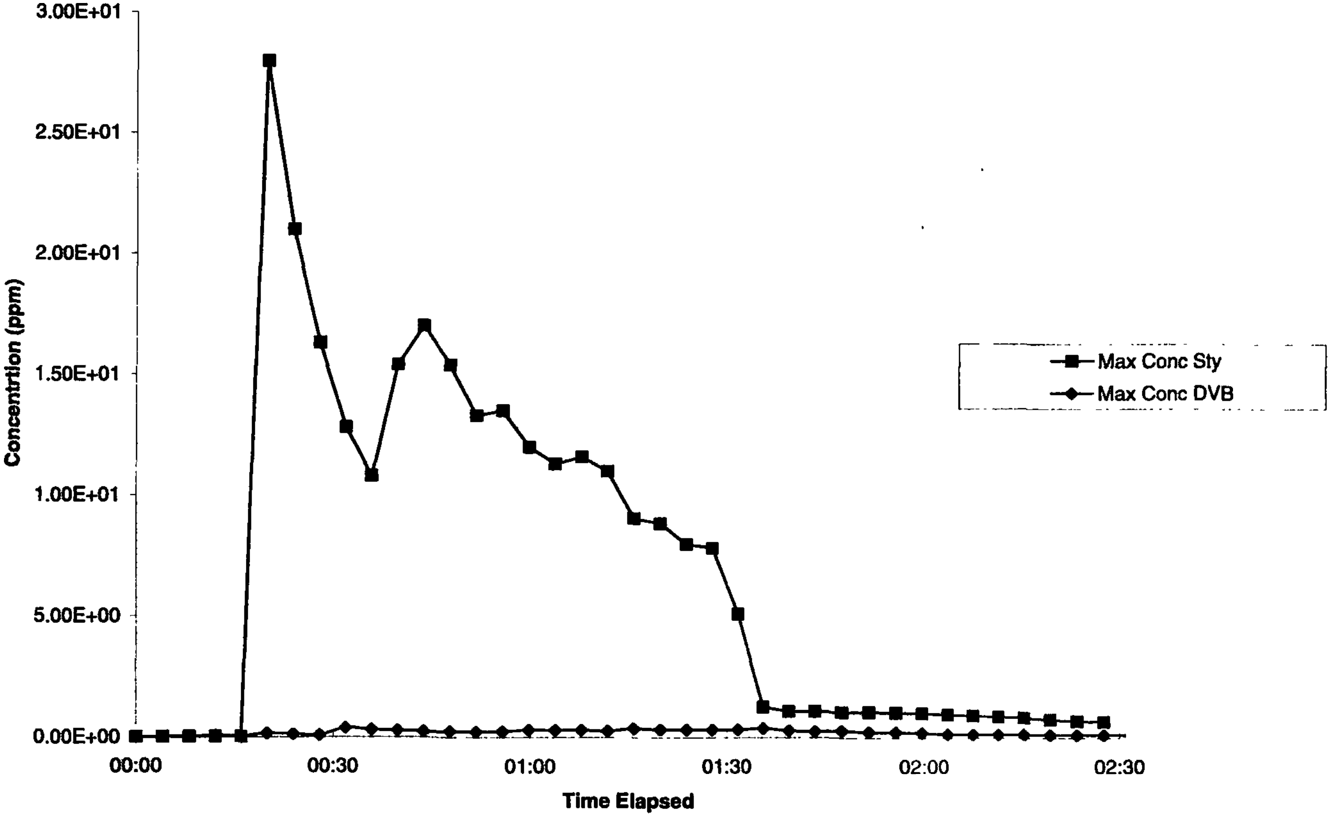
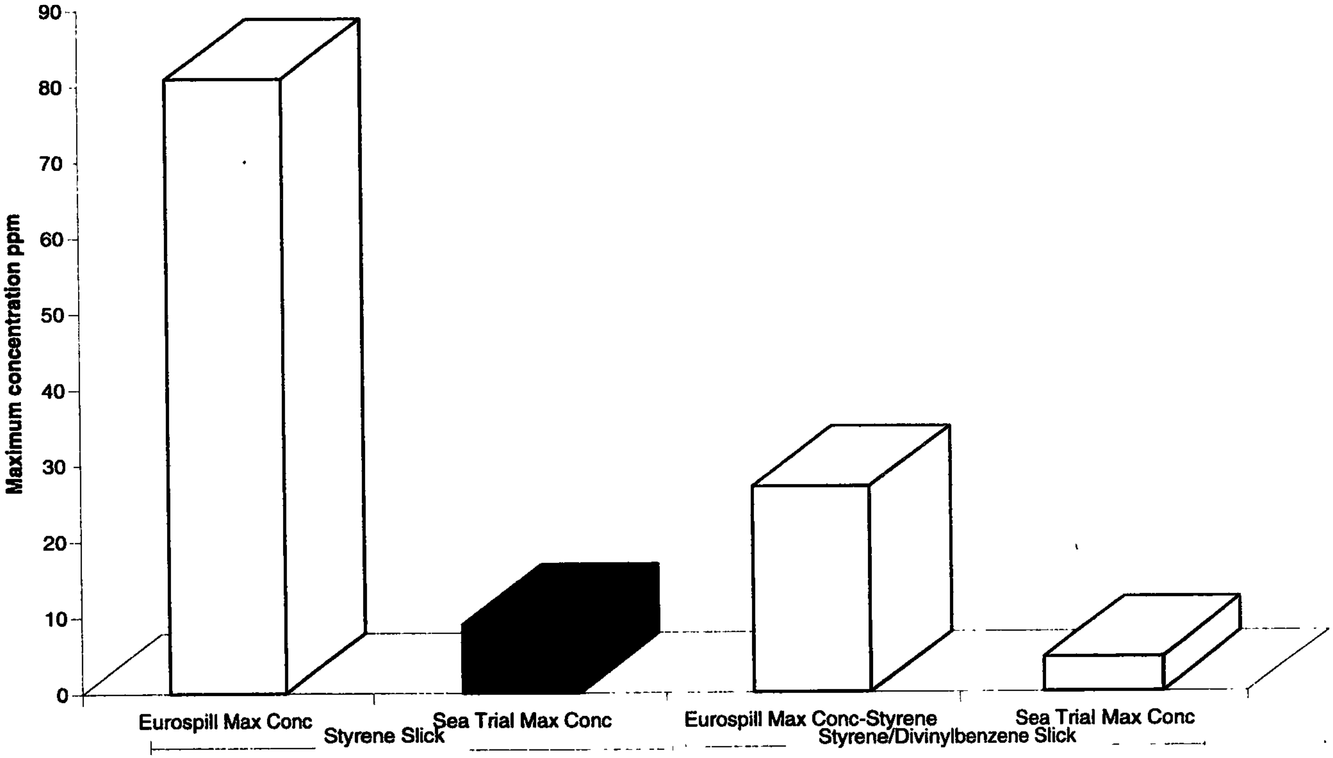


Figure 30. Comparison of maximum concentration predicted by EUROSPILL with maximum measured during sea trials '95



DETERMINATION OF XYLIDINES IN SOIL AND WATER CONTAMINATED WITH SAMIN MISSILE FUEL USING UV/Vis SPECTROPHOTOMETRY

Valdis Kokars[1], Shamil J. Cathum[2], Janis Avotins[1] and Harry Whittaker[2]

[1]*Faculty of Chemical Technology, Riga Technical University, Azenes St. 14, Riga, Latvia,* [2]Emergencies Engineering Division, Environmental Technology Centre, Environment Canada, 3439 River Road, Ottawa, Ontario K1A 0H3, Canada.

Abstract. Xylidine is an organic compound used in manufacturing azo-dyes and in missile fuel. The mixture of xylidine isomers is called xylidines and it is synthesized from coal-tar by nitrating isomeric xylenes, followed by reduction. The Emergencies Engineering Division of Environment Canada and a group of Latvian specialists have initiated a remediation project to clean soil and water from xylidine found in former Soviet Union bases. The need for a rapid method to detect xylidine in soil and water matrices has been addressed. A simplified spectrophotometric method that can be modified for field use, for the determination of xylidine in soil and water has been developed. The method is based on the reaction of xylidine with a colouring agent to shift the absorbance signal from the UV region toward the visible zone of the spectrum to minimize matrix interferences. A high level of 2,4-xylidine has been found in Latvian soils contaminated with SAMIN, a missile fuel in which 2,4-xylidine is a major component. It has been found that the soil matrix has no significant effect on xylidine measurements because it does not absorb at the analyte wavelength. Effects of the overall soil sorption capacity and pH on xylidine recovery and remediation processes are discussed.

INTRODUCTION

Xylidines are among many aromatic amines that are on the top list of Priority Substances of the Canadian Environmental Protection Act (Government of Canada, 1988). Xylidines are synthesized from xylenes obtained from coal-tar by nitrating isomeric xylenes without separation. Reduction of nitroxylenes with iron and hydrochloric acid gives xylidines. The chief constituent of the xylidine mixture is 2,4-xylidine. All xylidine isomers are liquid, except one which is solid. Xylidines are used in manufacturing azo-dyes and in missile fuel. They are one of the self-igniting fuels and can be thermally decomposed by mixing with nitric acid. When this happens, they release many contaminants (such as NO_2) to the environment. The NO_2 tends to generate the toxic and irritant ozone through a series of photochemical reactions. Patil et al., 1992 have examined exothermic reactions of some self-igniting fuels with HNO_3. They observed immediate evolution of NO_2 when xylidines, Mg, and HNO_3 are mixed together. Xylidines are also used as intermediates in the manufacture of azo dyes (Mark et al., 1978; Merck, 1989) and in the manufacture of pharmaceuticals, curing agents, antioxidants and antiozonants, as well as in the manufacture of gasoline additives and detergents. They are used in organic synthesis of wood preservatives, wetting agents for textiles, frothing agents, lacquers and metal complexes (Maguire, 1991). Craciunescu and Fruma (1977) have prepared xylidine complex compounds by reacting xylidines with $CuCl_2$, $CuBr_2$, CuI_2, $Cu(SCN)_2$, and H_2CuCl_4.

contamination in Canada (Maguire, 1977). However, In the former Soviet Union high level of xylidines concentration has been found in some of the missile sites. It is believed that xylidines are harmful compounds and adversely impact on human health (Maguire, 1991). Baird et al. (1977) have concluded from their study that 3,5-xylidine at 20 mg/L has an inhibitory effect on the respiration of activated sludge even after degradation suggesting that xylidines metabolites may be responsible for the observed toxicity. Exposure by inhalation and skin absorption causes anoxia due to the formation of methaemoglobin. In experimental animals, it causes damage to the lungs, liver and kidney. The threshold limit value (TLV) has been set to 5 ppm.

Although xylidines, like other aromatic amines, may not persist in the environment, there is concern on their sorption onto soils and sediments since the sorption/desorption processes may influence remediation processes and bioavailability of contaminants for microbiological degradation. Determination of xylidines in environmental samples, such as soil and water, is not reported in the literature. In this work a simplified spectrophotometric method has been developed to determine xylidines in soil and water.

The objectives of this study were to determine xylidines in water and soil by UV/Vis spectrophotometry and study the effects of soil matrices on the sorption/desorption processes, and investigate the effects of pH and concentration on the solubility and recovery xylidines from soil and water.

EXPERIMENTAL

UV/Vis Spectrometer. A UV/Vis spectrometer, Lambda 2, marketed by Perkin-Elmer, equipped with PECSS software (Perkin-Elmer) that allows communication with the instrument has been used. Basic methods such as direct concentration measurement, absorbance versus time, scanning, and calibration can be performed easily.

Preparation of standard solution. About 100-μL of 98% 2,4-xylidine (0.1038 g), is accurately weighed into a 100-mL volumetric flask and the volume is made up to the mark with dichloromethane, or distilled deionized water, and kept refrigerated. The final solution contains 1017.24 μg/mL of 2,4-xylidine. A series of working solution is prepared to test the dynamic range of the calibration curve.

Buffer solution. 1.92 g citric acid and 5.65 g disodium phosphate ($Na_2HPO_4.7H_2O$) are dissolved in a total volume of two litres distilled deionized water to give a pH of 5.4. The solution is stable and can be used for a long period of time.

p-Dimethylamino benzaldehyde. About 0.5 g of p-dimethylamino benzaldehyde (DMAB) is dissolved in 250 mL methanol containing 0.5 mL of concentrated HCl.

Trisodium pentacyanoamino ferroate (TPF). Ten grams of finely divided powdered sodium nitroprusside are treated in a flask with 32 mL of concentrated ammonium hydroxide and left overnight in the refrigerator. Absolute ethanol is added to the mixture and a yellow precipitate is obtained which is then washed with ethanol and anhydrous ether until dry. The resulting trisodium pentacyanoamino ferroate (TPF) is stored in a desiccator for subsequent use. Two solutions of 0.1% TPF, one in distilled deionized water and the other in buffer solution (pH = 5.4), are prepared separately to be used as colouring agents.

Solubility of 2,4-xylidine in water. Three separatory funnels are loaded with distilled deionized water, 100 mL each. The pH of the first separatory funnel is adjusted to two using 0.1M HCl. The second and the third ones are adjusted to pH 7 and 10, respectively, using 0.5M NaOH solution. A small amount of 2,4-xylidine is deposited slowly onto the water surface to avoid emulsion formation. The mixtures are left overnight to equilibrate. Then, 10 mL of the bottom layer of each separatory funnel is withdrawn into a test tube, shaken vigorously with 1 mL of dichloromethane and then centrifuged for 10 minutes at a speed of 3000 rpm. The bottom layer is withdrawn into a small vial, via Pasteur pipette, mixed with 5 mL of DMAB in methanol and allowed to stand for 30 minutes before UV/Vis measurement at 420 nm. A proper dilution is made to bring the analytical signal within the dynamic range of the calibration curve.

Preparation of spiked soil. About 2 kg of a synthetic soil is prepared by mixing different quantities of sand, black earth, peat and water in a ball mixer. The soil constituents are 70% sand, 10% black earth, 10% peat, and 10% water. Then, 200-mL of 2,4-xylidine solution (in methanol) is added to the soil mixture, mixed very well and transferred to a tray and left in the fumehood for two days to air-dry at room temperature. The final concentration of 2,4-xylidine in the soil is 132.5 μg/g on a dry basis.

Soil. Five grams of the synthetic-air-dried soil are weighed into a 40-mL VOC vial, followed by addition of a few drops of 2 M NaOH solution. Ten-mL of dichloromethane is added and the mixture is shaken vigorously for five minutes. One mL of the soil extract is withdrawn via Pasteur pipette into a vial and mixed with 5 mL of DMAB. A blank solution is prepared simultaneously to correct for background absorption. Both the blank and the sample are allowed to stand at room temperature for 30 minutes. The solution is then transferred to a UV/Vis cell for spectrophotometric measurement.

Water. For a small sample, 10 mL is shaken vigorously with 1 mL of dichloromethane in a test tube for 10 minutes. The mixture is centrifuged at 3000 rpm for 10 minutes. The bottom layer is then withdrawn via Pasteur pipette and mixed with 5 mL of DMAB, for UV/Vis measurement.

Sorption/desorption experiments. Five grams of the soil are accurately weighed into a 40-mL VOC vial, followed by addition of 30 mL of water, or

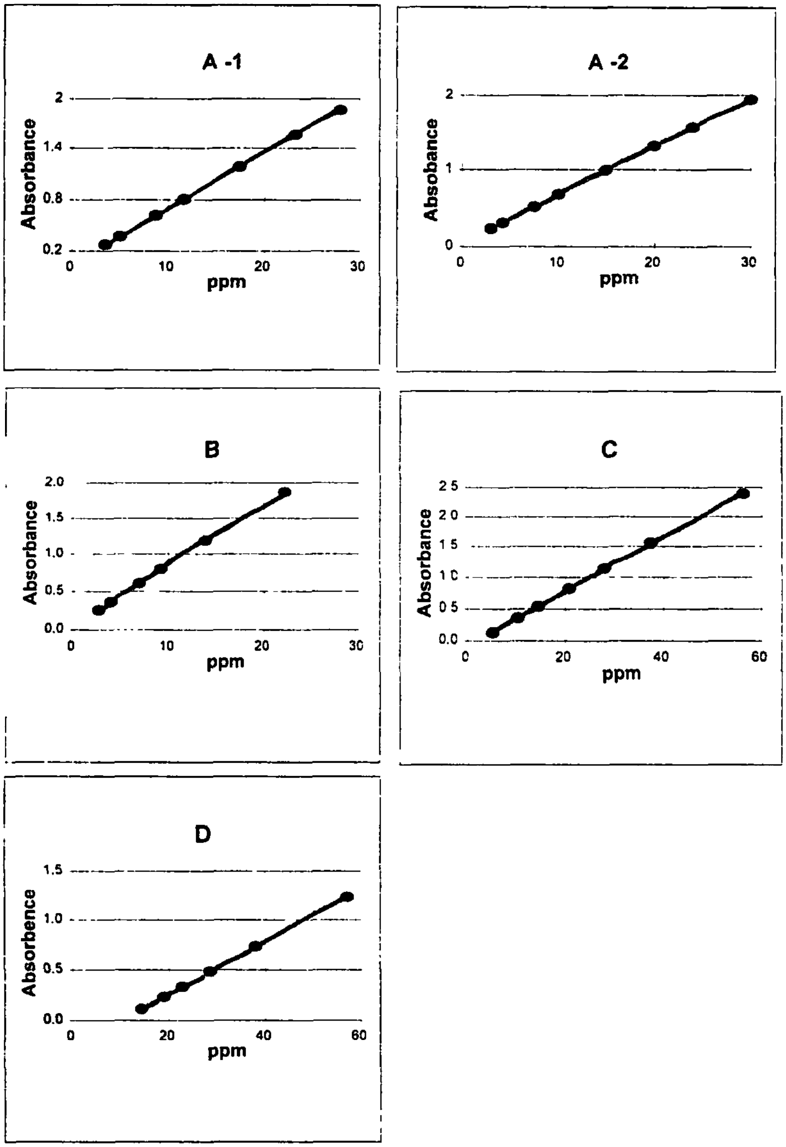


Figure 1. Calibration curves of xyldines; A-1: 2,4-xylidine reacted with DMAB in water; A-2: 2,5-xylidine reacted with DMAB in water; B: 2,4-xylidine reacted with DMAB in dichloromethane; C: 2,4-xylidine reacted with TPF in water (pH ≥ 7); D: 2,4-xylidine reacted with TPF in water (pH < 7).

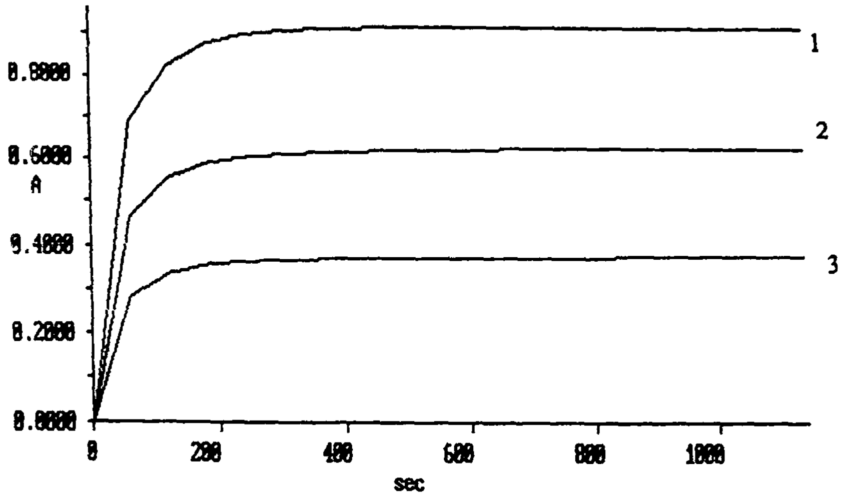


Figure 2. Reaction rate of 2,4-xylidine and DMAB at different concentrations; (1) 13.5 ppm; (2) 8.8 ppm; (3) 4.7 ppm.

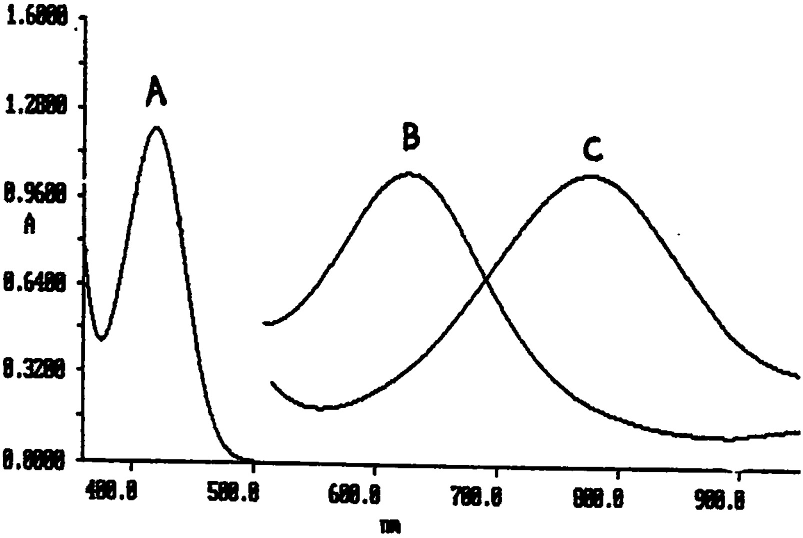


Figure 3. Spectra of 2,4-xylidine in different reaction media; (A) DMAB; (B) TPF (pH ≥ 7); (C) TPF (pH < 7).

dichloromethane. The mixture is shaken for a few minutes by hand and left to equilibrate at room temperature in the fumehood. A known amount of 2,4-xylidine is then added to the soil slurry. Immediately, 1.5 mL of the slurry is withdrawn using a disposable syringe, filtered through a microfilter (0.45 μm), and 1 mL is measured by a micropipette, mixed with 5 mL (DMAB) and allowed to stand for 20 minutes before measurement. The sorption/desorption processes are tracked over time for about one week. The filtrate measurement is the free 2,4-xylidine remaining in solution, and the difference between the initial and the filtrate concentration represents the sorbed 2,4-xylidine.

RESULTS AND DISCUSSION

The dynamic range of the calibration curve, using p-dimethylamino benzaldehyde (DMAB) and trsisodium pentacynaoamino ferroate (TPF) as colouring agents, was tested for quantitation in water and dichloromethane. Good results were obtained in both cases.

Figure 1 depicts various plots of absorbance versus concentration of xylidines reacted with DMAB and TPF in different media. It was found that a concentration of 0.1% of DMAB (in methanol) was suitable for colour development. A high concentration of DMAB, however, caused high background absorption that limited quantitation of the analyte in the soil. The optimum reaction time of 2,4-xylidine with DMAB in water was found to be 20 minutes and that of DMAB in dichloromethane was 30 minutes. These two reaction time were used throughout the experiment as they gave good reproducible measurements.

Trisodium pentacyanoamino ferroate (TPF). It is beneficial to have the analyte absorption far from the UV region since many chemical species absorb the radiation at this zone. The TPF is a good colouring agent and has been used to determine 1,1-dimethylhydrazine (UDMH) in air and water. The reaction of TPF and 2,4-xylidines has the advantage of shifting the absorbance toward the visible region, thereby reducing matrix interference appreciably. Direct determination of 2,4-xylidine without the use of a colouring agent may be possible if no significance interference from the sample matrix exists. This is because 2,4-xylidine has a strong absorption in the UV region and without shifting the absorbance to the visible zone it would be difficult to obtain reliable determination.

Figure 2 delineates the rate of chemical reaction between 2,4-xylidine and DMAB in two different media, i.e., water and dichloromethane. As can be seen, the chemical reaction in both cases is almost complete within a short time. The two hydrogen atoms of the NH_2 in 2,4-xylidine are readily replaceable.

Figure 3 shows spectra of 2,4-xylidine measured in different reagents. Absorption in the UV region suffers from severe matrix interferences. As a result, it is crucial that the absorbance is moved away from the UV region to the visible zone.

Figure 4 depicts spectra of 2,4-xylidine reacted with TPF for 12 hours in water adjusted to different pH. In the first spectrum, the reaction mixture was acidified with a drop of concentrated acetic acid prior to measurement. In the second spectrum, the solution mixture was left intact. The measurements were made on these two solutions, which clearly indicated that two absorbance profiles did exist, one at 645 nm $(pH \geq 7)$ and the other was at 765 nm $(pH < 7)$. The first absorbance was attributed to the formation of the TPF-xylidine complex. However, when the medium was changed to acidic the presence of high concentration of H_3O^+ would result in attacking more NH_2 groups in the xylidine molecule, thereby forming a protonated complex, i.e., a new chromophore that absorbed at a higher wavelength. The inflection points seen in the absorbance profiles at different pH indicated that the two compounds were in equilibrium with one another. The sensitivity of absorbance position to pH can be very useful to control the position of the analyte absorbance on the spectrum so that quantitative measurement can be made effectively with minimum matrix interference.

Effect of pH on recovery of 2,4-xylidine from water. Table I shows the recovery of 2,4-xylidine from water using dichloromethane at different pH. It was found that at higher pH the recovery of 2,4-xylidine from water was better. The recovery from a spiked soil was 93%. Table II shows the effect of concentration on the recovery of 2,4-xylidine. At pH 7, the recovery of 2,4-xylidine from water using dichloromethane was almost complete at different concentration levels. At this concentration range, no significant effect on the recovery from water was observed.

Table I. Recovery of 488 ppm of 2,4-xylidine from water at different pH.

pH	% Recovery
1	-
2	-
3	7 ± 5%
5	70 ± 3%
7	105 ± 4%
10	110 ± 3%

Effect of pH on solubility of 2,4-xylidine in water. Table III shows that the solubility of 2,4-xylidine in acidic, neutral and basic aqueous solutions is, respectively, 9.5%, 0.7% and 0.5%. This pH dependence in the solubility may be explained in terms of xylidine basicity. Xylidines are organic compounds that show an appreciable basicity (enough to change litmus paper to blue). Therefore, aqueous mineral acids or carboxylic acids may readily convert xylidines into their salts. Aqueous hydroxide ions readily convert the salts into the free form.

Table II. Recovery of 2,4-xylidine from water at different concentrations (pH 7).

ppm	% Recovery
30.5	114 ± 4%
61.0	113 ± 3%
122.1	111 ± 3%
240.1	110 ± 5%
488.3	105 ± 3%

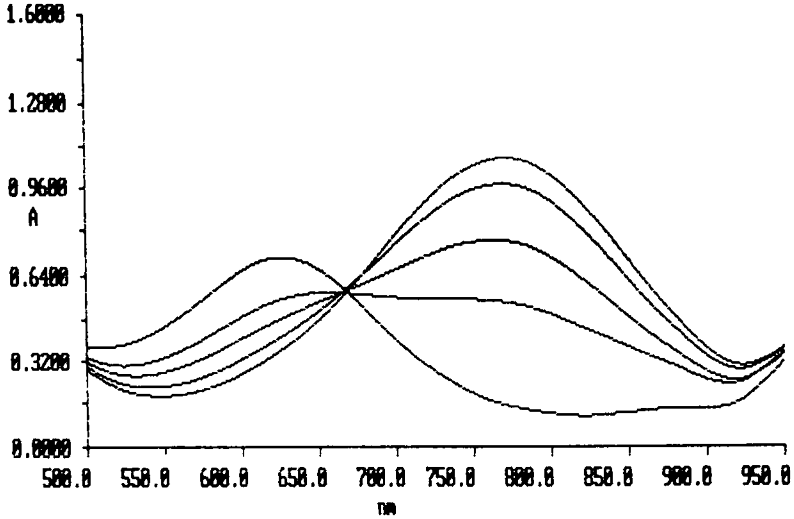


Figure 4. Effect of pH on the absorbance position of 2,4-xylidine reacted with TPF in buffer solution.

Determination of 2,4-xylidine in soil and water. A heavily samin-contaminated soil from Barta, Lativia, was washed with water to test the effectiveness of the soil washing processes for soil remediation. The proposed method was applied to monitor the contaminant level in the soil during the cleanup processes. Table IV summarizes the result of analysis using TPF as a colouring agent. In this method, the xylidine isomers 2,4-xylidine and 2,5-xylidine could not be separated from each other and appeared as one absorbance. Hence, the determination was based on total xylidines as characterized by the two isomers. No significant matrix interferences from water and soil were found by use of this method.

Table III. **Solubility of 2,4-xylidine in water.**

pH	g/100 mL
2	9.5 ± 6.8%
7	0.7 ± 9.5%
10	0.5 ± 0.1%

Sorption/desorption processes. When a contaminant is brought in contact with the soil, a rapid wetting of soil aggregates by water molecules is expected which transport contaminant molecules to the soil particles. Within a short time small concentration of a surface-sorbed contaminant may develop. This results in retaining contaminant molecules on soil particles as water moves in the soil. The movement of the sorbed contaminant molecules is then determined by forces of interactions between the soil and contaminant. The phenomenon likens that observed in the thin layer chromatography in which organic compounds are separated according to their differential movements through a porous media under the influence of a moving solvent. After the sorbed water reaches some sort of distribution equilibrium, there will be a redistribution of contaminant molecules over the soil particles, and sorption-desorption processes become effective.

Table IV. **Determination of 2,4-xylidine in Barta's soil and water.**

Water/soil ratio L/kg	Concentration in soil μg/g	Concentration in water μg/mL
0	6230	-
3	-	3398
5	-	4162
8	-	4665

The sorption may be regarded as occurring in three steps, diffusion of the free contaminant molecules from aqueous solution to soil particles, adsorption onto the surface, and diffusion toward the interiors of the soil particles. Many authors have reported that the initial adsorption is followed by a second stage that is relatively slower. The contaminant taken up by this second process cannot be recovered by a quick extraction (Karickhoff and Morris, 1985; Talbert and Fletchall, 1965; Mill, 1980; Macalady and Wolfe, 1984). Hamaker et al. (1966) have suggested that organic chemicals slowly diffuse into the interiors of the soil particles. In the absence of other processes (hydrolysis, microbiological degradation, etc.) the mechanism for the mass transfer is expected to have two consecutive steps. The following equation represents this, with M_t representing the contaminant in solution and on the category of sorption sites from which it can be immediately desorbed.

$$M_t + S_o \rightleftarrows M_tS_o \rightarrow M_tS_o \quad \textit{(Diffusion)}$$

S_o represents unoccupied sorption sites in the soil. Locations within soil particle interiors at which contaminant can be physically trapped are labelled "Diffusion." During the very early interval of the contaminant uptake onto the soil, the number of occupied sorption sites is so small that Step II has no measurable effect on Step I.

Figure 5 presents the sorption/desorption experiment of 2,4-xylidine onto soil (A) and sand (B) in aqueous medium. A control solution was run parallel to the sample. In soil suspension, it was found that 2,4-xylidine sorbed strongly onto soil as time elapsed. The free 2,4-xylidine decreased exponentially and then level off. In sand, however, the sorption was very low. This observation is consistent with the fact that more organic matter in the soil will result in more sorption. The sand contained trace amounts of organic matter and expected to sorb organic contaminants slightly. It can be stated that in soil-water system an appreciable amount of 2,4-xylidine exists as "bound residue." Another sorption/desorption experiment was run exactly under the same condition except that dichloromethane had been used as the reaction medium instead of water.

Figure 6 depicts the sorption/desorption experiment of 2,4-xylidine onto soil (A) and sand (B) in dichloromethane. Clearly, different sorption/desorption processes did indeed exist in dichloromethane. In the soil-dichloromethane system, the free 2,4-xylidine remaining in solution was much higher than that observed in the soil indicating that dichloromethane is a good solvent that can be used to extract 2,4-xylidine from the soil. In the sand, however, 2,4-xylidine in presence of dichloromethane is likely to slightly be sorbed onto sand particles. This phenomenon may be explained in terms of competition of 2,4-xylidine and solvent molecules for active sites in the soil.

In summary, the difference in soil uptake for 2,4-xylidine in different media can be beneficial for soil cleanup processes. A contaminated soil, for example, can be washed out with dichloromethane to remove most of the xylidines effectively. Dichloromethane is found to be a good solvent to extract 2,4-xylidine from soil and water and can be used for quantitation purposes.

Acknowledgement. The technical help of Dario Velicogna is greatly appreciated.

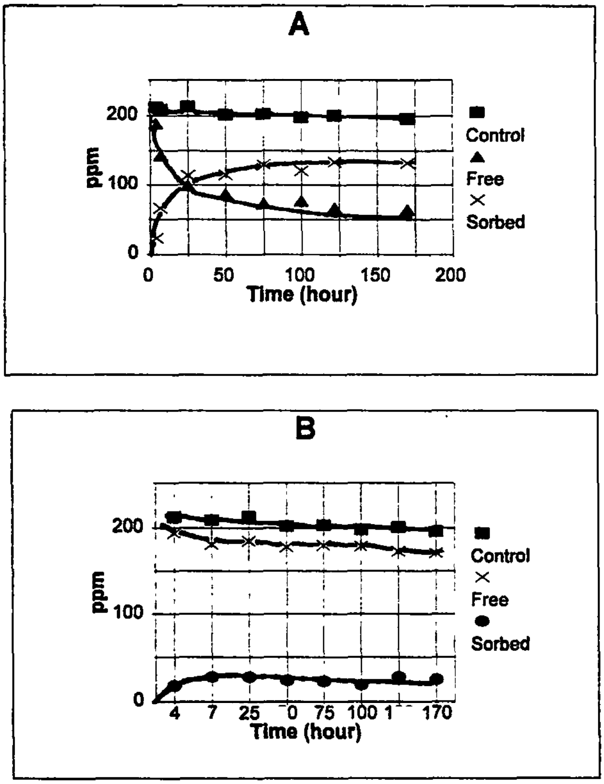


Figure 5. Rate of sorption/desorption reactions of 2,4-xylidine onto soil particles in water; (A) soil; (B) sand.

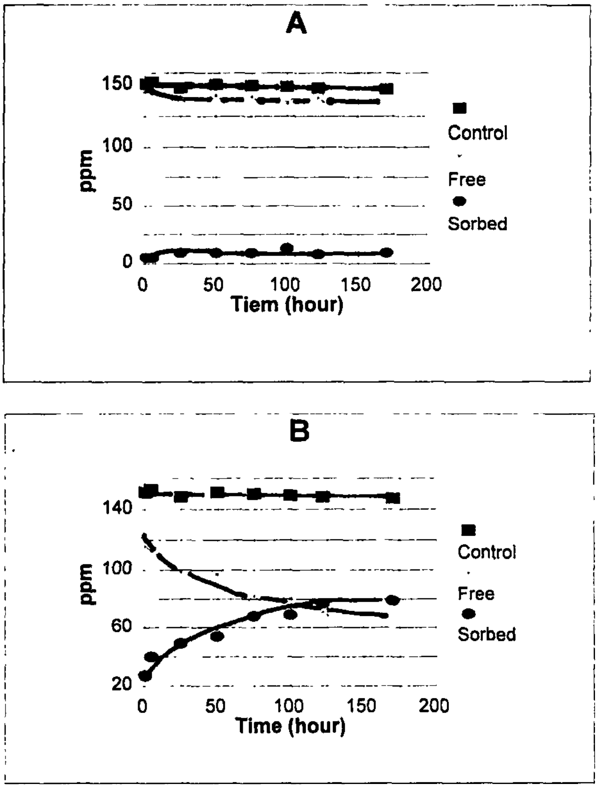


Figure 6. Rate of sorption/desorption reactions of 2,4-xylidine onto soil particles in dichloromethane; (A) soil; (B) sand.

REFERENCES

Baird, R., Carmona, L. and Jenkins, R.L. Behaviours of Benzidine and Other Aromatic Amines in Aerobic Wastwater Treatment, *J. Water Pollut. Contr. Fed.*, 1977, 49, 1609-1615.

Craciunescu, D.; Fruma, Al. *Collect. Czech. Chem. Commun.* **(1970)**, 35(8), 2502-5.

Government of Canada (1988). An Act Respecting the Protection of the Environment and of Human Life and Health. Hansard, Chapter 22, pp. 1-96. Queen's Pronter,. Ottawa, Ontario.

Hamaker, J.W.; Goring, C.A.L.; Youngson, C.R. Organic Pesticides in the Environment: American Chemical Society; Washington, DC., **1966**, p.23.

Karickhoff, S.W.; Morris, K.R. Sorption Dynamics of Hydrophobic Pollutants in Sediment Suspensions. *Environmental Toxicology and Chemistry*, **1985**, 4, 469-479.

Macalady, D.L.; Wolfe, N.L. Abiotic Hydrolysis of Sorbed Pesticides. *ACS Symp. Ser.* **1984**, 259, 221-244.

Maguire, R.J. Environmental Chemistry of the Four Aromatic Amines to be Assessed Under the Canadian Environmental Protection Act: Aniline, 3,5-Dimethylaniline, Benzidine and 3,3'-Dichlorobenzene, Rivers Research Branch, National Water Research Institute, Canada Centre for Inland Waters, Burlington, Ontario, 1991, p. 8.

Mill, T. Data Needed to Predict the Environmental Fate of Organic Chemicals. In Dynamics, Exposure and Hazards Assessment of Toxic Chemicals; Hague, R.Ed. Ann Arbor, MI., **1980**, pp. 297-322.

Patil, D. G.; Jain, S. R.; Brill, T. B. *Propellants, Explos., Pyrotech.* **(1992)**, 17(5), 260-4.

Talbert, R.E.; Fletchall, O.H. The Adsorption of some s-Triazines in Soils. *Weeds*, **1965**, 13, 46-52.

DETERMINATION OF UNSYMMETRICAL DIMETHYLHYDRAZINE IN WATER AND SOIL BY DERIVATIZATION WITH AROMATIC ALDEHYDES USING GC/MS

Vladimir Atamaniouk[1], Lioudmila Ananieva[2], Caroline Ladanowski[3], Shamil Cathum[3] and Harry Whittaker[3]

[1] Ukrainian Academy of Science
Kyiv, Ukraine

[2] Ukrainian Ministry of Defence
Kyiv, Ukraine

[3] Emergencies Engineering Division
Environmental Technology Centre
Environment Canada
3439 River Road
Ottawa, Ontario K1A OH3

INTRODUCTION

Unsymmetrical Dimethyl hydrazine (UDMH) is widely used as a rocket fuel, frequently as a 1:1 mixture with Hydrazine called Aerozine-50 [1]. UDMH as a high-energy propellant is used in large volumes for a space shuttle programme and for other aerospace operations. It has number of commercial applications, including its role as essential building blocks to the synthesis of various polymers, pesticides, pharmaceuticals, and chemotherapeutic agents [2]. UDMH is a degradation product of Daminozide (succinic acid 2,2-dimethylhydrazide; Alar) which is a plant growth regulator used to make fresh fruit firmer, control flowering, prevent spoilage and watercore development, reduce fruit dropping, and enhance storability and colour [3]. It has been marketed since 1963 and has been used primarily on apples, although it has also been used on grapes, cherries, peaches and other fruits and vegetables to improve harvest quality and/or reduce harvest cost.

Daminozide is possibly carcinogenic [4] and is known to degrade to UDMH when present in an apple homogenate that is subsequently boiled [5]. UDMH residues in food are of particular concern because the compound has been identified not only as a toxin [6-11] but also as a potential carcinogen with laboratory animals [12-17].

Despite the fact that Daminozide was prohibited in USA and Canada since 1989 UDMH was found in apples in 1995 [18]. N-Nitrosodimethylamine (NDMA) was also detected in drinking water supply in Ontario [19]. NDMA is a dangerous carcinogenic agent and is a major by-product of UDMH oxidation.

The large volumes of hydrazines and their derivatives being used in the public and private sectors have generated concern for the health and safety of persons in close contact with these chemicals. The toxicological problems associated with the inhalation or ingestion of the hydrazines have been monitored in laboratory animals, and they include damage to internal organs, creation of blood abnormalities, irreversible deterioration of the nervous system, and documented teratogenic and mutagenic effects [20,21]. Therefore, the American Conference of Governmental Industrial Hygienists (ACGIH) has recommended that the threshold limit values (TLVs) for UDMH be lowered from 500 ppb to 10 ppb in air [22].

Several different analytical techniques have been used for the detection of hydrazines. Examples include coulometry [23], potentiometry [24], titration [25], colorimetry [26], dosimetry [27,28], fluorescence [29,30], mass spectrometry [31], ion-mobility spectrometry [32], gas chromatography [33], and liquid chromatography [34]. Each of these techniques has merits in specific applications; however, none has combined the sensitivity, selectivity, and real-time monitoring capability necessary for determining hydrazines in environmental samples.

Currently, there was insufficient attention devoted to GC and GC/MS methods for determining UDMH in different media. Unfortunately, the direct determination of hydrazines by GC and GC/MS methods have some difficulties. The sensitivity for detection of hydrazines by GC and GC/MS can be improved by converting hydrazines to organic derivatives with high carbon (or even some halogen) content, such as hydrazones, azines or pentafluorobenzoyl derivatives [35-37].

UDMH is easily derivatized using acetone [35], furfuraldehyde [1], salicylaldehyde [38], 2-nitrobenzaldehyde [18,39]. The reported methods [38,39] have a much improved detection limit of 10 ppb but has some shortcomings as the product of derivatization (2-nitrobenzaldehyde-2,2-dimethylhydrazone) is light sensitive and can undergo destruction during analysis.

Literature revealed that the analysis of UDMH by derivatization with aldehydes showed promise and thus became the focus of this research.

OBJECTIVES

The objective of this research was to investigate the feasibility of determining UDMH by derivatization using the following seven aldehydes :
4- nitrobenzaldehyde, 2- nitrobenzaldehyde, 4- cyanobenzaldehyde,
4- chlorobenzaldehyde, 4- dimethylaminobenzaldehyde, benzaldehyde, and furfuraldehyde.

EXPERIMENTAL PROCEDURE

Chemicals

All chemicals were used as received. Benzaldehyde (99%), furfuraldehyde (99%), 2- nitrobenzaldehyde (98%), 4- nitrobenzaldehyde (98%), 4-cyanobenzaldehyde (98%), 4- chlorobenzaldehyde (97%), 4- dimethylaminobenzaldehyde (99%), UDMH (98%), titanium (111) chloride (99%), acetic acid (99.8%) and pyrogallol (98%) were obtained from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin.

Solvents such as dichloromethane, toluene, methyl alcohol, ethyl alcohol were received from Caledon Laboratories Ltd., Georgetown, Ontario.

Aldehyde Reagents

Fresh solutions of benzaldehyde, furfuraldehyde, 2-nitrobenzaldehyde, 4-nitrobenzaldehyde, 4-cyanobenzaldehyde, 4-chlorobenzaldehyde, 4-dimethylaminobenzaldehyde (Aldrich Chemical Co., Inc., Milwaukee, Wisconsin) were prepared in dichloromethane (Caledon Laboratories Ltd., Georgetown, Ontario) so that the final concentration was 5 g/L. 10 uL of acetic acid (Aldrich) was added to the reaction mixture.

Standard UDMH solution

A standard UDMH solution was prepared by dissolving 100 uL of UDMH (Aldrich) in dichloromethane purged with argon gas (Matheson Gas Products Canada, Ottawa, Ontario) in the head space of the storage container. An antioxidant solution was prepared by weighing 20 g of $TiCl_3$ (Aldrich) in argon purged distilled water, bringing the final volume to 100 mL. The final UDMH solutions were 1-250 ppm.

Preparation of Hydrazones

Hydrazone compounds were prepared by one of the following methods.

Method 1.

0.83 g of UDMH was weighed into a 100 mL flask, followed by addition of 3 mL of acetic acid, 50 mL of methanol and 6.2 g of 4-nitrobenzaldehyde. The mixture was stirred for 3 hours at room temperature and then 30 mL of water was added. The precipitate was collected, washed with water and dried. Recrystallization from ethanol-water gave a 4-nitrobenzaldehyde 2,2-dimethylhydrazone [40].

Method 2.

2-nitrobenzaldehyde 2,2-dimethylhydrazone and 4-nitrobenzaldehyde 2,2-dimethylhydrazone were prepared by mixing 1 g of UDMH, 0.833 g of 2-nitrobenzaldehyde or 4-nitrobenzaldehyde, 1 mL acetic acid (pH5) and 20 mL of absolute alcohol (ethanol) in a 50 mL distillation flask in a fume hood.

2-nitrobenzaldehyde 2,2-dimethydrazone and 4-nitrobenzaldehyde 2,2-dimethylhydrazone are light sensitive and therefore were stored in amber vials and wrapped with aluminum foil. Decreased concentration of UDMH over the course of analysis would occur without this protection.

GAS CHROMATOGRAPHY - MASS SPECTROSCOPY ANALYSIS

A Varian Saturn Ion Trap GC/MS System (Varian Analytical Instruments, 220 Humboldt Court, Sunnyvale, California 94089) equipped with Saturn II software was used for the analysis. A Star 3400 CX Gas Chromatography and 8100 CX Auto Sampler were included in this system. A 30 m by 0.25 mm i.d. (J & W Scientific, Folson, CA) DB- 5 capillary column was employed.

The following temperature program was used: initial temperature was 60^0C for 1 min ramped at the rate of 25^0C to a final temperature of 260^0C. The final temperature was maintained for 1 min to complete the process. The ion source temperature of the mass spectrometer was maintained at 280^0C during the analysis. Ionisation was performed at 70 eV and the instrument was scanned in selected-ion monitoring mode to achieve good sensitivity and selectivity.

RESULTS AND DISCUSSION

Determination of UDMH in Water

UDMH was reacted with seven aldehydes in dichloromethane. A 10-12 point calibration curve was linear within the concentration range of 1-250 ppm for all compounds excluding benzaldehyde and furfuraldehyde. The chromatogram for 4-nitrobenzaldehyde -2.2 dimethylhydrazone is shown in Figure 1 as a single high purity product.

UDMH reaction with benzaldehyde was not extensively studied in literature because the benzaldehyde has insufficient purity and the derivatization reaction gives various products as shown in Figure 2. This results in a low sensitivity of 25 ppm for UDMH determination. UDMH reaction with furfuraldehyde was previously used for UDMH determination [38] but has the same shortcomings as with benzaldehyde. UDMH reaction with 4-dimethylaminobenzaldehyde gave high sensitivity for UDMH determination; however, the reaction time of 18-24 hours was relatively long [35]. Benzaldehyde and furfuraldehyde were not further studied because of their poor recovery and sensitivity. 2-nitrobenzaldehyde has similar behavior to 4-nitrobenzaldehyde and was not studied in detail. Table 1 shows the chromatographic conditions and characteristic masses for hydrazones. Figures 3-14 show the mass spectra and calibration curves for hydrazones.

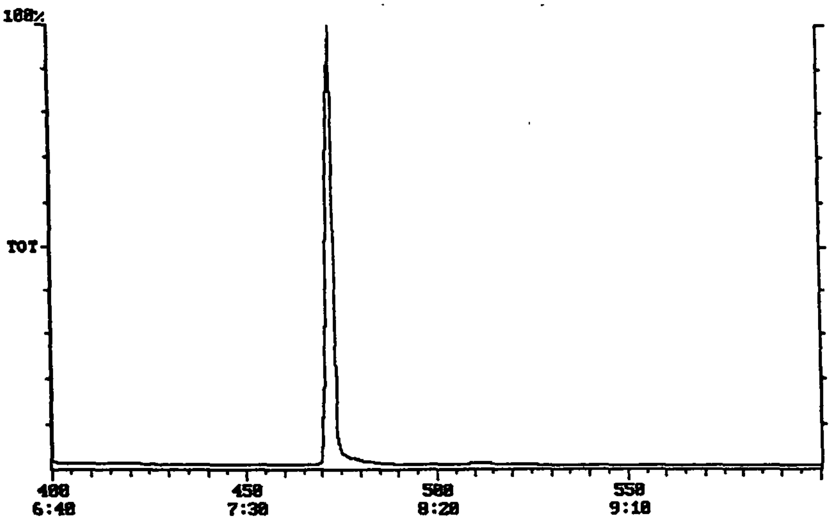


Figure 1. Chromatogram of 4-nitrobenzaldehyde-2,2-dimethylhydrazone in dichloromethane.

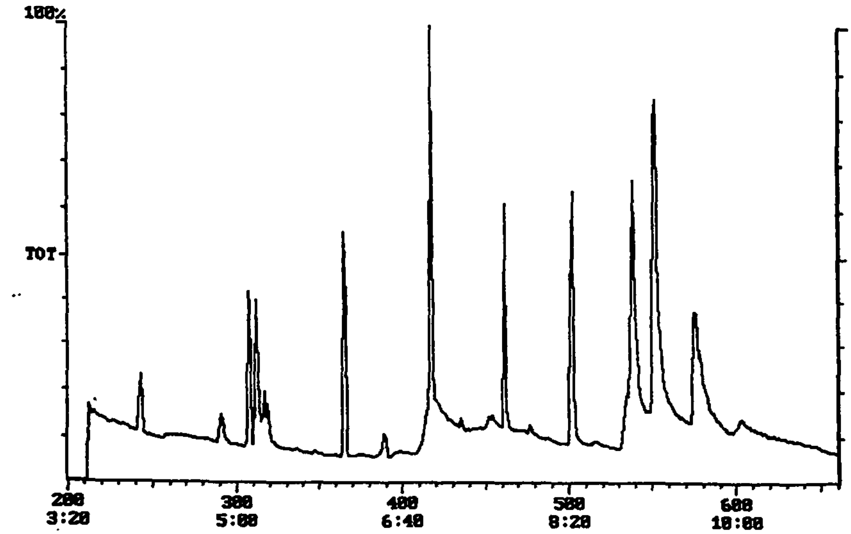


Figure 2. Chromatogram of UDMH reacted with benzaldehyde in dichloromethane.

Table 1. Chromatographic Conditions and Characteristic Masses for Hydrazones

UDMH derivatisation reagent	Retention time (min)	Molecular ion	Relative abundance	Mass spectrum (Figure)	Calibration curve (Figure)
4-nitrobenzaldehyde	7.53	193	100%	3	4
2-nitrobenzaldehyde	7.09	193	100%	5	6
4-cyanobenzaldehyde	7.11	173	100%	7	8
4-chlorobenzaldehyde	6.21	182	100%	9	10
4-dimethylaminobenzaldehyde	7.39	191	100%	11	12
benzaldehyde	5.13	148	100%	13	14
furfuraldehyde	2.56	95 and 97	100%	-	-

Five different methods for UDMH analysis were studied and their results are presented in Tables 2, 3 and 4.

Method # 1. Dichloromethane extraction of UDMH from water solution followed by derivatization.

Method #2. Derivatization of UDMH with aldehyde in water followed by dichloromethane extraction of the resulting hydrazone.

Method #3. Derivatization of UDMH with aldehyde in water, in presence of pyrogallol, followed by dichloromethane extraction of the resulting hydrazone.

Method #4. Toluene extraction of UDMH from water solution followed by derivatization.

Method #5. Derivatization of UDMH with aldehyde in water, in presence of $TiCl_3$, followed by dichloromethane extraction of hydrazone.

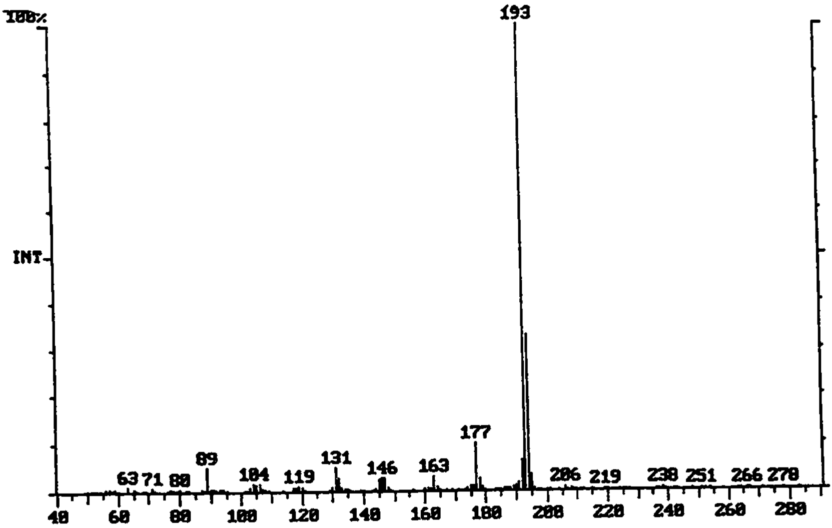


Figure 3. Mass spectrum of 4-nitrobenzaldehyde-2,2-dimethylhydrazone.

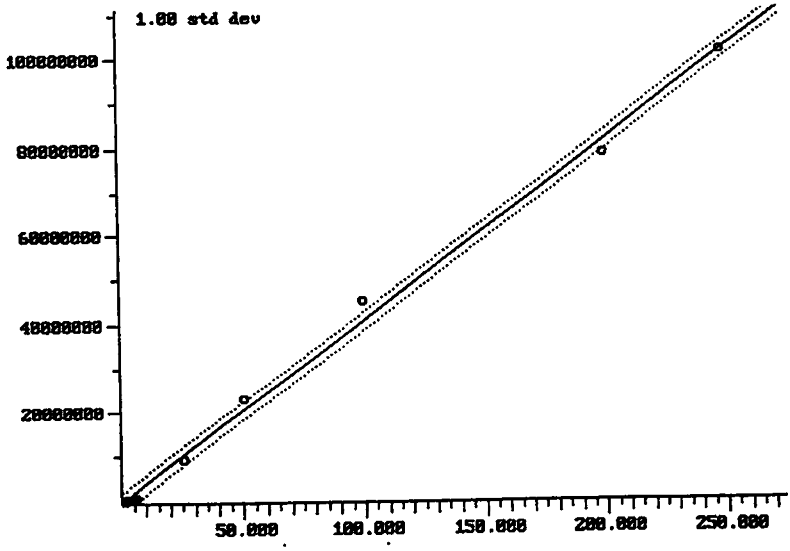


Figure 4. Calibration curve of 4-nitrobenzaldehyde-2,2-dimethylhydrazone.

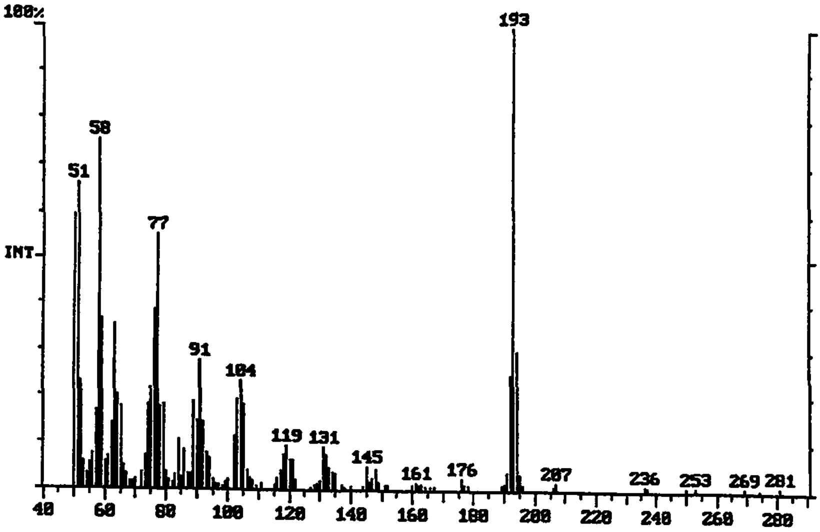


Figure 5. Mass spectrum of 2-nitrobenzaldehyde-2,2-dimethylhydrazone.

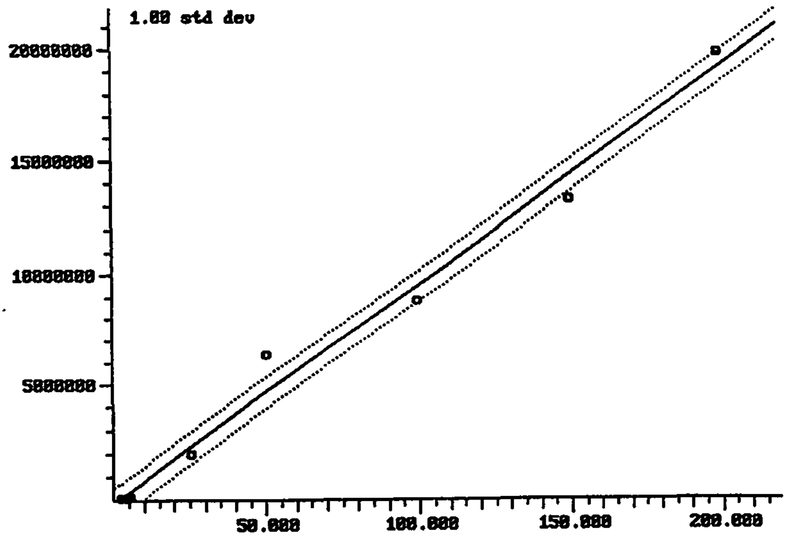


Figure 6. Calibration curve of 2-nitrobenzaldehyde-2,2-dimethylhydrazone.

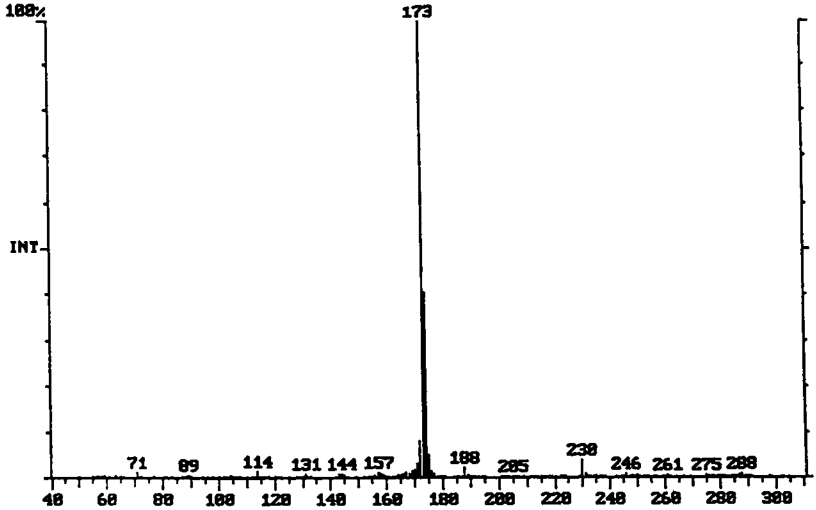


Figure 7. Mass spectrum of 4-cyano-2,2-dimethylhydrazone.

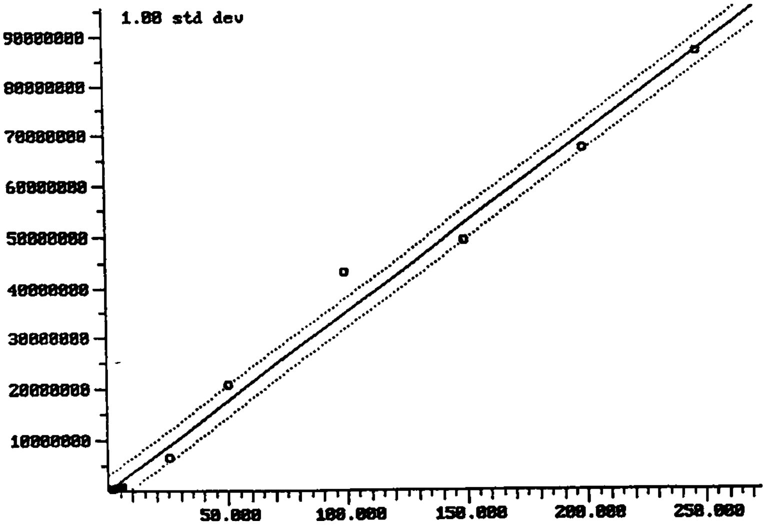


Figure 8. Calibration curve of 4-cyano-2,2-dimethylhydrazone.

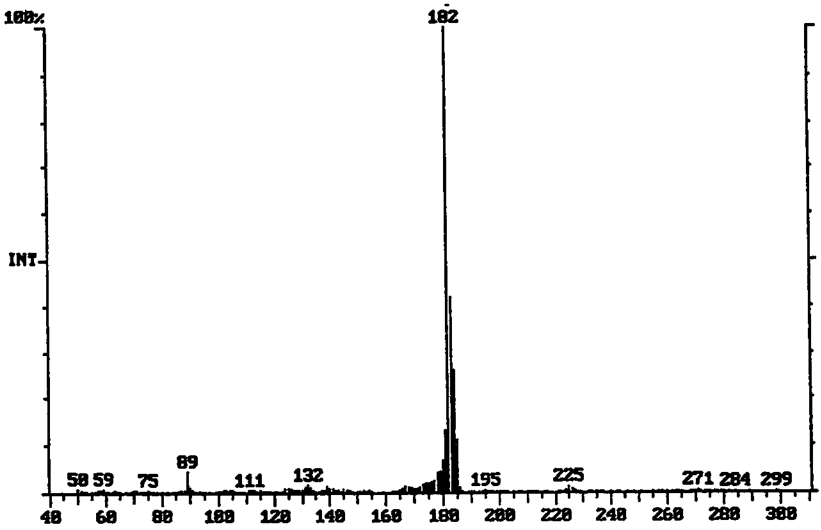


Figure 9. Mass spectrum of 4-chloro-2,2-dimethylhydrazone.

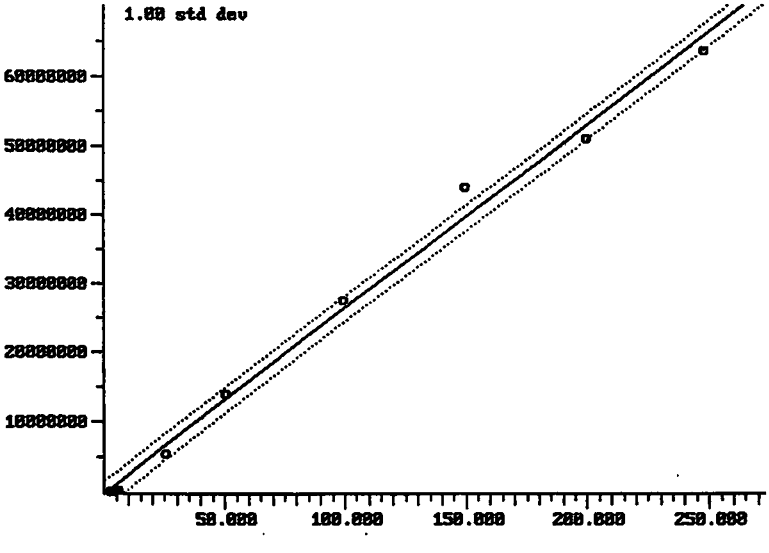


Figure 10. Calibration curve of 4-chloro-2,2-dimethylhydrazone.

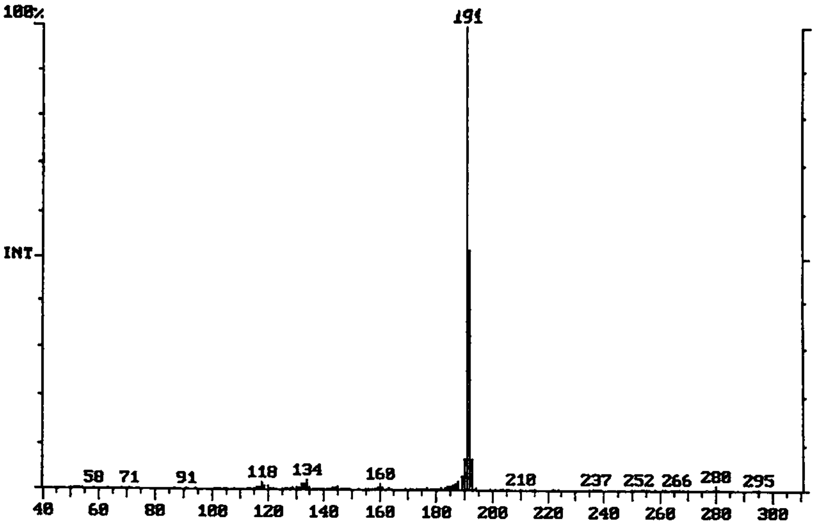


Figure 11. Mass Spectrum of Dimethylaminobenzaldehyde-2,2-dimethylhydrazone

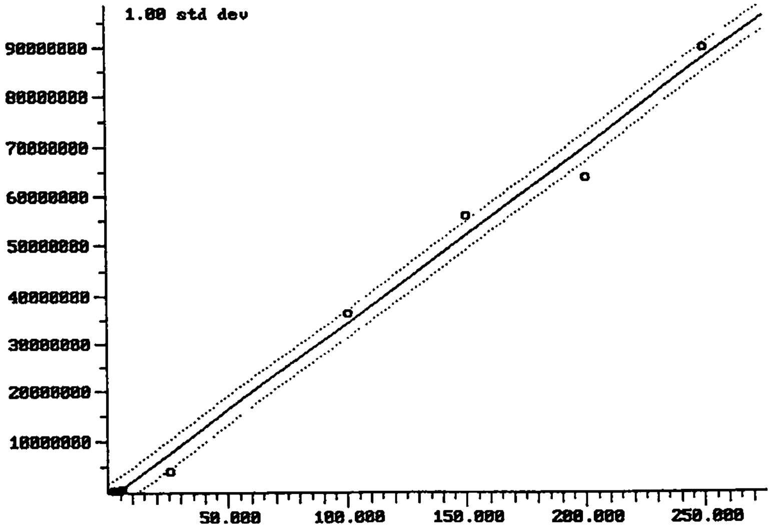


Figure 12. Calibration Plot for Dimethylaminobenzaldehyde-2,2-dimethylhydrazone

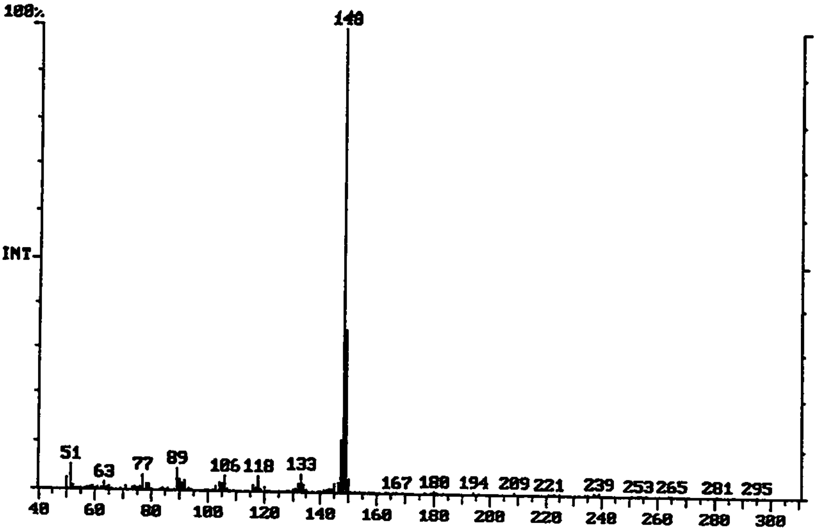


Figure 13. Mass Spectrum of Benzaldehyde-2,2-dimethylhydrazone

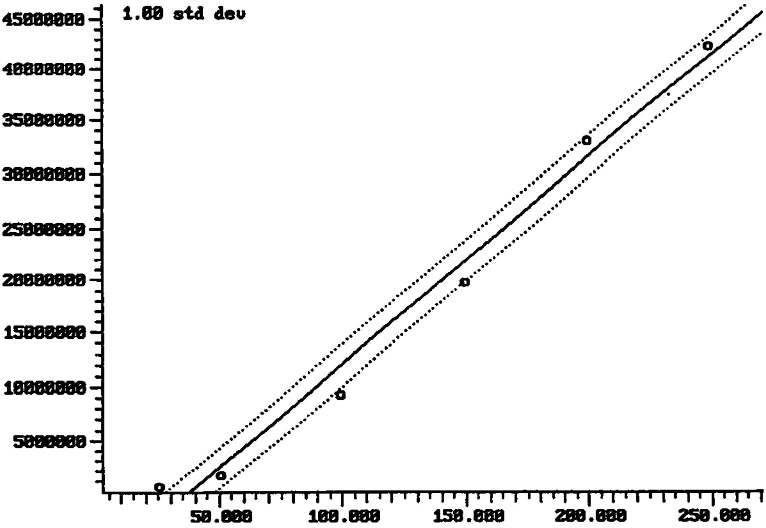


Figure 14. Calibration Plot for Benzaldehyde-2,2-dimethylhydrazone

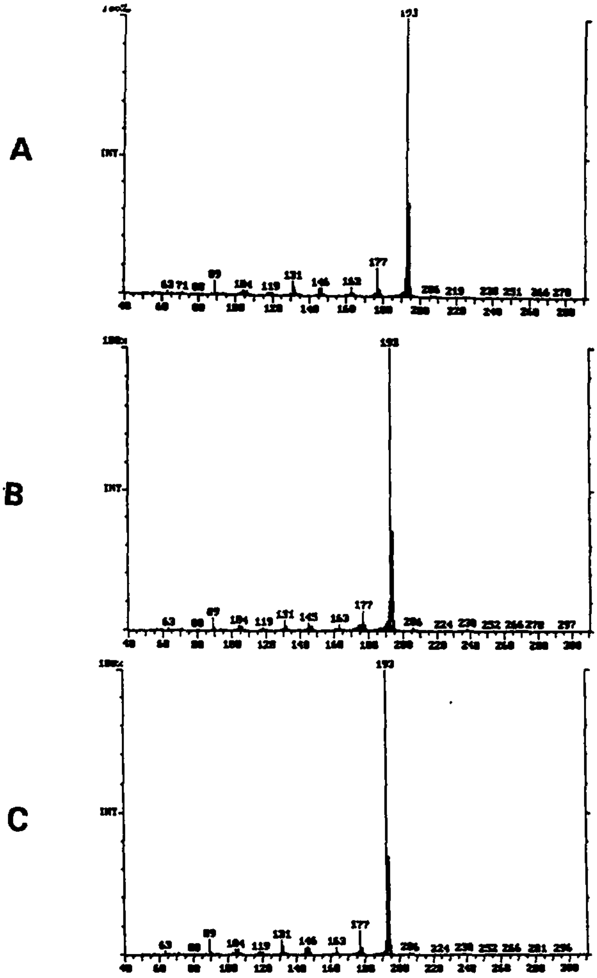


Figure 15. Mass spectrum of 4-nitrobenzaldehyde-2,2-dimethylhydrazone; (A) synthesized by an independent method; (B) by derivatization and extraction from water; (C) by derivatization and extraction from soil.

Select experiments were performed in a nitrogen atmosphere and in the presence of antioxidant solution (pyrogallol) since UDMH is unstable in oxygen atmosphere and traces of oxygen dissolved in water can react with UDMH. $TiCl_3$ has previously been used as an antioxidant [18] and in these experiments gave low recovery which may be attributed to destruction of UDMH by reducing it to dimethylamine, nitrogen and other products.

TABLE 2. Recovery of UDMH with 4-Nitrobenzaldehyde

Method #	Atmosphere	Sample ID	Final Concentration of Hydrazone (ppm)	% Recovery
1	air	ATW-8	19.16	8
		ATW-9	21.11	9
		ATW-10	23.84	10
1	nitrogen	AVW-5	40.55	16
		AVW-6	39.49	16
		AVW-7	42.86	17
2	air	ATW-17	51.07	21
		ATW-18	61.91	25
		ATW-19	61.14	25
2	nitrogen	ATW-14	92.61	37
		ATW-15	97.56	39
		ATW-16	95.99	39
3	air	ATW-20	111.55	45
		ATW-21	118.01	48
		ATW-22	110.11	44
4	air	ATW-26	2.62	1
		ATW-27	2.32	1
		ATW-28	2.23	1
5	air	AW-5	not detected	-
		AW-6	not detected	-
5	nitrogen	AW-7	not detected	-
		AW-8	not detected	-

TABLE 3. Recovery of UDMH with 4-Chlorobenzaldehyde

Method #	Atmosphere	Sample ID	Final Concentration of Hydrazone (ppm)	%Recovery
1	air	ATW-20	14.91	6
		ATW-21	19.51	8
		ATW-22	19.39	8
1	nitrogen	AVW-8	62.35	25
		AVW-9	31.57	13
		AVW-10	67.01	27
2	nitrogen	ATW-17	47.31	19
		ATW-18	44.79	18
		ATW-19	45.19	18
5	air	AW-9	not detected	-
		AW-10	not detected	-
5	nitrogen	AW-11	not detected	-
		AW-12	not detected	-

TABLE 4. Recovery of UDMH with 4-Cyanobenazaldehyde

Method #	Atmosphere	Sample ID	Final Concentration of Hydrazone (ppm)	%Recovery
1	air	ATW-5	20.47	8
		ATW-6	18.19	7
		ATW-7	21.18	9
1	nitrogen	AVW-2	29.79	12
		AVW-3	37.33	15
		AVW-4	30.79	12
2	air	ATW-14	93.42	38
		ATW-15	99.89	40
		ATW-16	103.29	42
2	nitrogen	AVW-11	217.88	88
		AVW-12	205.49	83
		AVW-13	238.23	96

Table 5 presents method detection limits determined at 95% level of confidence determined by the method of Kuselman and Shenhar [43]. It also shows that the lowest limit of detection (LLD) has been obtained when 4-nitrobenzaldehyde, 4-chlorobenzaldehyde and 4-cyanobenzaldehyde were used as derivatization agents. More than ten points have been used to construct the calibration curve to determine the detection limits. This may have a negative impact on the instrument detection limit (IDL) and method detection limit (MDL) since the noise level increases appreciably at high concentrations. The purpose of using this high concentration level, however, is to discover the dynamic range of the calibration curve to be used for quantitation.

Table 5. Detection Limits for Select Hydrazones

UDMH derivatisation Reagent	Retention time (min)	Molecular ion	Standard deviation	Variance	IDL ppm	LLD ppm	MDL ppm
4-nitrobenz-aldehyde	7.53	193	3.2	10.2	9.6	14.7	0.8
4-chlorobenz-aldehyde	6.19	182	3.1	13.7	11.1	17.1	1.1
4-cyanobenz-aldehyde	7.11	173	2.1	4.6	6.4	9	0.5

Determination of UDMH in soil

The method developed for the analysis UDMH in water has also been applied to the analysis of this fuel in soil. The properties of soil depend very much upon composition and structure (e.g., particle size, fertility, capillarity, porosity, aeration, water content, acidity or alkalinity, dashes of inorganic and organic compounds). Consequently, four different types of soil were spiked with UDMH to account for the varying properties. The spiked soils included: sand; natural soil; dried natural soil; and soil treated with hydrochloric acid. Soils were spiked with UDMH to a concentration of 480 ppm. Soils were then extracted with dichloromethane and treated with a solution of 4-Nitrobenzaldehyde. Tables 6 and 7 show the results of soil analyses.

Table 6. **Results of Soil Analysis (Immediately)**

Sample ID	Description of Soil	Final Concentration of Hydrazone (ppm)	% Recovery
SAUPN-1	sand	460.1	96
SAUPN-2	dried natural soil	2.2	0.5
SAUPN-3	soil washed with HCl	11.8	2
SAUPN-4	natural soil	251.5	52

Table 7. **Results of Soil Analysis (After 4 hours)**

Sample ID	Description of soil	Final Concentration of Hydrazone (ppm)	% Recovery
SAUPN-5	sand	251.5	52
SAUPN-6	dried natural soil	1.1	0.2
SAUPN-7	soil washed with HCl	8.7	2
SAUPN-8	natural soil	47.7	10

Tables 6 and 7 show that UDMH contaminated soil have a strong dependence on soil properties, exposure time and content of metal ions. It is known from the literature that copper and chromium are used as catalysts for UDMH oxidation and can accelerate the UDMH destruction. The authors believe that iron may play a role. Preliminary results showed that UDMH mixed with iron can form a compound with a red colour thereby inhibiting UDMH destruction in aqueous solutions. This experimental observation is supported by literature [38]. Contrarily, this reaction may decrease the recovery of UDMH from soil and formation of hydrazones. Table 8 shows the analysis for the initial soil sample obtained using inductively coupled plasma - atomic emission spectrometry (ICP-AES).

Table 8. ICP Analysis for Initial Soil Sample

Element	Units	MDL	Concentration
Aluminium	%	0.01	1.55
Antimony	ug/g	5	<5
Arsenic	ug/g	5	9
Barium	ug/g	5	82
Beryllium	ug/g	0.2	0.9
Bismuth	ug/g	5	<5
Cadmium	ug/g	1	<1
Calcium	%	0.01	0.39
Chromium	ug/g	1	25
Cobalt	ug/g	1	10
Copper	ug/g	1	15
Iron	ug/g	0.01	1.81
Lead	ug/g	1	12
Lithium	ug/g	1	12
Magnesium	%	0.01	0.31
Manganese	ug/g	1	670
Molybdenum	ug/g	1	1
Nickel	ug/g	1	24
Niobium	ug/g	5	<5
Potassium	ug/g	0.05	0.24
Silver	ug/g	0.5	<0.5
Sodium	%	0.01	<0.01
Strontium	ug/g	1	21
Tin	ug/g	20	<20
Titanium	ug/g	5	286
Tungsten	ug/g	20	<20
Vanadium	ug/g	1	30
Yttrium	ug/g	1	10
Zinc	ug/g	1	69

CONCLUSION

1. A GC/MS method of determining UDMH in water by derivatisation with aldehydes was developed.

2. 4-nitrobenzaldehyde, 4-chlorobenzaldehyde and 4-cyanobenzaldehyde gave satisfactory results as derivatisation reagents for UDMH determination with the best results obtained using 4-cyanobenzaldehyde.

3. Different sequence of UDMH extraction from water and derivatisation with aldehyde was studied and showed that the extraction of hydrazone is preferable to the extraction of aldehyde.

4. Using pyrogallol as antioxidant and purging solutions with nitrogen gave better analytical results than using air-saturated UDMH solutions. Using $TiCl_3$ as antioxidant is not convenient and gave negative results.

ACKNOWLEDGEMENTS

The authors would like to thank Mr. Dario Velicogna for his assistance in conducting analysis and Mr. Ivan Tchletchko for his assistance in preparing this paper.

REFERENCES

1. Schmidt. E.W., "Hydrazine and its Dervatives", Preparation, Properties, Applications. John Wiley & Sons, Inc., New York, 1984.

2. Schiessl. H.W., "Encyclopedia of Chemical Technology", ed. Othmer, K., Wiley, New York. 3rd edition, 1980, Vol. 12, p.734.

3. Dozier, W.A., Jr., Rymal, K.S.. Knowles, J.W., Pitts, J.A., and R.B. Reed. "Residue Levels of Daminozide in Apple Trees Sprayed the Preceding Spring and Summer". J. Food Protect., 1985, Vol. 48, p.1058.

4. Toth, B., Wallcave, L., Patil.K., Schmeltz, I., and D. Hoffmann, "Induction of Tumors in Mice with the Herbicide Succinic Acid 2,2-Dimethylhydrazide", Cancer Res., 1977, Vol. 37, p. 3497-3500.

5. Newsome, W.H., "Determination of Daminozide Residues on Foods and Its Degradation to 1.1-Dimethylhydrazine", J. Agric. Food Chem., 1980, Vol.28. p.3199.

6. Tuazon, E.C., Carter, W.P.L., and J.N. Pitts. Jr., "Reactions of Hydrazines with Ozone Under Simulated Atmospheric Conditions", Environ. Sci. Technol., 1981, p. 823; Excerpta Med., 1982, Vol. 19, p.68 (Series 46).

7. Chevrier, J.P. and A. Pfister. "Toxicity of 1,1-dimethylhydrazine in Animals. II Chromic Poisoning", Eur. J. Toxicol., 1974, Vol. 7, p.242; Excerpta Med., 1975, Vol. 34, p.806 (Section 30).

8. Simpson, C.J. and Barrow, M.V. "Toxicity of a Substituted Hydrazine for Turkeys". Arch. Environ. Health., 1972, 25, p.349; Excerpta Med., 1973, 27, p.624 (Section 30).

9. Rouganne, J.P.; Cier, A., and P. Dura. "Hepatic Effects of Subacute Poisoning with Hydrazine and Dimethylhydrazine", C.R. Soc. Biol.,1962, Vol. 163, p.192; Excerpta Med., 1970, Vol. 23, p.349 (Section 30).

10. Cornish, H.H. and P. Hartung, "The Subacute Toxicity of 1,1-Dimethylhydrazine", Toxicol. Appl. Pharmacol., 1969, Vol. 15, p.62. Excerpta Med., 1970, Vol. 23, p.279 (Series 30).

11. Barth, M.L., Geake, C.L. and H.H. Cornish, "1,1-Dimethylhydrazine-Induced Diuresis", Toxicol. Appl. Pharmacol., 1976, Vol. 11, p.26.

12 Kimura, O., Kaibara, N., Miyano, Y., Okamoto, T., Tamura, H., Yurugi, B., and S. Aoga, "Nuclear DNA Content in Dimethylhydrazine-Induced Colonic Carcinoma and Mucosal Dysplasia in Rats", Cancer, 1984, Vol. 53, p.1918. Excerpta Med., 1985, Vol. 5, p.140 (Section 52).

13. Sakita, M., Imai, H., Kasuga, M., Kageyama, N., Imaki, S., Tamai, M., Fujita, V., and S. Majima, "Effect of Protein-Bound Polysaccharide Preparation, PS-K, on Dimethylhydrazine Induction of Intestinal Tumors in Rats", GANN, 1983, Vol. 74, p.351. Excerpta Med., 1984, Vol.3, p.279 (Section 52).

14. Schmeltz, I., Abidi, S., and D. Hoffmann, "Tumorigenic Agents in Unburned Processed Tobacco", Cancer Lett., 1977, Vol. 2, p.125. Excerpta Med., 1977, Vol. 41, p.2612 (Section 30).

15. Christenson, H. and T.Luginbyhl, "Suspected Carcinogens, A Subfile of the NIOSH Toxic Substances List", U.S. Government Printing Office: Washington, DC, 1975; pp.51, 191, 192. Code of Federal Regulations. Daminozide: Tolerances for Residues. Title 40, Section 180.246, 1975.

16. Roe, F.J., Grant, G.A., and D.M. Millican, "Carcinogenesis of Hydrazine and 1,1-Dimethylhydrazine for Mouse Lung", Nature, 1967, Vol. 216, p.373-376.

17. Saxton W. L., Steinbrecher, K., and E. Gunderson, "Results of a Survey for the Presence of Daminozide and Unsymmetrical Dimethylhydrazine in Food", J. Agric. Food Chem., 1989, Vol. 37, p.570-573.

18. Majumdar, T.K., Geno, P.W., and A. Yau, "Determination of Daminozide Residues at Very Low Levels in Fruits by Gas Chromatography/Mass

Spectrometry", J. Agric. Food Chem., 1995, Vol. 43, No. 6.

19. Taguchi, V.Y., Jenkins, S.W.D., Wang, D.T., Palmentier J.-P.F.P., and E. J. Reiner. "Determination of N-Nitrosodimethylamine by Isotope Dilution, High-resolution Mass Spectrometry", Can. J. Appl. Spectr., 1994,Vol. 39, No. 3.

20. Vernot, E.H., MacEwen. J.D., Bruner, R.H., Haun, C.C., Kinkead, E.R., Prentice, D.E., Hall, A. III, Schmidt, R.E., Eason, R.L., Hubbard, G.B., and J.T.Young, Fundament. Appl. Toxicol., 1985, Vol.5, p.1050.

21. Wald, N., Boreham, J., Doll, R., and J.Br. Bonsall, J. Ind. Med., 1984, Vol.41, p.31.

22. American Conference of Governmental Industrial Hygienists: "Documentation of the Threshold Limit Values and Biological Exposure Indices", 6th edn., Cincinnati, OH, 1991.

23. Olsen, E.C., Anal. Chem., 1960, Vol. 38, p.487.

24. Stetter, J.R., Blurton, K.F., Valentine, A.M., and K.A. Tellefsen, J. Electrochem. Sos., 1978, Vol. 125, p.1804.

25. Malone, H.E., Anal. Chem., 1961, Vol. 33, p.575.

26. George, G.D. and J.T.Stewart, Anal. Lett., 1990, Vol. 23(8), p.1417.

27. Holtzclaw, J.R., Rose, S.L., Wyatt, J.R., and C.M. Hawkins, US Pat., 4 780 282, 1988.

28. Taffe, P.A., and S.L. Rose-Pehrsson, US Pat., 4 900 681, 1990.

29. Weeks, R. W., Jr., Yasuda, S.K., and B.K. Dean, Anal. Chem., 1976, Vol. 48, p.159.

30. Danielson, N.D. and C,M. Conroy, Talanta, 1982, Vol. 29, p.401.

31. Knox, B.E. and E.J. McHale, Anal. Chem., 1966, Vol. 38, p.487.

32. Leasure, C.S. and G.A. Eiceman, Anal. Chem., 1985, Vol. 57, p.1890.

33. Holtzclaw, J.R., Rose, S.L., Wyatt, J.R., Rounbehler, D.P., and D.H. Fine, Anal. Chem., 1984, Vol. 56, p.2952.

34. Ravichandran, K. and R.P. Baldwin, Anal. Chem., 1983, Vol. 55, p.1782.

35. Holtzclaw, J.R., Rose, S.L., and J. R. Wyatt, "Simultaneous Determination of Hydrazine, Methylhydrazine, and 1,1-Dimethylhydrazine in Air by

Derivatization/Gas Chromatography", J. Anal. Chem., 1984, Vol. 56, No. 14, p.2953.

36. Newsome, W.H., "Determination of Daminozide residues on foods and its degradation to 1,1- Dimethylhydrazine by cooking", J. Agric. Food Chem., 1980, Vol. 28, p.319-321.

37. Rutschmann, M.A. and H-R. Buser, "Determination of Daminozide and dimethylhydrazine residues in Swiss apple juice concentrates using gas chromatography-mass spectrometry", J. Agric. Food Chem., 1991, Vol. 39, (1), p.176-181.

38. Conditt, M.K., Baumgardner, J.R., and L.M. Hellmann, "Gas chromatographic/ mass spectrometric determination of Daminozide in high protein food products", J. Assoc. Off. Anal. Chem., 1988, Vol. 71, (4), p.735-739.

39. Wright, D., Jr. "New method for the determination of 1,1- Dimethylhydrazine residues in apples and peaches" J. Assoc. Off. Anal. Chem., 1987, Vol. 70 (4), p.718-720.

40. Ueno K. and T. Umeda, "Electrochemical and chromatographic properties of selected hydrazine and hydrazide derivatives of carbonyl compounds", J. Chromatogr., 1991, Vol. 585, p.225-231.

41. Karst U., Binding N., Cammann K., and U.Witting, "Interferences of nitrogen dioxide in the determination of aldehydes and ketones by sampling on 2.4-dinitrophenylhydrazine-coated solid sorbent", Fresenius J. Anal. Chem., 1993, Vol. 345, p.48-52.

43. Kuselman, I. And A. Shenhar, Anal. Chim. Acta, 1995, Vol. 306, pp.301-305.

TRENTON SOIL BIOREMEDIATION: METHODOLOGIES FOR CHEMICAL ANALYSES

Shamil Cathum, Laura Ouellette and Harry Whittaker

Emergencies Engineering Division, Environmental Technology Centre,
Environment Canada, Ottawa, Ontario, Canada K1A 0H3

Abstract. The Trenton soil bioremediation project is a joint research activity between the Department of National Defense (DND) and the Emergencies Engineering Division (EED) of Environment Canada. The objective of the project is to compare and analyze the effectiveness of several bioremediation processes in cleaning up hydrocarbons contaminated soils at a firefighter training area at CFB Trenton. Protocols for laboratory chemical analyses to determine the concentration of contaminants in the soil have been proposed. Seven tests including soil moisture, pH, purgeable hydrocarbons, mineral oil and grease (MOG), extractable petroleum hydrocarbons (TPHs) polynuclear aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCB's) are performed to interpret contaminant levels in the soil. The quality assurance (QA) and quality control (QC) have been addressed in greater detail.

INTRODUCTION

Due to the high cost of the low temperature thermal desorption cleanups, the Department of National Defense (DND) has conducted a bioremediation project to evaluate and compare various technologies for bioremediating heavy hydrocarbons contaminated soils. Batches of 50-100 tons of petroleum contaminated soil are setup as "windrows" in the field for this purpose. Each windrow is treated by a different bioremediation process and the level of contaminants are determined over time.

The effectiveness of any soil bioremediation process is normally tested by analyzing many soil samples carefully sampled and transported to the laboratory for analyses following standard operation procedures. In order for the analytical results to be meaningful the tests have to be made on a well-characterized soil sample. Because the soil is a complex mixture of materials made up of interacting mineral, organic, water, and air components, with both biotic and abiotic features, a distinction must be made as to what fraction of the soil is to be analyzed (Carter, 1993; Lewis et al., 1994). For remediation purposes, the soil means everything, with no restriction on soil particle size. Typically, soil encompasses the mass of unconsolidated weathered rocks and loose materials, and may be defined as all minerals and naturally occurring organic materials that is 2 mm or less in size. This definition is normally used to differentiate between soil consisting of sand, silt and clay and gravels, and is currently accepted in North America (Carter, 1993; Lewis et al., 1994). Moreover, precise measurement of contaminants in a soil sample without a certain level of uncertainty is difficult to achieve, because of variations in the physicochemical properties of the natural soil system (Mason, 1983; Barcelona, 1989; Calabrese and Kostecki, 1991; Rayment, 1993). Spatial and temporal variations in the soil composition, for instance, may make the measurement even more difficult. Therefore, it is imperative to define the objectives and scope of the analysis and specify the uncertainty and level of confidence in the data to be generated so that effective site assessment and interpretation of contaminant impact on the environment can be achieved (Calabrese and Kostecki, 1991).

The Emergencies Engineering Division (EED) of Environment Canada has been approached to conduct the chemical analyses of the hydrocarbon contaminated soils in the laboratory. Environment Canada agreed with the Department of National Defense (DND), to conduct seven tests for this purpose. Moreover, many biological and chemical tests have been carried out in replicas by Integrated Explorations Environmental Research Consultans to perform interlaboratory QA/QC to get a global picture on contaminants levels. Environment Canada tests included purgeable hydrocarbons, total petroleum hydrocarbons (TPHs), polynuclear aromatic hydrocarbons (PAHs), mineral oil and grease (MOG), polychlorinated biphenyls (PCBs), total soil moisture content, and measurement of soil pH. Some of these tests have been modified from the U.S. Environmental Protection Agency (EPA) and the Canadian Society of Soil Science (CSSS) methods (Carter, 1993). For these measurements to be reliable, an effective and easy method to check the quality of the measurement, has to be developed and formatted for the analyst need.

One objective of this work was to sample hydrocarbon-contaminated soils from a fire fighter area at CFB Trenton, analyze them in the laboratory, and apply rigorous statistical analysis on the measurements so that the results can be reported with a certain level of confidence. Another objective was to train a team of Latvian and Ukrainian specialists how to perform various environmental analyses and site assessments on a real contamination problem.

EXPERIMENTAL SECTION

(A) Sampling of soil

From each location, five grab soil samples are placed in a clean plastic bag. Stones, wood, etc., that are greater than 0.5 inch are removed from the soil sample. The sample is mixed by hand from outside the bag very well, and if the soil is very wet and cannot be mixed by this manner, it is mixed by hand inside the bag using clean latex gloves. The soil is then transferred from the bag into the glass sampling jar and sealed with an aluminum liner cover. The jars are labelled randomly with the names of contaminants to be analyzed, locations, and date the sample is taken and placed into a plastic bag. Sampling equipments are cleaned from soil by washing with water and drying before performing another sampling. Along with the hydrocarbon contaminated soil, a background soil from a designated area is also sampled following the same procedure. The jars are then placed in a cool box containing ice packs to keep the samples refrigerated, and transported to the Laboratory for analyses.

(B) Preparation of soil samples for chemical analysis

The determination of purgeable hydrocarbons and soil moisture is performed immediately after minor treatments such as removing large objects (metals, pebbles, twigs, etc.). For THPs, PAHs, MOG, PCBs, and pH, the soil sample is spread on a tray, mixed and rolled to break down clods, and left in the fumehood to air-dry for two days. The soil is then sized down to 2 mm by gentle grinding and sieving using mortar and pestle. Fragments of metals, stones, etc., that do not break down and pass through the 2-mm sieve are rejected. (Discard ranged between 35-47%).

(C) Measurement of soil pH

A solution of 0.01 M $CaCl_2$ is prepared by dissolving 1.1 g in 1 litre of distilled deionized water. The pH of this solution should be between 5.0 and 6.5. If not $Ca(OH)_2$ or HCl should be added to adjust it. A ten-gram portion of the 2-mm air-dry soil sample is stirred in a small beaker with 20 mL of 0.01 M $CaCl_2$ solution for 10 minutes. The suspension is allowed to settle down and the pH electrode is immersed into the soil suspension. (Care should be taken not to immerse the electrode to the bottom of the container.) Once the pH metre stabilizes, the pH value is recorded to one decimal place.

(D) Gravimetric determination of soil moisture and mineral oil and grease in the soil

1. **Determination of soil moisture content using a gravimetric method.** While preparing the soil sample for the purge and trap measurement, about one gram of the non-dry soil sample is accurately weighed into an aluminum weighing dish and left for two days to air-dry. The soil moisture is the difference between the initial and final weight.

2. **Determination of mineral oil and grease in the soil using a gravimetric method.** About a five-g portion of the air-dry soil is accurately weighed into a solvent cleaned mason jar. Five g of anhydrous Na_2SO_4 is added and the mixture is shaken vigorously for one minute. Then, 60 mL of dichloromethane is added to the mixture and placed on a mechanical shaker for 10 minutes. The solvent is decanted into a 500-mL Erlenmeyer flask. The extraction steps are repeated two more times. The combined extract is filtered through a Whatman No.1 filter paper containing Na_2SO_4 and received into a 250-mL Erlenmeyer flask. The filtrate is reduced to 5 mL using a rotary evaporator which is then transferred quantitatively to a solvent cleaned silica gel column. The transfer is completed with 60 mL dichloromethane rinsings. The column is a glass tube, plugged with glass wool and packed with 2 cm of Na_2SO_4, 10 cm silica gel, and 3 cm of Na_2SO_4. The eluate is collected into a pre-weighed 100 mL beaker and left for 24 hours to air-dry in the fumehood. The weight of the oil residue is the mineral oil and grease content of the soil, expressed in mg/kg.

(E) Gas chromatography

1. **Quantitation of purgeable hydrocarbons using purge and trap gas chromatography - flame ionization detector (GC-FID).** The method is based on introduction of purgeable hydrocarbons into a gas chromatography column. The procedure is applicable for use with aqueous samples directly and to solids, wastes, soils, sediments, and water-miscible liquids following appropriate sample preparation. In this method, nitrogen is bubbled through the sample that will efficiently transfer the purgeable hydrocarbons from the aqueous phase to the vapour phase. The vapour phase passes through a sorbent trap where the purgeables are trapped. After purging is complete, the trap is heated and back flushed with nitrogen to desorb the purgeables into the gas chromatographic column. Purgeable hydrocarbons are detected by flame ionization detector (FID). The equipment and experimental conditions are as follows:

Gas Chromatography	Varian 3400
Purge and trap	Tekmar, ALS 2016, Tekmar, LSC 2000
Column	DB-624, 30 m x 0.25 mm ID fused silica, 0.25 μm film or equivalent.
Carrier Gas	Nitrogen
Purging gas	Nitrogen
Detector temperature	220 °C
Injector	180 °C
Oven	40 °C for 2 min, to 180 °C at 7.5 °C/min and hold 2 min.
Detector	FID
Calibration	Gasoline is used to prepare a 5-point calibration curve

About a 5-g portion of the non-dry soil is accurately weighed into a purge and trap vial, mixed with 5 mL H_2O and attached to the instrument (Tekmar, ALS 2016 and Tekmar, LSC 2000) for GC-FID measurement.

2. **Quantitation of total petroleum hydrocarbons (TPHs) using gas chromatography - flame ionization detector (GC-FID).** The method is based on gas chromatography to detect extractable hydrocarbons. Soil samples are mixed with pentane and placed in the fridge for cold extraction for 24 hours at 4 °C. A small fraction of the soil extract is injected into a gas chromatography column using an autosampler and the compounds in the column effluent are detected using a flame ionization detector. The method is semi-quantitative because the diesel standard used to calibrate the instrument response does not have exactly the same composition as the hydrocarbons found in the soil sample. The gas chromatography conditions are as follows:

Gas Chromatography	Hewlett Packard 5890
Column	DB-5, 30m x 0.25 mm ID fused silica, 0.25 μm film or equivalent.
Autosampler	HP 7673
Carrier Gas	Hydrogen
Injection	1 μL
Oven	50 °C for 3 min, to 75 °C at 5 °C/min, to 250 °C at 15 °C/min, to 325 °C at 35 C°/min and hold 7 min.
Detector	FID
Calibration	Diesel is used to prepare a 5-point calibration curve

About a 5-g portion of the air-dry soil is accurately weighed into a 40-mL VOC vial, followed by addition of 5 g of anhydrous Na_2SO_4. The mixture is shaken until there are no clumps. Then, 10 mL of pentane is added to the mixture, shaken for one hour on a mechanical shaker and placed in the fridge at 4 °C for 24 hours. About 1.5 mL of the extract is capped into a small vial for GC measurement.

3. **Determination of polychlorinated biphenyls (PCBs) using gas chromatography elector capture detector (GC-ECD).** The soil sample is extracted with acetone and hexane, filtered and evaporated to reduce the volume to 5 mL. The soil extract is cleaned up on a Florisil column to separate unwanted soil matrixes from the sample. A gas chromatography instrument equipped with a capillary column and electron capture detector is used for the analysis. Instrumentation and parameters are given below:

Gas Chromatography	Hewlett Packard 5890
Column	DB-5, 30m x 0.25 mm ID fused silica, 0.25 μm film or equivalent.
Autosampler	HP 7673
Carrier Gas	5% methane in Argon, 20 mL/sec
Injection	1 μL
Oven	90 °C for 2 min, to 180 °C at 10 °C/min, to 240 °C at 3 °C/min, to 285 °C at 10°C/min and hold 5 min.
Detector	ECD
Calibration	Arochlor 1242 is used to prepare a 5-point calibration curve

<u>Solvent extraction</u>. Extraction of PCBs from the soil is repeated three times. About a 10-g portion of the homogenized soil is accurately weighed into a mason jar, followed by addition of 35 mL of acetone. The mixture is vigorously shaken for 10 min using a mechanical shaker. Seventy-mL aliquot

of hexane is added to the mixture and shaken for another 10 minutes. The solvent mixture in each extraction step is decanted into a one litre separatory funnel containing 500 mL deionized water. The combined soil extract is swirled vigorously in the separatory funnel (no shaking). The organic layer is separated into a 250-mL Erlenmeyer flask. Anhydrous sodium sulphate is added, shaken and filtered through a Whatman No.1 filter paper into a 500-mL round bottom flask. One mL of isooctane is added, and the extract is reduced to 5 mL using a rotary evaporator at 35 °C.

Cleanup and fractionation. About 20 g of Florisil (60-100 mesh) is added to a chromatography column, plugged with glasswool. The column is tapped gently to ensure a homogenous layer of Florisil. The column is topped off with 1-2 cm of Na_2SO_4, and rinsed with 60 mL of hexane. Just prior to exposition of sodium sulphate to air, the elution is stopped by closing the stopcock. The eluate is discarded at this stage. The five-mL hexane extract is transferred quantitatively to the column and the flask is rinsed twice with hexane. The column is drained to the top level of Na_2SO_4 into a 500-mL round bottom flask, and then eluted with 200 mL of 3% (v/v) ethyl ether in hexane using a drip rate of 5 mL/min. The eluate in both cases is collected into the same round bottom flask, which is then concentred to 3 mL using a rotary evaporation at 35 °C.

4. **Determination of polynuclear aromatic hydrocarbons using gas chromatography - mass spectrometry (GC-MS).** The soil sample is extracted with a solvent mixture containing acetone, dichloromethane and hexane, cleaned by a chromatography technique and fractionated for quantitation by GC-MS. A certified reference material (EPA 610) is used to calibrate the instrument response.

Soil extraction. The soil sample is extracted three times with a mixture of organic solvents containing 10% acetone, 40% dichloromethane and 50% hexane. About 5 g of the air-dry soil is accurately weighed into a mason jar, followed by addition of 5 g of anhydrous Na_2SO_4 to absorb the moisture. In each extraction step, 75 mL of the solvent mixture is added to the sample and shaken for 10 minutes. The solvent is decanted off into a 500-mL Erlenmeyer flask. About 2 g of Na_2SO_4 is added to the combined extracts and swirled. The mixture is filtered through a Whatman No.1 filter paper containing Na_2SO_4 and received into a 500-mL round bottom flask. The soil extract is reduced to about 1 mL using a rotary evaporator at 35 °C. About 50 mL of hexane is added to the extract to change solvent and evaporation is continued until the volume is reduced to 1 mL.

Cleanup. A glass cleanup column, 25 cm x 1.5 cm, plugged from the bottom with glass wool is prepared as follows: About 10 g of the activated silica gel is added to the column, followed by 2 g of Na_2SO_4. The column is tapped gently to ensure uniform packing, pre-eluted with 50 mL hexane and *drained just to top of the Na_2SO_4 layer. The sample is loaded to the column quantitatively. The round bottom flask is rinsed three times with hexane (1 mL) to complete the transfer. The column is eluted with 5 mL of hexane, followed by 5 mL of benzene. The eluate is discarded at this stage. The PAHs fraction is then eluted from the column with two 5-mL aliquots of benzene into a calibrated centrifuge tube. The extract is concentrated to 1 mL by blowing with nitrogen and capped into a small vial for GC-MS measurements.*

The final purified extract is analyzed under the following conditions:

Instrument:	Varian Saturn GC-MS.
Column:	30 m x 0.32 mm ID DB-5 fused silica column (0.25 μm film thickness)
Autosampler:	Varian 8100
Inlet:	Splitless.
Gases:	Carrier: helium, 1.0 mL/min, nominal
Injector volume:	1 μL
Injector temperature:	290 °C
Detector temperature:	280 °C (transfer line temperature)
Temperature program:	For target PAHs, 80 °C for 1 min, then 25 °C/min to 160 °C, then 8 °C/min to 300 °C, hold 15 min.
Calibration:	Calibration is performed using EPA 610 mixture. The external method is used for quantitation.

The presence of a target compound in the sample extract is confirmed when the sample mass spectrum and the retention time match with that of the external standard.

RESULTS AND DISCUSSION

Sampling

In general, a chemical analysis is performed on a small fraction of the whole sample. The composition of this small fraction must reflect as closely as possible the average composition of the bulk of the material. Often, sampling is the most difficult step in the entire analytical process and the step that normally limits the accuracy of the procedure. There are three steps that have to be considered in sampling bulk materials: (a) identification of the population from which the sample is to be obtained; (b) collection of a gross sample that is truly representative of the population being sampled; and (c) reduction of the gross sample to a small size of a homogeneous laboratory sample that is suitable for the analysis. The effects of the uncertainty arising from these steps on the overall uncertainty should not be overlooked. The determinate and indeterminate errors in analytical data, for instance, can be traced back to instrument, method, and personal causes, and may be eliminated by exercising care, by calibration, and by proper use of standards, blanks, and certified reference materials (CRM). Errors due to sampling, however, are different in the sense that they are not controllable by the use of blanks and standards or by controlling experimental variables.

For random uncertainties in an analytical measurement, the overall standard deviation s_o is related to the standard deviation of the sampling process s_s and to the standard deviation of the method s_m by the relationship (Youden, 1981; Skoog et al. 1988):

$$s_o^2 = s_s^2 + s_m^2 \tag{1}$$

In many cases, the method variance will be known from replicate measurements on the product of a single laboratory sample. Under this circumstance, s_s can be computed from the measurements of s_o for a series of laboratory samples each of which is obtained from several gross samples. Once the measurement uncertainty has been reduced to one third or less of the sampling uncertainty (i.e., $s_m < \frac{1}{3}s_s$), further improvement in the measurement uncertainty is fruitless (Youden, 1981). If the sampling uncertainty is large and cannot be improved, it is wise to switch to a less precise but rapid method of analysis so that more samples can be analyzed within a short period of time, thus improving precision.

Ideally, the gross sample is a miniature replica of the entire mass of material to be analyzed. It corresponds to the whole not only in chemical composition but, equally important, in particle-size distribution (Skoog et al., 1988, Carter, 1993, Lewis et al., 1994). The size of the gross sample is determined by: (a) uncertainty that can be tolerated between the composition of the gross sample and that of the whole; (b) degree of heterogeneity of the whole; and (c) level of particle size at which heterogeneity begins. The latter point is important and warrants amplifications. Suppose that it is required to analyze mineral oil and grease in a sample consisting of soil and manure. Let us further assume that the manure contains the higher percentage of oil P_1 and the soil contains the lesser amount P_2. Furthermore, the average density d of the soil mixture differs from the densities of d_1 and d_2 of the manure and soil, respectively. We are now interested in deciding what number of mixture particles and thus what weight we should take to ensure a sample possessing the average percent of mineral oil and grease P with a sampling relative standard deviation %RSD. The following equation gives the mathematical description for this argument (Benedetti-Pichler, 1956; Skoog et al. 1988):

$$n = p(1-p)\left(\frac{d_1 d_2}{d^2}\right)^2 \left(\frac{P_1 - P_2}{\%RSD\,P}\right)^2 \tag{2}$$

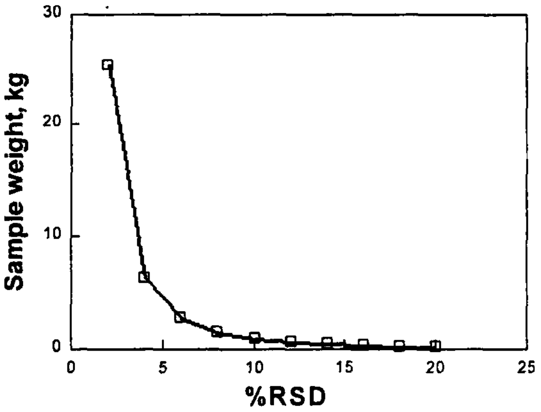


Figure 1. Weight of sample versus relative standard deviation, %RSD.

Where p is the fraction of manure particles, 1-p is the fraction of soil particles. From this equation, we see that the demand for accuracy is costly, in terms of the sample size required, because of the inverse-square relationship between the allowable standard deviation and the number of particles taken. Furthermore, a greater number of particles must be taken as the average percentage P of the mineral oil and grease becomes smaller. The degree of heterogeneity as measured by P_1-P_2 has a profound effect on the number of particles required, with the number increasing as the square of the difference in composition of the two components of the soil mixture.

Figure 1 delineates the effect of particle size, expressed as radius r (in cm), on the weight of the soil sample (in g) that has to be taken. If the particles of the soil sample are big, the weight has to be increased so that the measurement will be representative to the population from which the sample is taken. There is always some uncertainty due to the heterogeneity of the soil. This uncertainty has to be defined in advance because it plays a significant role on the size of the soil that has to be taken from the population, and the subsequent sample preparations such as grinding and sieving.

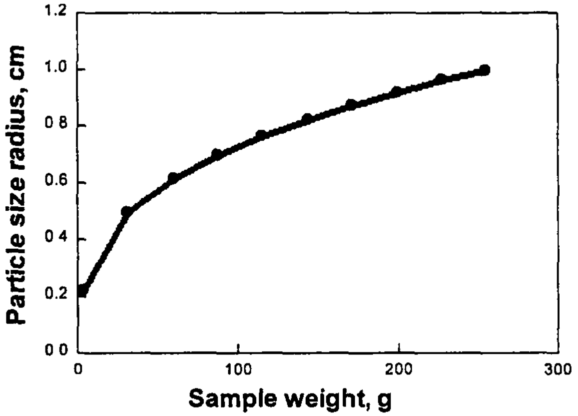


Figure 2. Sample particle size versus weight of sample.

Figure 2 shows weight of the soil sample in grams that has to be sampled, versus the tolerable scattering in the measurement expressed as a relative standard deviation, %RSD. Less scattering requires that greater weight will have to be taken from the population.

In conclusion, proper sampling is the basis for precise measurement of contaminants in the soil. The soil sample taken should be representative of the whole soil. For the best sample, the soil should be homogeneous and free from roots, organic matter, and stones (Pande, 1975; Lewis et al., 1994). Changes in distribution of contaminants laterally and vertically must be taken into account. Glass jars with Teflon liner cover are suggested and should be used for field sampling and transportation to the laboratory (used in this work). The gross soil samples may be nonhomogeneous and weigh too much, and so reduction and homogenizing the gross sample to a finely ground laboratory sample, weighing at the most a few hundred grams, is necessary (Skoog et al., 1988, Carter, 1993). This process involves crushing and grinding, sieving, and mixing the samples. During each sample reduction, a weight of a sample that contains the number of particles has to be retained. Because crushing and grinding tends to change the chemical composition of the sample, the particle size should be reduced no more than is required for homogenizing and ready attack by reagents.

Soil moisture content

Soil samples often contain water. As a consequence, the composition of the sample depends upon the moisture content at the time it is analyzed. To deal with this problem, it is common practice to remove the moisture from the soil sample prior to weighing or, if this is not possible, to bring the moisture content to some reproducible level (Carter, 1993). Another way to deal with this problem is to determine the soil moisture content at the time the sample is weighed for analysis so that the results can be corrected to a dry basis. Table I presents various methods that are currently used to dry soil samples for chemical analysis. Water may present in soils in many different forms, and it is difficult to establish accurate boundaries among these different varieties of soil moisture. Essential water, for example, is an integral part of the molecular or crystalline structure of a compound in its solid state. It can be found as water of crystallization, such as, $CaC_2O_4.2H_2O$ or water of constitution, such as, $KHSO_4$ and $Ca(OH)_2$. The latter yield stoichiometric amounts of water when heated,

$$2KHSO_4(s) \rightleftharpoons K_2S_2O_7(s) + H_2O(g) \tag{3}$$

$$Ca(OH)_2(s) \rightleftharpoons CaO(s) + H_2O(g) \tag{4}$$

Nonessential water is retained in the solid as a consequence of

Table I. Drying of soil for chemical analysis (Carter, 1993).

Province (Canadian)	Drying method	Grinding method	Sieve size	Soil sample measurement
Newfoundland	40 °C	Mortar & pestle	2 mm (1 mm for mineral soil)	Volume
Prince Edward Island	35 °C	Mechanical	2 mm	Weight
Nova Scotia	35 °C	Mortar & pestle	2 mm	Weight (Volume for mineral soil)
New Brunswick	Air dry	Mortar & pestle	2 mm	Volume
Quebec	<37 °C	Mortar & pestle	2 mm	Volume
Ontario	35 °C	Flail	2 mm	Volume
Manitoba	<35 °C	Heavy duty grinder	2 mm	Volume
Saskatchewan	30 °C	Flail	2 mm	Volume
Alberta	60 °C	Flail	2 mm	Weight (or volume)
British Columbia	55 °C	Wood blocks	2 mm	Volume

physical forms. It can be adsorbed water retained by the soil by the forces of adsorption. It can exist as sorbed water held as a condensed phase in the small spaces or capillaries of the solid, e.g., water in silica gel, charcoal, and soil. The quantity of the sorbed water is relatively high. The other form of the nonessential water is the occluded water. Examples are liquid water entrapped in microscopic pockets spread irregularly throughout the solid particles. Such cavities often occur in minerals, rocks and soils.

Soil moisture content can be determined by different methods, such as, gravimetric, electrical resistance, dielectric, and thermal conductivity method. The gravimetric method is the most direct method and is used to calibrate the other methods (Pande, 1975, Carter, 1993). The method involves collecting a soil sample, weighing the sample before and after drying it, and calculating its moisture content. The conventional way is to dry the soil in an oven at 105 °C until constant weight is obtained (Carter, 1993). The air dry method is another way to bring the soil moisture to a reproducible level (Carter 1993). It should be noted, however, that both methods do not yield all of the soil moisture content. This is because clay minerals, such as, kaolinite retains certain level of moisture even after heating to 105 °C for a long time (Pande, 1975).

Analysis of soil

Table II shows a layout of the bioremediation project at CFB Trenton and locations of the soil samples taken from different windrows. Table III presents a summary of the chemical analyses for target analytes in windrow 3, determined at the start of the bioremediation project. The results are just an example for a typical analysis report that can be generated by these methods. All measurements are reported on a dry basis and corrected for recoveries. Undetected contaminants are marked with ND (not detected). Contaminants that are less than the method detection limits (MDL) are accounted as <MDL. The use of MDL does not indicate that the soil sample is free from contaminants. Rather, it is an indication that the analyte concentration in the sample is not high enough to bring the instrument response to a measurable quantity having the stated level of confidence. Figure 3 shows a comparison of IDL, LLD, and MDL values for TPHs, expressed as percentages relative to that of MDL. As expected, the MDL is much greater than IDL and LLD. This is because analyte concentration in the soil sample is corrected for recovery, and that the measurement is done on a diluted sample solution. In other cases, however, MDL may be very close to the value of LLD or even less, if high recovery of analyte is obtained and that the soil sample extract is reduced to a small volume before measurement.

Table II. Locations of soil samples on windrows (not to scale).

<table>
<tr><th>Windrow No.</th><th colspan="6">Location of soil sample</th></tr>
<tr><td>1</td><td colspan="2">w</td><td colspan="2">c</td><td colspan="2">e</td></tr>
<tr><td></td><td colspan="3">a</td><td colspan="3">b</td></tr>
<tr><td>2</td><td>w</td><td>c</td><td>e</td><td>w</td><td>c</td><td>e</td></tr>
<tr><td></td><td colspan="3">a</td><td colspan="3">b</td></tr>
<tr><td>3</td><td>w</td><td>c</td><td>e</td><td>w</td><td>c</td><td>e</td></tr>
<tr><td>4</td><td colspan="2">w</td><td colspan="2">c</td><td colspan="2">e</td></tr>
<tr><td>5</td><td colspan="2">w</td><td colspan="2">c</td><td colspan="2">e</td></tr>
<tr><td>6</td><td colspan="2">w</td><td colspan="2">c</td><td colspan="2">e</td></tr>
<tr><td>7</td><td colspan="2">w</td><td colspan="2">c</td><td colspan="2">e</td></tr>
</table>

Table III. Summary of analysis of heavy hydrocarbons contaminated soils (week 0).

Location	pH	Moist (%)	Concentration, μg/g				
			Purgeables	TPHs	MOG	PAHs	PCBs
3ac	8.0	11	76	<MDL	1431	<MDL	<MDL
3ae	8.0	10	147	<MDL	2096	<MDL	<MDL
3aw	8.0	17	62	<MDL	1061	<MDL	<MDL
3bc	8.0	15	51	<MDL	2049	<MDL	<MDL
3be	7.9	14	85	<MDL	1333	<MDL	<MDL
3bw	8.2	12	82	<MDL	1308	<MDL	<MDL

Quality assurance (QA) and quality control (QC)

Quality assurance (QA) and quality control (QC) are practices and procedures used to evaluate and minimize errors in all phases of environmental analyses. Error or variation in the results may be attributed to population variability and measurement variability. The latter can be subdivided into sampling variability, handling, transport and preparation variability, and laboratory analysis variability. In most cases, the error arising from field sampling is much greater than that associated with sample preparation, handling, or analysis (Carter, 1993). The U.S. Environmental Protection Agency (EPA) has proposed a systematic approach to control variation in soil sampling based on the use of split, spiked, calibration, and duplicate samples (van Ee et. al., 1990). These laboratory operating principles and measures, if strictly followed during sample collection and analysis, will yield data of known and defensible quality (Greenberg et. al., 1992).

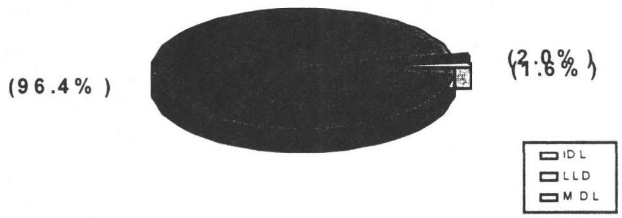


Figure 3. **Values of IDL and MDL relative to that of MDL for TPHs; n = 5, m = 3.**

The quality assurance (QA) plan included:

1. Plan approval (Joint Project between the Department of National Defense and the Emergencies Engineering Division of Environment Canada)
2. Organization and responsibilities section describing the chain-of-command and assigning specific functions to each person involved
3. Sample control and documentation procedures that permit tracing analytes through all steps from sample collection to final results
4. Training and expertise of the analyst to ensure good laboratory practice (GLP) and good measurement practice (GMP) for the proposed methods

5. Equipment maintenance procedures to reduce an instrument malfunction and maintain calibrations
6. Correction action to ensure high data quality
7. Internal and external quality control activities
8. Data assessment procedures for bias and precision
9. Data reporting

The quality control (QC) provisions included:

1. Operator competence to ensure that the reportable work can be delivered
2. Recovery of known analyte addition
3. Analysis of externally supplied standards
4. Analysis of blank (sand)
5. Calibrations with standards (five points calibration curve)
6. Analysis of duplicates (5% of samples provided)
7. Maintenance of control charts [average, standard deviation (s), warning limits (2s) and control limits (3s)]
8. Analysis of spiked matrix

Detection limits

The detection limit is an important parameter that has to be determined so that the result can be reported with confidence. Current practice identifies several limits of detection (Taylor, 1987; Greenberg et al., 1992). These are the instrument detection limit (IDL), lower limit of detection (LLD), method detection limit (MDL), limit of quantitation (LOQ), and the practical quantitation limit (PQL). The relationship, for water samples, is approximately as follows: IDL:LLD:MDL:LOQ:PQL = 1:2:4:10:20 (Greenberg et al., 1992; Kuselman and Shenhar, 1995).

Determination of detection limits. Determination of the instrument detection limit (IDL), lower limit of detection (LLD), and method detection limit (MDL) is summarized as follows: A series of standard solutions is prepared from a certified reference material (CRM) to construct a calibration curve in which the instrument response, R, is plotted versus analyte concentration, C_i,

$$R = b_o + b_1 C_i \qquad (5)$$

Where b_0 and b_1 are, respectively, the intercept and the slope of the regression equation. The dynamic range of the calibration curve must be tested at the start of the analysis, and an effort has to be devoted to derive a best straight line from the analyte concentrations. The regression analysis, using the least-squares method, is then applied to the data to obtain a straight line, and to specify the uncertainties associated with it (Skoog, et. al., 1988, Greenberg et al., 1992; Kuselman and Shenhar, 1995).

The IDL is determined as follows:

$$IDL = \frac{3S_o}{b_1} \tag{6}$$

Where S_0 is the standard deviation of b_0.

In order for an analytical measurement to be reliable the level of confidence has to be stated prior to the analysis. The confidence level means how much error in a measurement can be tolerated. Two types of error are reported in the literature (Taylor, 1987; Greenberg et al., 1992, Kuselman and Shenhar, 1995). The first one is known as false positive (α) or, type I error, in which the analyte concentration is reported to be there while in fact it is absent from the sample. The second type is false negative (β) or, type II error, in which the sample is reported to be free from the contaminant while the latter is there. They can be equal, i.e., $\alpha = \beta$. The tolerable error in both types, however, should be known in advance so that the number of replicas, calibration points, and the dynamic range of the calibration curve can be determined to meet the confidence level required. All of these experimental parameters (i.e., n, m, α, β and dynamic range of the calibration curve) will have to be considered when determining LLD and MDL.

The value of LLD can be determined as follows (Wernimount,1985; Kuselman and Shenhar, 1995),

$$LLD = C_u + \frac{t_{1-\beta}}{b_1}\sqrt{(1/m + 1/n)S_o^2 + (2C_u - \sum C_i/n)^2 S_b} \tag{7}$$

such that,

$$C_u = \frac{t_{1-\alpha}}{b_1}\sqrt{(1/m + 1/n)S_o^2 + (\sum C_i/n)^2 S_{b_1}} \tag{8}$$

where,

C_u = concentration corresponding to the upper confidence limit of the blank reading

t = statistical parameter called one-sided t distribution, depending on the degree of freedom (mn-2)

m = number of replicates
n = number of calibration points (typically, $n = 5$)
C_i = concentration of standard solution
$\sum C_i/n$ = average of the concentrations used in the calibration curve
S_0 = standard deviation of b_0
S_{b1} = standard deviation of b_1
α = type I error
β = type II error

The method deletion limit (MDL), which differs from the LLD in that the sample containing the analyte being processed throughout the complete analytical procedure (Greenberg et al., 1992), is determined as follows:

$$MDL = \frac{LLD \times mL_{extract}}{\%Recovery \times g_{soil}} \qquad (9)$$

Where g_{soil} is the weight of the soil sample in grams and $mL_{extract}$ is the volume of the sample extract analyzed in millilitres.

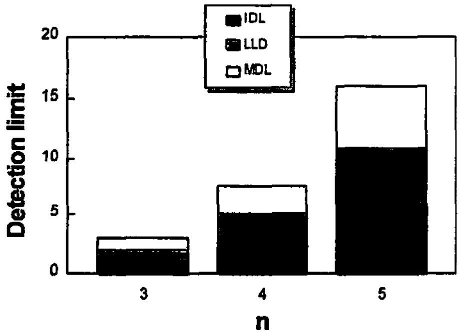


Figure 4. Values of IDL, LLD and MDL of TPHs determined at different number of calibration points.

Figure 4 shows values of various detection limits, IDL, LLD, and MDL determined at different number of calibration points, i.e., number of standard solutions used to construct the calibration curve. The number of replicas for all calibration points was kept constant at $m = 3$. As can be seen from Figure 4, IDL, LLD and MDL increased as the number of calibration solutions, n, was increased. For the case of LLD and MDL, this is because the average value of the calibration solutions $\sum C_i/n$ was involved in the calculation, which means that if a low level of MDL has to be maintained, a narrow calibration curve must be used.

Figure 5 demonstrates that the more we repeat the measurement, the lower the limit of detections (LLD, and MDL) will be. This is explained by the degree of freedom upon which the values of LLD and MDL depend. The value of IDL, however, is not influenced by the degree of freedom and $\sum C_i/n$. The degree of freedom, DOF, is the combination of the number of replicas m and calibration points n, given by the following expression (Kuselman and Shenhar, 1995),

$$DOF = (mn - 2) \qquad (10)$$

Figure 6 depicts the effect of the level of confidence on the value of LLD and MDL for TPHs. Clearly, the more confidence is requested in a measurement, the

Table IV. Experimental parameters.

Contaminant	Weight, g	Volume of extract, mL	%Recovery	Solvent	Solvent density
Purgeables	5	5	69	Methanol	0.793
TPHs	5	10	70	Pentane	0.626
PAHs	5	1	90	Dichloromethane	1.336
MOG	5	-	90	-	-
PCBs	10	3	100	Hexane	0.659

Table V. Values of detection limits for various contaminants in the soil.

Parameter	Variance $(\mu g/g)^2$	$\mu g/g$		
		IDL	LLD	MDL
Purgeables	0.4	2	3	4
TPHs	8×10^4	850	1000	2000
PAHs	6	7	190	60
MOG	1×10^4	300	450	500
PCBs	0.03	0.5	0.8	0.2
Moisture	1×10^4	300	450	-

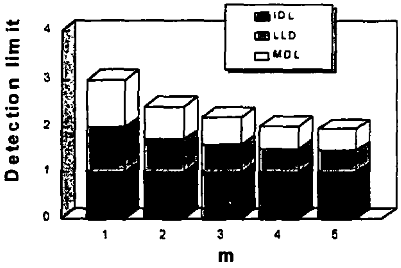


Figure 5. **Effect of measurement replication for TPHs on IDL, LLD and MDL;** *n = 5; m = 3.*

higher the limit of detection will be. The value of IDL is not sensitive to the confidence level.

Table IV shows experimental parameters used in the calculations of detection limits. The values of LLD and MDL are greatly affected by the weight of sample, sample solution, recovery of analyte from the matrix, and the density of the solvent used for preparing standard solutions, whereas, values of IDL and variance are not influenced by them.

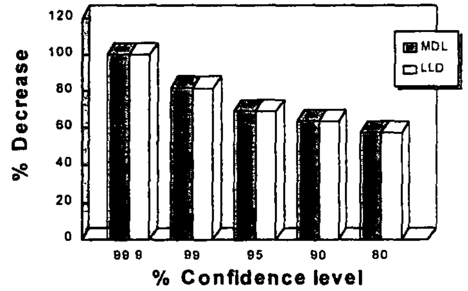


Figure 6. **Values of IDL, LLD and MDL as a function of confidence level; n = 5; m = 3.**

Table V presents values of variance, IDL, LLD, and MDL, for purgeable hydrocarbons, total petroleum hydrocarbons (TPHs), polynuclear hydrocarbons (PAHs), mineral oil and grease (MOG), polychlorinated biphenyls (PCBs) and soil moisture content, expressed in μg/g, except for the variance which is given in $(\mu g/g)^2$. The values of LLD and MDL were determined at $\alpha = \beta = 0.05$, i.e., at a level of confidence of 95%. The demand for high level of confidence, as characterized by error I and error II, will increase the LLD and MDL values. Increasing the number of calibration points will improve LLD and MDL values appreciably. The average value of the calibration concentrations, however, may have a negative effect on LLD and MDL, as shown in equations 7 and 8. If lower values of LLD and MDL have to be maintained, the calibration concentrations must be kept narrow and as low as possible.

The mineral oil and grease (MOG) were determined in soil samples using a gravimetric method. Figure 7 delineates a plot of average MOG in μg/g versus time in weeks for windrow 3. As can be seen, MOG concentration in windrow 3 decreased appreciably to a low level. Detailed description of the project engineering can be found in another publication from this centre (Ouellette et al., 1996).

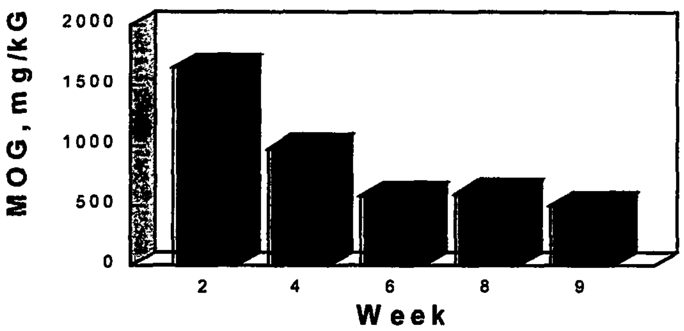


Figure 7. Mineral oil and grease (MOG) in the soil.

Conclusion

Determination of contaminants in the soil can be made effectively if well-defined procedures for sampling and treatment are used. When reporting a soil analysis result, the variations in sampling and measurement have to be taken into account. This requires that a rigorous statistical analysis has to be applied so that the data generated are defensible and can be reported with a certain level of confidence. The proposed methodologies can be used to test the level of mineral oil and grease (MOG), total petroleum hydrocarbons (TPHs), total purgeable hydrocarbons, polynuclear aromatic hydrocarbons (PAHs), and polychlorinated biphenyls (PCBs) in various soil samples. An easy and effective method to check the quality of the analytical measurements, based on daily calibrations has been developed.

Acknowledgment. The authors are grateful to Major John Critchley of the Department of National Defense for helpful comments on this work. The technical help of Mr. Dario Velicogna is greatly appreciated.

REFERENCES

Barcelona, M.J., Principles of Environmental Sampling, Keith, L.H., Ed., American Chemical Society, Washington, DC, **1989**, pp. 3-23.

Benedetti-Pichler, A.A. , Physical Methods in Chemical Analysis, W.G. Berl, Ed., Vol. 3, New York: Academic Press, **1956**, p.192.

Calabrese, E.J. and P.T. Kostecki (editors), Hydrocarbon Contaminated Soils, Volume 1, Lewis Publishers, Michigan, **1991**, pp.206-207.

Carter, M.R. (Editor), Soil Sampling and Methods of Analysis, Lewis Publisher, Florida, **1993**, p. 20.

Kuselman, I., and A. Shenhar, *Anal. Chim. Acta*, **1995**, 306, 301-305.

Lewis, T.E., A.B. Crockett and R.L. Siegrist, *Environmental Monitoring and Assessment*, **1994**, 30 (213-246).

Mason, B.J. Preparation of Soil Sampling Protocol: Techniques and Strategies, EPA-600/4-83-020. U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, Las Vegas, NV, **1983**.

Ouellette, Laura, Shamil Cathum, John Critchley, Janis Avotins, Valdis Kokars and David Cooper, Soil Bioremediation at CFB Trenton: I. Evaluation of Bioremediation Processes, a paper presented in the Artic and Marine Oilspill Program Technical Seminar (AMOP) on June 12-14, **1996**, Calgary, Alberta, Canada.

Pande, A. Handbook of Moisture Determination and Control, Marcel Dekker Inc., New York, Vol. 3, Chapter 12, **1975**.

Rayment, G.E. *Australian Journal of Experimental Agriculture*, **1993**, 33, 1015-1028.

Skoog, D.A., D. M. West and F.J. Holler, Fundamentals of Analytical Chemistry, **1988**, Holt, Rinehart and Winston, 111 Fifth Avenue, New York, p.678.

Taylor, J.K. Quality Assurance of Chemical Measurements, Lewis Publishers, **1987**, p.80.

van Ee, J.J.; L.J. Blume, and T.H. Starks, U.S. Environmental Protection Agency, Environmental Monitoring Systems Laboratory, EPA/600/4-90/013. Las Vegas, NV., **1990**, pp.57.

Youden, W.J. *J. Assoc. Off. Anal. Chem.* **1981**, 50, 1007.

Wernimount, G.T. Use of Statistics to Develop and Evaluate Analytical Methods, Association of Official Analytical Chemists, Washington, DC, **1985**, p.76.

A Critical Review of Total Petroleum Hydrocarbon (TPH) Analysis

P. Lambert [1], M. Goldthorp [2], B. Fieldhouse [1], M. Fingas [1]

1. Emergencies Science Division, Environmental Technology Centre, Environment Canada, Ottawa, Ontario.
2 Goldthorp Consulting, Nepean, Ontario.

Abstract

The Emergencies Science Division has an on-going program to evaluate commercially available person-portable instruments and field analysis kits, with the intent to review their applicability to the on-site determination of chemical hazards in the environment.

The on-site measurement of hydrocarbons in the environment has historically been an active area. Recently this field, due in part to new regulations regarding ozone depleting substances and the appearance of new technologies, has seen a resurgence in the number of new apparatus arriving on the scene More specifically, the increase is in the field of the determination of total petroleum hydrocarbons (TPH) in soil and water.

This paper provides an overview of the problems associated with measuring the concentration of petroleum products in the field and summarizes information on various types of available instrumentation As well, a comparison is made between the TPH values from an immunoassay based field kit (EnviroGard, Millipore Canada, Mississauga, ON) to those of standard laboratory analysis techniques (U.S. EPA Method No. 8011 and No. 3810) on environmental field samples, and finally a comparison of different field kits using prepared diesel fuel-in-sand samples and environmental field samples. The field kits were the EnviroGard Petroleum Fuels in Soil Test kit, PetroFlag Hydrocarbon Test Kit for Soil (Dexsil, Hamden, CT) and a modified version of the method for oil and grease and petroleum hydrocarbons solvent extraction with infrared (IR) analysis (Buck Scientific, East Norwalk, CT)

Objectives

The objectives of this project are to provide a summary and critique of the instrumentation available for measuring petroleum hydrocarbons in the environment and to follow with a comparison of the results from different field kits and with those results from standard laboratory methodologies.

Introduction

The popularity of on-site analysis in general has continued to grow This is due in part to its advantages of lowering analysis costs and reducing the turn around time required to obtain results. Petroleum spills, be they crude oil or refined oil products, have traditionally been the most commonly reported type of spill incidents. As such field analysis procedures have existed for some time. Most of these approaches were instruments capable of measuring volatile organic hydrocarbons or adaptations of the procedure from Standard Oil and Grease and Petroleum Hydrocarbons The Montreal Protocol, calling for the reduction in the use of ozone depleting substances such as trichlorotrifloroethane, has resulted in the aforementioned method decreasing in popularity, due to the lack of availability and a substantial escalation in the cost of the reagent. For the purposes of meeting environmental regulatory requirements, the need for field results comparable to laboratory data has gained importance, which in turn has produced improvements in existing field methodologies and aided in bringing forth several new field test kits incorporating recently developed technologies.

Petroleum hydrocarbon analysis in the laboratory and field is an evolving process. No hard definition of what constitutes total petroleum hydrocarbon, exists. Instead, as technology changes so to does the ability to detect, isolate, identify and quantify very specific chemical compounds in the petroleum product. With this, the understanding of the complexity of petroleum products and fuels improves, but the meaning of total petroleum hydrocarbon becomes clouded.

Due to the complex chemical composition of petroleum, different approaches can be taken when attempting to measure the amount of petroleum hydrocarbons in the environment. Instruments designed to measure lighter, volatile hydrocarbon concentrations in air are commercially available and diverse. The reference by Bissonnette (Bissonnette et al., 1994) provides a listing of available portable instrumentation for this purpose. The majority of the instruments employ either a photo-ionization detector (PID) or a flame ionization detector (FID). The PID uses an ultraviolet light energy source which is more suited to detect aromatic compounds while a FID, more sensitive to alkane hydrocarbons, uses a flame to ionize the gas particles (Fitzgerald, 1993). A detailed report comparing the PID, FID and field GC instruments during an actual field investigation of a contaminated site can be found in Denahan et al., 1993. One of the conclusions was the FID, due to its calibration with methane, had superior detection limits as compared to the PID. On-going improvements have been made to these technologies including their incorporation into portable gas chromatographs (GC). This has resulted in improving detection limits, making the instrument more compound specific, and producing results which can be more easily compared to laboratory methods. However, they still primarily detect only the volatile component of petroleum hydrocarbons and do not portray an accurate picture of the total petroleum hydrocarbon content of a sample.

A second class of instrumentation are those which measure petroleum hydrocarbons on a real-time basis without any sample preparation These instruments focus mainly on air and water analysis The principle means available are fluorometers and a new technique, a fibre optic chemical sensor. Fluorometers operate on the basis of the detection and quantification of the amount of petroleum present in relation to the presence of a group of fluorescing compounds in the petroleum. The percentage of a petroleum product made up of these compounds varies from product to product As such, difficulty has been experienced with attempting to quantify the petroleum concentration in the sample without prior knowledge of the chemical make-up of the petroleum hydrocarbon. Although a promising new technology, the fibre optic analysers measure, the amount of dissolved hydrocarbons in the medium. In the environment, dissolved hydrocarbons are a very select portion of the total present making it difficult to relate this value to the total amount of hydrocarbons present

This report presents data dealing with another class of instruments used for the field analysis of petroleum hydrocarbons in soil These are methodologies marketed as being capable of measuring the TPH concentration in soil. Each operates on the principle of extraction of the petroleum hydrocarbon from the soil followed by quantification of the contaminant The techniques used to quantify the TPH levels differ for each procedure. The three procedures examined were a field version of the trichlorotrifluoroethane extraction and IR quantification method, a colourimetric-based test kit, and an immunoassay based kit. Evaluations were carried out on equipment possessed by the Emergencies Science Division. Other portable kits are commercially available and new instruments are regularly developed. Information was not available to present an accurate reflection of their capabilities. For this reason, they have not been addressed in this report.

Procedures

The following paragraphs describe the measures taken to prepare the samples and the methods used to determine the petroleum hydrocarbon content. Two distinct types of experiments were performed and the format in which the procedures are outlined reflect this. Procedures employed for the comparison of immunoassay based field kits versus standard laboratory methodologies are presented first and followed by a description of the approach used to compare results of the different field methods.

Comparison of Immunoassay Based Field Kits versus Standard Laboratory Techniques

Environmental samples, from a historic fuel contaminated area, were used. Soil sampling procedures were based on the U.S. EPA, *Standard Operating Procedure #2012, Soil Sampling* (U.S. EPA, 1988). Samples were collected at a depth of less than 20 cm. Steel garden hand tools and spades were used to collect soil samples. A sample-handling protocol was initiated to reduce chances of potential cross-contamination. Sampling equipment was decontaminated on a regular basis using manual cleaning techniques followed by multiple washes with water, followed by methanol, and finally distilled water. In addition, disposable gloves were used by the operators during sampling operations. The samples were stored in new, certified clean, glass bottles with Teflon lined caps (Fisher Scientific, Nepean Ont.; VWR Scientific, London, ON.). Certification was to U.S. EPA protocols for extractable organics including pesticides and PCB. A temperature-controlled sample cooler (Canadian Coleman Co., Toronto, ON.) was used to store and transport the samples at a suitably reduced temperature. A chain of custody form was prepared and used to log the progress of samples. Samples were forwarded to the contract laboratory for analysis using the same equipment and handling practices.

Field analysis of TPH was performed using immunoassay technology Analysis was performed in the field using the manufacturer's instructions. A summary of the method is as follows. Prior to analysis, each sample was homogenized by manually rotating the sample bottle. A 5 g aliquot of the sample was removed and extracted with 10 mL of methanol. A micro litre portion of the extract was accurately transferred to the reaction tube along with prescribed amounts of reagents. The colour change occurring is compared to those of standards prepared concurrently. A portable spectrophotometer was used to quantify results. Total petroleum hydrocarbon results from the field analysis are reported as a value within a range of two standards. Two kits were required, having lot numbers of IM4JM00794-D and IM5DM0495-S. A background sample, defined as a sample collected from a location at the site with no apparent contamination, was examined in conjunction with the other samples for the purpose of providing information on potential systematic interference in the procedure.

Laboratory analysis was performed on the same samples by a contract facility, MDS Environmental Services Limited (Mississauga, ON). A contract laboratory was employed to provide independent and unbiased analysis. Laboratory analysis was carried out using standard methodologies. The analysis included extractable hydrocarbon analysis by solvent extraction and GC analysis (U.S EPA Method No. 8011, micro extraction, 1986) and analysis of benzene, toluene, ethylbenzene, xylenes and purgeable hydrocarbons by Static Headspace Capillary GC PID/FID (U.S. EPA Method No. 3810, modification, 1986). Instrumentation were Hewlett-PackardII, dual injector, dual FID, A/S GC/FID/FID and a Varian 3400 GC/PID/FID with a Genesis Headspace Analyser. A review of quality assurance and quality control criteria showed the data generated by the laboratory to be within acceptable limits.

Comparison of Results of Field Kits

Environmental samples were collected at the same time and manner as described previously. Samples were stored, following the completion of the field work, at ESD in a temperature-controlled room at 5 °C.

The diesel fuel-in-sand samples were prepared using 8%, by weight, artificially weathered diesel fuel. The diesel fuel was the fuel used in the 1994 Mobile burn experiments (Fingas et al., 1996; Walton et al., 1995). The weathered sample was generated from the roto-evaporation of the original fuel using an established method (Jokuty and Fingas, 1994). Fresh and weathered fuels, when not in use, are stored in a temperature-controlled refrigerator at 5 °C. Prior to use, the diesel fuel was brought to ambient temperature and mechanically mixed for 2 hours The washed, all-purpose sand is a commercially available product sold under the name Sakret (King Paving and Materials Ltd., Paris, ON) Samples were prepared by adding a known volume of fuel to a weighed amount of sand. The density of the fuel (0.84 g/mL) was used to convert the concentration of the samples to µg/g (parts per million, ppm). Samples were mechanically shaken for 9 hours over a two day period, and then allowed to remain undisturbed for 3 days to permit interaction of the fuel with the soil matrix. Five samples were prepared over the concentration range of 0 µg/g to 836 µg/g.

Analysis, by each field kit, was carried out on a weighed aliquot from the same sample. Both the environmental samples and prepared samples were manually shaken prior to the removal of the aliquot. A summary of the procedure for the EnviroGard kit has already been included A differential photometer, as recommended in the instructions, was used to quantify results. Total petroleum hydrocarbon results are reported as a value within a range of two standards. The samples were examined twice using two kits, from the same lot number IM5DM0495-S. The measurement range of the kit is 5 to 1250 ppm.

Determination of TPH, via the PetroFlag kit, was done using the manufacturers instructions. In summary, a weighed amount of the sample (1 g or 10 g depending on concentration levels) is placed in an extraction tube, to which a proprietary solvent is added. A standard is provided and prepared in a manner similar to the samples. Following extraction, the contents of the tubes are filtered and collected in a vial. The extracting solvent contains an additive which produces turbidity in the sample in proportion to the concentration of the hydrocarbons present. An analyser is used to quantify the result using the prepared standard as a reference and a calibration factor specific to the type of petroleum product. A calibration factor of 5 was input into the analyser and used to measure the concentration. The measurement range of the kit is 10 to 2000 ppm.

A modified version of the ASTM method D 3921-85 (reapproved 1990), Standard Test Method for Oil and Grease and Petroleum Hydrocarbons in Water (ASTM, 1995), was employed for the measurement of hydrocarbons in soil. Although portable field infrared (IR) analysers are commercially available, no complete kit containing necessary supplies is marketed. Labware and reagents used in the experiments were obtained separately. The reagents were of high quality and the labware was suitably prepared. In general, a weighed amount of the sample (2 g to 3 g) was transferred to a 125 mL separatory funnel containing 30 mL of deionized water and mixed. The mixture was extracted with 25 mL of trichlorotrifluoroethane. The solvent layer was drained to a vial. A series of diesel fuel-in-solvent calibration standards were prepared. The concentration of the standards extended over the range of 0 to 84 µg/mL. The standards were used to obtain an absorbance versus concentration calibration curve. Readings were taken, following the manufacturers instructions, using a fixed wavelength model 404 IR analyser (Buck Scientific, East Norwalk, CT). The wavelength is fixed at 2924 cm^{-1} , a commonly used value for the detection of petroleum hydrocarbons. The extracts from the samples were individually transferred to a cuvette, placed in the spectrometer and the absorbance noted. From the calibration curve and sample absorbance reading, the concentration of the petroleum in the samples was calculated. The measurement range of the IR is 2 to 20,000 ppm.

Results

The results section of this paper includes three tables of data. The first lists results from the analysis of environmental samples comparing the EnviroGard immunoassay based test kits with laboratory examination. Table 2 consists of four sets of results for the same samples, using the EnviroGard kit, and provides an indication of the repeatability of the method. Table 3 offers a comparison of results of the three available TPH field procedures.

In regard to the first set of results, all analysis was carried out in conjunction with a recent project undertaken by the Emergencies Science Division. Field measurements were carried out on an aliquot of the original sample, while on-site, using the manufacturers instructions. The laboratory analysis was performed on the original samples by a contract laboratory employing standard methodologies. Laboratory results are presented as a total extractable hydrocarbon value and total purgeable hydrocarbon value. For comparison purposes, the laboratory total petroleum hydrocarbon result is the sum of the total extractable and total purgeable hydrocarbon values. The chemical resemblance of the hydrocarbon, as identified by the laboratory, and a description of the soil matrix has been included. The intent was to provide additional information which can be used to evaluate the effects of the sample matrix and hydrocarbon composition on results.

Table 1: A Comparison of Immunoassay Field Results to Laboratory Results

Sample ID Cape Race Lightstation	TPH Field Results (mg/kg)	Laboratory Results (mg/kg)	Chemical Resemblance	Sample Description
C623-1115 Area 2	<50	5070 Extractable Hydrocarbons nd Purgeable Hydrocarbons	Diesel fuel	Contains dry, sandy soil with small stones , fuel odour detected, moisture content 8%.
C623-1125 Area 2	<250	944 Extractable Hydrocarbons nd Purgeable Hydrocarbons	Diesel fuel	Contains dry, sandy soil with small stones , fuel odour detected, moisture content 16%.
C623-1130 Area 2	<250	88 Extractable Hydrocarbons nd Purgeable Hydrocarbons	Diesel Fuel	Contains dry, sandy soil with small stones , fuel odour detected, moisture content 5%
C623-1145 Area 2	<250	nd Extractable Hydrocarbons nd Purgeable Hydrocarbons	Not Applicable	Contains sand/clay mixture, no fuel odour, moisture content 5%.
C623-1155 Area 2	<50	nd Extractable Hydrocarbons nd Purgeable Hydrocarbons	Not Applicable	Contains sand with gravel and stones, no fuel odour, no root material, moisture content 6%.
C623-1220 Area 2	<250	nd Extractable Hydrocarbons nd Purgeable Hydrocarbons	Not Applicable	Contains dry, sand and small stones. no vegetation, or fuel odour, moisture content 5%.
C623-1235 Area 2	<250	nd Extractable Hydrocarbons nd Purgeable Hydrocarbons	Not Applicable	Contains dry, sand and small stones, no vegetation, or fuel odour, moisture content 4%.
C623-1240 Area 2	<50	1800 Extractable Hydrocarbons nd Purgeable Hydrocarbons	Motor Oil	Contains few stones, no vegetation, possible faint fuel odour, moisture content 6%.
C623-1250 Area 2	<50	3050 Extractable Hydrocarbons nd Purgeable Hydrocarbons	Motor Oil	Contains few stones, no vegetation, no fuel odour, moisture content 6%.
C623-1255 Area 2	<50	2820 Extractable Hydrocarbons nd Purgeable Hydrocarbons	Motor Oil	Contains sand and gravel. no fuel odour or vegetation, moisture content 4%
C623-1705 Area 4	<50	768 Extractable Hydrocarbons trace Purgeable Hydrocarbons	Diesel Fuel	Contains moist, gravel with clay/sand soil mixture, fuel odour present, moisture content 15%.
C623-1717 Area 4	<250	2020 Extractable Hydrocarbons nd Purgeable Hydrocarbons	Diesel Fuel /Motor Oil	Contains dark brown wet soil, very sandy (silty), small stones, fuel odour present, moisture content 16%.
C623-1720 Area 4	<1000	5020 Extractable Hydrocarbons 6 Purgeable Hydrocarbons	Diesel Fuel /Motor Oil	Contains moist sand/clay soil, stones, fuel odour present, moisture content 9%.
C623-1730 Area 4	>1000	5220 Extractable Hydrocarbons 12 Purgeable Hydrocarbons	Diesel Fuel	Contains wet clay, fuel odour present, moisture content 14%
C623-1625 Area 4	>1000	3720 Extractable Hydrocarbons 19 Purgeable Hydrocarbons	Diesel Fuel	Contains moist soil, fuel sheen and odour present, moisture content 23%
C623-1637 Area 4	<250	4790 Extractable Hydrocarbons trace Purgeable Hydrocarbons	Diesel Fuel	Contains moist soil, fuel sheen and odour present, moisture content 12%.

The data listed in Table 2 is from the TPH analysis of actual samples from a recent field project. Testing was carried out on four separate occasions using the EnviroGard test kits. Some variations existed in the procedure between each set of analysis but these would not have affected results. The four runs were done over a period of eight months. Two runs (two left-most columns) were performed during the course of a field project while the final sets were analysed at the same time as the laboratory evaluation of the field kits occurred. A spectrophotometer and differential photometer were used to quantify results during the field project and laboratory evaluation respectively.

Table 2: Reproducibility of EnviroGard Kit Results

Sample	Millipore EnviroGard Immunoassay Kit µg/g	Millipore EnviroGard Immunoassay Kit µg/g	Millipore EnviroGard Immunoassay Kit µg g	Millipore EnviroGard Immunoassay Kit µg/g
Cape Race Lightstation S623-1125	0<x<250	0<x<250	0	0
Cape Race Lightstation S623-1150	50	0<x<250	0	0
Cape Race Lightstation S623-1235	0<x<50	0<x<50	0	0
Cape Race Lightstation S623-1300	50<x<250	0<x<250	0	0
Cape Race Lightstation S623-1645	0<x<50	0<x<250	0	0
Cape Race Lightstation S623-1655	0<x<50	0<x<250	0	0
Cape Race Lightstation S623-1845	0<x<50	0<x250	0	0

Results listed in Table 3 were generated from experiments carried out in the laboratory using prepared diesel fuel-in-sand samples and actual environmental samples collected during a recent project. Analysis for all the field kits was performed in the laboratory using an aliquot from the same samples. Tests with the PetroFlag and EnviroGard kits were carried out according to the manufacturers instructions, where, the infrared analysis procedure followed a modified version of the ASTM method D3921-85. A description of the soil matrix has been included. The intent was to provide additional information which can be used to evaluate the effects of the sample matrix and hydrocarbon composition on results.

Table 3. A Comparison of Field TPH Methodologies

Sample	Solvent Extraction and IR Quantification µg/g	Dexsil PetroFlag Colour Analyser Kit µg/g	Millipore EnviroGard Immunoassay Kit µg/g	Description
Diesel-in-sand 0 µg/g Sample	16 11*	0	0 0	Contained dry sand and 8% (wt%) weathered diesel.
Diesel-in-sand 8 µg/g Sample	18 17*	0	0 0	Contained dry sand and 8% (wt%) weathered diesel.
Diesel-in-sand 83 µg/g Sample	68 17*	91	0 0	Contained dry sand and 8% (wt%) weathered diesel.
Diesel-in-sand 419 µg/g Sample	342 46*	542	0 50<x<250	Contained dry sand and 8% (wt%) weathered diesel.
Diesel-in-sand 836 µg/g Sample	692 131*	1,327	0 50<x<250	Contained dry sand and 8% (wt%) weathered diesel.
Cape Race Lightstation S623-1125	3,545 533*	>20,000	0 0	Contains dry, brown/black soil with a high sand content, little to no root mat, a fuel odour was detected.
Cape Race Lightstation S623-1150	656 310*	3,810	0 0	Contains dry, brown/black soil with a high sand content, little to no root mat, a fuel odour was detected.
Cape Race Lightstation S623-1235	3.781 2.146*	11.450	0 0	Contains black/brown soil, stones, some root material, no fuel odour
Cape Race Lightstation S623-1300	>20,000 >20,000*	>20,000	0 0	Contains black soil with some root material, many small stones, fuel odour.
Cape Race Lightstation S623-1645	2,205 652*	8,370	0 0	Contains dark brown/black soil, silt, rocks, stones, samples fuel odour present.
Cape Race Lightstation S623-1655	200 123*	3,270	0 0	Contains dark brown/black soil, silt, rocks, stones, samples fuel odour present.
Cape Race Lightstation S623-1845	12 11*	1.227	0 0	Background sample containing moist soil and root material

* solvent extract was filtered through silica gel

Discussion

Comparison of Immunoassay Based Field Kits to Standard Laboratory Techniques

A comparison of field TPH analysis to laboratory analysis data was presented in Table 1. The chemical resemblance of the hydrocarbon is determined by a general comparison of the size and location of the peak in the sample chromatogram to that of a generic standard. This is not a definitive identification, as all of the generic standards are petroleum hydrocarbon based. Some naturally occurring hydrocarbons will resemble low level motor oil contamination Chemical resemblances described as "Not Applicable" are a result of the insufficient amount of hydrocarbons. Samples C623-1115 through C623-1717 and C623-1637 have field TPH values of <250 mg/kg and have an inconsistent correlation with laboratory data. Sample C623-1720 to C623-1625 display field TPH values of near or greater than 1000 mg/kg. This is a satisfactory relationship to laboratory results as 1000 mg/kg or 1250 mg/kg (depending on the set of calibration standards used) are the upper detection limit of the field kits and results in excess of the limit are reported in this manner. The standards included in the kit are home heating fuel. TPH results for the field kits are reported in terms of "equivalent" to home heating fuel.

Results from field analysis methodologies and those from laboratory analysis are seldom numerically equivalent. This is a result of the fact that each technique employs different sample preparation procedures and each type of instrument has its own unique limitations. Field TPH analysis showed similar trends to laboratory analysis, however the numerical values were not similar. The kits are marketed as a semi-quantitative tool. Although they did not always produce results which were numerically equivalent to laboratory analysis, they were capable of detecting the presence of the fuel within the limits of the kits. The detection limit of the kits was dependent on the soil matrix and calibration standards employed. The advantage of these kits is that they can significantly reduce the time and cost of analysis and this technology is one of the few commercially available as a portable kit. A kit can analyse a maximum of 17 samples. Estimated cost of a complete kit, the sample preparation labware and solvent is $450. A one-time purchase of reusable pipettes would be an additional $350.

The effect of the sample matrix can be seen in the correlation between field and laboratory for the immunoassay test kit. Water content, the make up of soil, and type of contaminant will influence the performance of the immunoassay kits. Methanol is the solvent used in the procedure to extract the contaminant from the soil. It is used for two reasons; its chemical composition differs enough from the contaminant of interest so that it will not compete for, or interfere with, the reaction and it is not toxic to the antibody. However, the extraction efficiency of methanol is low for samples containing motor oil or weathered fuel. Extraction of a chemical from soil is affected by soil type. Soils with a high organic content contain naturally occurring oils which are somewhat similar in structure to motor oil and contaminants often bind strongly to the organic compounds. Clay based soils tend to absorb the solvent, reducing the recovery. Sand and gravel soils generally have the best extraction efficiencies. Water contents above 30% may influence the results. As methanol is water soluble, when diluted its ability to remove the chemical from the soil is reduced. This being said, several samples with high water contents were tested in the field with good correlation between laboratory and field results.

Already briefly mentioned was the effect of the fuel type on field results. Note that with samples C623-1720, C623-1730 and C623-1625 the presence of a small amount of purgeable hydrocarbons has resulted in a significant improvement in the numeric correlation between field and laboratory results. The enzyme antibody used in the TPH kit is the same one as incorporated into the BTEX test kit. The difference between the kits is an alternate set of calibration factors was used to calculate TPH values. The presence or absence of the purgeable hydrocarbons, such as BTEX, in the fuel appears to play a major role in the capability of the EnviroGard kit to generate results numerically similar to those from a laboratory.

Potential sources of systematic errors, such as those from unrepresentative sub-sampling, for the purposes of field analysis, from the original 250 mL sample, were reduced by instituting proper quality control and assurance measures. These included the use of standard methodologies, where available, regular maintenance and calibration of the instruments, duplicate analysis, and a sampling/analysis log system. As well, a background sample was collected at each site and was included during analysis. The purpose of which was to obtain results which could be compared to those from samples collected in identified areas of concern. Any naturally occurring chemical compounds, which may skew results, would be noted and compensated for in the results for the contaminated samples. In addition, it provides a valuable tool for comparison to false positive sample results, as often the same positive value appears in the background sample

Table 2 shows a collection of four sets of TPH results from the same environmental samples as measured by the EnviroGard immunoassay test kits. These results provide an indication of the repeatability of the EnviroGard kits. The results in the two left columns were from analysis carried out during a field project while the other two sets were from tests performed at a later date. Because results are displayed as within a range, the final presentation of the results is affected by the selection of the standards. A review of the raw data showed results from both field runs to be equivalent to each other. Differences between the field values and those obtained in the final two runs is explained by the absence of the lighter purgeable hydrocarbons. Although none of these samples underwent laboratory analysis, several samples collected in the same areas did. Laboratory analysis of these samples showed "not detectable" amounts of purgeable hydrocarbons. Assuming the laboratory and field kit analysed samples have similar fuel contamination, the samples analysed by field methods would have had a minimal amount of the compounds remaining, during field testing, which could be detected by the enzyme antibody. With time, this amount has decreased further, below the detection limits of the kits, resulting in zero values for the final two data sets. In view of the aforementioned discussion, repeatable results are obtained within the limits of a semi-quantitative test kit.

Comparison of Results of Field Kits

Each of the methodologies examined in this study claim to be able to quantify the amount of petroleum hydrocarbons in soil. Testing was carried out using the manufacturers instructions, thus the sample preparation and detection principle differs for each method. A comparison of the TPH results from three field methodologies is present in Table 3. The results make it possible to compare the responses of different technologies evaluated under the same conditions Two separate types of samples were examined. The first were a series of five prepared diesel fuel-in-sand samples with known concentrations while the second set of seven samples were samples collected from a contaminated site.

The purpose of the prepared samples was to determine the capability of the various procedures to accurately quantify the amount of petroleum hydrocarbons in a soil sample. Prewashed sand was used as the soil matrix and should represent an optimal situation, as sand usually is the easiest matrix to remove contaminants from. A diesel fuel, in which 8% by weight of the lighter components had been evaporated away, was used as the contaminant to simulate conditions commonly found in the field.

The samples from the contaminated site provide information on the capability of the field kits when dealing with difficult samples where the fuel has had an opportunity to weather and adsorb into the sample matrix. The soil itself is a mixture of sand, gravel and organic material which lends to the difficulty of analysis. None of the samples used in this portion of the experiment were analysed by standard laboratory methods. However, several samples collected in the same area did undergo laboratory analysis. Their results are included here for information purposes only. Laboratory data on the sample from the same area as the environmental samples S623-1125 to S623-1300 had a petroleum hydrocarbon concentration of 227 mg/kg. No purgeable hydrocarbons were detected. Samples S623-1645 and S623-1655 were collected in an area where laboratory analysis of subsequent samples showed petroleum hydrocarbon concentration of between 1710 to 4830 mg/kg. Again, no purgeable hydrocarbons were detected in the samples.

The results from the EnviroGard immunoassay kits show similar trends to those discussed in the previous paragraphs. With the exception of the two prepared diesel fuel-in-sand samples, having the highest concentration, the immunoassay kits could not detect the presence of the petroleum hydrocarbons. Testing was repeated to confirm results, with both sets of analysis producing similar responses. The weathered diesel used in the prepared samples and the natural weathering of the fuel in the environmental samples has resulted in the inability of these kits to extract sufficient material to produce accurate responses. As described earlier, the low level of lighter components in the fuel and the soil matrix affected the capabilities of EnviroGard kits.

The PetroFlag kit appears to have the capability to deal with weathered fuels. From the results of the prepared samples, it can be seen that the PetroFlag methodology can differentiate between different levels of contamination. Results from the field kit are higher than the true concentration of prepared samples. The soil composition and matrix of the environmental samples had little affect on the capability of the kit to obtain reasonable data. Like the prepared samples, the results are higher than those from the other test procedures. Sample S623-1846 is a background sample with low petroleum hydrocarbon content. The result for that sample is a false positive. It is not uncommon for field kits to generate high results as they are sometimes designed to err on the side of caution. The reaction in the test vessel produces turbidity in proportion to the amount of hydrocarbons. Interferences such as suspended particulate can affect results. In general the kit was capable of detecting and approximating the concentration of petroleum hydrocarbons in soil. The PetroFlag test kit is entirely self contained, operationally easy to use, has a purchase price of $700 and can analyse ten samples before requiring additional stock. Replacement reagent packages for ten samples are approximately $100.

The infrared test procedure is not a commercially available field kit In fact, it was only with the development of portable IR spectrometers that this laboratory procedure has been made field portable. Necessary equipment and reagents, in addition to the IR, must be purchased separately. Costs for these can be as high as $1000. The solvent employed in the procedure, trichlorotrifluoroethane, is an ozone depleting substance and regulated under the Montreal Protocol. This has seen a drastic increase in the solvent price ($500 per 4 L bottle), if it is available at all. The cost of the spectrometer is $8000, however the prices have begun to slowly decrease with market competition.

A review of the results shows the procedure can satisfactorily detect petroleum hydrocarbons in soil and appears to have the lowest detection limits of the kits evaluated. Two separate runs were performed. In the first set (results are indicated by an asterisk, *) the extracts were filtered through silica gel, as described in the procedure. The purpose of the silica gel is to remove the naturally occurring hydrocarbons from the extract so that the final results reflect a true petroleum hydrocarbon value. As filtration through the silica had the effect of inconsistently reducing the results by up to 75%, the second set of extracts were not filtered. Measured petroleum hydrocarbon concentrations were generally about 80% of the expected value for the prepared samples. Results from the environmental samples showed similar trends between the IR method and the PetroFlag kit, however the IR procedure generated numerically lower values. Results from the IR procedure were closer to the expected hydrocarbon concentrations based on the laboratory results of subsequent samples collected in the area. This is not unexpected as experience has shown the solvent employed possesses above average extraction capability in comparison to the solvents from the other kits. Unlike the other kits, which have a subsequent reaction in the detector portion of the procedure, the accuracy of the IR test is primarily dependent on the extraction efficiency of the solvent.

Conclusion

A series of results have been presented, comparing the TPH results from a commercially available immunoassay based field kit to those from standard laboratory methodologies. The field kit was found to be able to detect the presence of petroleum hydrocarbon contamination in soil Immunoassay results showed similar trends to that of laboratory analysis, however, the field kit results did not consistently compare to the numeric value of laboratory results for environmental soil samples The primary influence on the responsiveness of the immunoassay field kit tested appears to be presence or absence of the lighter, purgeable hydrocarbons in the fuel, where the presence of purgeable hydrocarbon improves the capability of the test kit

An experiment was carried out to review the performance of three field procedures under similar testing conditions. Results from the EnviroGard Petroleum Fuels in Soil Test kit showed it to be the least responsive and appeared to be significantly effected by the sample matrix. The PetroFlag Hydrocarbon Test Kit for Soil was less affected by the sample matrix but generated high results. Both of these commercially available test kits are relatively user friendly. The modified solvent extraction and IR method appears to be the most sensitive method. Results are more likely to represent the real hydrocarbon value of a sample, however the procedure requires expensive reagents and instruments, and some training.

Instructions provided by the manufacturer for each of the procedures were found to lack sufficient measures to ensure adequate quality control over results. Additional steps should be instituted by the analyst.

References

American Society for Testing and Materials, *1995 Annual Book of ASTM Standards - Water and Environmental Technology, Water(II)*, Vol. 11.02, Philadelphia, Pennsylvania, 896p., 1995.

Bissonnette, M., M. Goldthrop, M. Fingas, J. Bélanger and J. Paré, *Person-Portable Instrument Review*, Environment Canada Manuscript Report Number EE-150, Ottawa, Ontario, 283p., 1994.

Denahan S., B. Denahan, W. Elliott, W. Tucker, M. Winslow, " Relationship Between Chemical Screening Methodologies for Petroleum Contaminated Soils: Theory and Practice", *Principle and Practices for Petroleum Contaminated Soils*, E. Calabrese and P. Kostecki Ed., Lewis Publisher, Chelsea, Michigan, pp. 67-84, 1993.

Fitzgerald, J., "Onsite Analytical Screening of Gasoline Contaminated Media Using a Jar Headspace Procedure", *Principle and Practices for Petroleum Contaminated Soils*, E. Calabrese and P. Kostecki Ed., Lewis Publisher, Chelsea, Michigan, pp. 49-66, 1993.

Fingas, M., F. Ackerman, P. Lambert, K. Li, Z. Wang, R. Nelson, M. Goldthorp, J. Mullin, L. Hannon, D. Wang, A Steenkammer, L. Graham, S. Schutz, P.R. Campagna, R.D. Turpin, and R. Hiltabrand, "Emissions From Mesoscale In-Situ Oil (Diesel) Fires: The Mobile 1994 Experiments", in *Proceedings of the Nineteenth Arctic Marine Oilspill Program Technical Seminar*, Environment Canada, Ottawa, Ontario, in print, 1996.

Jokuty, P. and M. Fingas, "Oil Analytical Techniques for Environmental Purposes", in *Proceedings of the 17th Arctic and Marine Oil Spill Program Technical* Seminar, Environment Canada, Ottawa, Ontario, pp. 245-260, 1994.

U.S. EPA (U.S. Environmental Protection Agency), *Standard Operating Procedure #2012, Soil Sampling*, U.S. EPA Environmental Response Team, Edison, New Jersey, 17 p., 1988.

U.S. EPA (U.S Environmental Protection Agency), "Volume 1C: Laboratory Manual Physical/Chemical Methods, Method 3810 and 8011", *Test Methods for Evaluating Solid Waste*, Office of Solid Waste and Emergency Response, SW-846, Third Edition, Washington, DC, 1986

Walton, W., W. Twilley, and A. Putorti, in *Proceedings of the 18th Arctic and Marine Oil Spill Program Technical* Seminar, Environment Canada, Ottawa, Ontario, pp. 1053-1074, 1995

AN EVALUATION OF RAPID SAMPLE EXTRACTION BY MICROWAVE-ASSISTED EXTRACTION

Ken Li[1], Jacqueline M. R. Bélanger[1], M. F. Fingas[1], María Llompart[1], Raj Singhvi[2], Rodney D. Turpin[2], Lois B. Jassie[3], Todd Kierstead[3], and J. R. Jocelyn Paré[1]

1. Environment Canada, Microwave-Assisted Processes Division & Emergencies Science Division, Environmental Technology Centre, Ottawa, ON, Canada K1A 0H3;

2. United States Environmental Protection Agency, Environmental Response Branch, Edison, NJ 08837, USA;

3. CEM Corporation, 3100 Smith Farm Road, Matthews, NC 28106, USA.

ABSTRACT

The main objective of this study is to evaluate the applicability of microwave-assisted extraction and subsequent GC/MS determination of toxic substances including PAHs. PCBs, base-neutrals. chlorinated pesticides and substituted phenols. Mixtures of representative compounds were spiked into typical environmental matrices including sand, soil and glass-fibre filters and analysed. Recoveries from these matrices were mostly above 80% with the exception of some volatile components; precision was generally in the 10% (RSD) range. The method was validated using standard reference materials including marine sediments, harbour sediments and a creosote contaminated soil certified with PAH and PCB. Split samples were also obtained from a contract laboratory and the consensus results were used to evaluate recoveries of PAHs and organochlorinated pesticides. The potential problem of degradation of thermally labile pesticides was addressed by measuring degradation products of DDT and endrin after microwave-assisted extraction. Spiked samples before and after the extraction procedure did not result in additional decomposition products.

INTRODUCTION

Several microwave-assisted processes have been patented by Environment Canada [1-4]. As a result, the Trademark MAP ™ [1] (for Microwave-Assisted Process) has been secured to cover various extraction, chromatography, and synthesis activities. Several reports are now available in the open literature on the use of microwave energy to assist in the extraction of a broad range of substances from various matrices. For example, drug residues in tissues [5], various herbicides, pesticides, organochlorinated pesticides, and petroleum hydrocarbons from soils and

---

[1] MAP is a Trademark of Her Majesty the Queen in Right of Canada as represented by the Minister of the Environment.

sediments [6-12], and PAHs, PCBs, BNAs and others from soils and sediments [13-16] were all reported. All these studies reported recoveries similar or better than Soxhlet and sonication methods.

With the potential of rapid sample turn-around, most important in emergencies response work, an evaluation of this type of extraction method for environmental pollutants from soils and sediments has been conducted. To minimise method development time, only one extraction condition was used which was 115° for 10 min. under full power. We have performed matrix spike studies, replicating 5 extractions for each matrix. The extent of analyte loss during sample preparation was also evaluated which included extraction and the subsequent sample workup. Certified soil/sediment samples were then used to measure the accuracy of the entire method from sample workup and analysis. Finally, split soil samples from actual contaminated sites were obtained from an EPA contract laboratory and analysed to compare performance of extraction/analysis between two independent laboratories different extraction and analytical protocols.

EXPERIMENTAL

Standards and Solvents

All solvents including toluene, *n*-hexane, acetone and dichloromethane were purchased from Caledon (Belleville, Canada).

For matrix spiking, a Method 525 kit (organics in drinking water by liquid-solid extraction and capillary GC/MS determination) from Accustandard (New Haven, CT) was used. The kit consisted of 5 mixtures of PAH (13 components), PCB (8 components from monochloro- to octachloro-), chlorinated pesticides (12 components), base-neutral (9 components) and pentachlorophenol (Table 1). Each mixture was run individually on the GC/MSD using the condition described above and then combined to give a final spiking solution of 25 µg/mL. A surrogate mixture of 4 deuterated PAH compounds (Supelco, Mississauga, Ontario) was added to the sample matrix to assess loss in the extraction and sample workup.

For pesticide samples, a surrogate mixture of tetrachloro-m-xylene and dibutyl-chlorendate (Supelco) was used. Native organo-chlorine compounds used for GC/ECD quantitation were purchased from Hewlett-Packard (Mississauga, Ontario). For these analysis, a d4-1,4-dichlorobenzene internal standard (Supelco) was also used. Phenol compounds were purchased from Supelco. PCB native compounds and a Aroclor 1242, 1248 and 1254 mixtures were obtained from Ultrascience (Kingstown, RI).

Standard Reference Materials and Split samples

Eight reference materials: four reference marine sediments, one creosote contaminated soil, and three lake sediments were used in the validation. The marine sediments include HS 3, 4 and 5 marine sediments collected from three harbour in Nova Scotia and were purchased from the National Research Council of Canada. The other marine sediment is SRM 1491 purchased from NIST (Gaithersburg, MD) collected from the Chesapeake Bay at the mouth of Baltimore Harbour. The SRS103-100 natural soil matrix is contaminated with creosote and certified for a number of PAH and PCP. It was purchased from Fisher Scientific, Fairlawn, New Jersey. For PCB validation, the Great Lake sediments EC-1 to 3 were from National Water Research Institute, Environment Canada, Burlington. They have PCB as a natural contaminant, but only EC-1 was certified; the other two have provisional values only.

Split samples were from an EPA contract laboratory (Roy F. Weston, REAC, Edison, N. J.). They included one soil contaminated with creosote and four soils with pesticides.

In the spike study, topsoil was collected from Environmental Technology Centre (ETC), Ottawa and air dried. It was then crushed and homogenised in a mortar and pestle and screened to 250-µm mesh size. The ETC soil is a typical urban sandy/loam soil which was previously analysed to make sure no detectable levels of analytes were found. Glass-fibre filter (37-mm) was obtained from Whatman and used as received. Sea sand was obtained from a local yard supply and used as received.

Microwave-Assisted Extraction

An aliquot of soil or sediment material (1-5 g) was weighed in an extraction vessel. In the matrix spike studies, the native analyte mixture was added to the material and allowed *ca.* 1/2 hr for the solvent to evaporate. Prior to extraction, an aliquot of an appropriate surrogate mixture was added. Contents of the vessel was extracted in thirty ml of 1:1 hexane/acetone using full power at 115° C for 10 min. To make sure each vessel received the same amount of microwave energy in each study, there were always six vessels in the microwave oven. After extraction, the sample carousel was removed from the microwave oven and cooled in a water bath for *ca.* half an hour. Solvent loss was checked in a few instance and found to be below 1%. Post extraction manipulations involved drying/filtration through *ca.*1 gm anhydrous sodium sulphate (previously dried at 120° C) on a medium porosity filter paper inside a glass funnel which was pre-washed with 5 mL of acetone/ hexane. Using a glass pipette, the clear supernatant was transferred to the filtration apparatus, collecting the filtrate in a small round bottom flask. The soil was rinsed three times using a 1-mL aliquot of acetone hexane and transferred to the filtering funnel. Finally, the sodium sulphate was rinsed with acetone/hexane. One mL toluene was added to the filtrate as a keeper and the volume reduced by evaporation *in vacuo* to about 1-2 mL. The extract was transferred to a pre-calibrated test tube and made up to volume. An internal standard (d_{14}-terphenyl for GC/MSD or dichlorobenzene for GC/ECD) was added to give a final concentration of 2 µg/ml before analysis.

Sample Cleanup

Sample extract cleanup, if required (judging from the colour of the extract and the chromatogram of the raw extract), was performed by filtering the raw extract through a silica solid phase extractor (SPE, Varian) which removed the very polar compounds from the extract. The analytes of interest were recovered by rinsing with 10 mL of dichloromethane.

A more rigorous cleanup for PAH compounds was performed by silica adsorption chromatography in which the raw extract was fractionated by eluting with hexane to remove the saturated compounds, followed by dichloromethane/hexane to recover the PAH fraction. In either case, the fraction was concentrated by evaporation *in vacuo* and blow-down to a known volume before instrumental analysis.

For PCB in sediment analysis, an acid/base-modified silica column was used to remove easily oxidised background material in the raw extract. Sulphur, if present, was removed by shaking a 1-mL aliquot of the raw extract in an auto-sampler vial with copper filings. The copper was activated by 1 molar hydrochloric acid and washed with acetone before use.

Analysis of extracts

All extracts from spiking experiments were carried out on the GC/MSD system which included a HP 5890 Series II GC equipped with a HP 5973 automatic liquid sampler (ALS) and interfaced directly to a HP 5971A mass selective detector (MSD). A DOS-ChemStation was used as system control and data manipulation. A 30 M HP-1 capillary column (0.2 mm id, 0.3-µm film) was used for separation. Oven temperature used was 40º C for 1 min, heated to 170º C @ 30º/min; to 240º @ 4º/min; to final temperature of 300º @12º/min and held 10 min. Injection volume was 1-µL in the split-less mode with a 0.75 min purge off. Temperature of the injector and the direct interface were maintained at 270º and 290º C respectively. The MSD was operated in linear scan mode. scanning 40-500 amu at *ca.* 1 scan/sec. Tuning was by Auto-tune using PFTBA and electron multiplier voltage was nominally at 1400 V.

In addition to GC/MSD analysis, other GC analyses were also carried out for confirmation or in the case where higher sensitivity was required.

GC-ECD parameters. A 6890 GC equipped with ECD was used for chlorinated compounds. A HP-5MS 30 M (0.32 mm i.d. column with 0.25-µm film) was used. Oven temperature were similar to that of GC/MSD. One µL was injected split-less via an auto-sampler. Injector and detector temperature was 250° and 270° respectively. The GC was operated in constant flow mode in which a 2-mL column flow was maintained at all times.

GC-FID parameters. A 5890 Series II GC was used to supplement the GC/MSD for phenol analysis. A SPB-1 column (30 M*0.53 mm i.d. with 1.5-µm film) was used. Oven temperature was 50° for 1 min and heated to 250° at the rate of 10°/min. One µL was injected split-less via an auto-sampler. Injector and detector temperature was 250° and 280° respectively. The GC column flow was nominally 5 mL per min.

Prior to injection, an internal standard of d_{14}-terphenyl was added to give a final concentration of 2 µg/mL. For PCB and pesticides, 1,4-dichlorbenzene was used instead. Quantitation was based on the internal standard method. A 6-point calibration curve was constructed initially covering the range of 0.2-10 µg/mL. Daily calibration was by injecting a 2.5 µg/mL standard. Results were not corrected for surrogate recovery. Reporting was by means of the custom reporting feature of the MSD software in which the target, confirmation ions, area responses and all pertinent information were extracted and formatted as an Excel spreadsheet.

RESULTS AND DISCUSSION

Using a mixture of 41 compounds in the EPA525 covering several classes of environmentally important pollutants, calibration and optimisation of the GC/MSD were carried out initially. In addition to the native compounds, surrogate standards of 4 deuterated PAH plus an internal standard of d_{14}-terphenyl was also monitored (Table 1). The total ion chromatogram (TIC) of 46 compounds are shown in Figure 1. Separation on the HP-1 column was excellent under the GC condition given above. The only native analytes that were not resolved were a tetrachloro-PCB isomer/heptachlor pair at 18.2 min and an octachloro-PCB isomer/methoxychlor at 26.0 min. Each peak represents 2.5 ng/µL (ppm) with the exception of pentachlorophenol at 2.0 ng/µL. Peak shape and sensitivity of the full scan analysis was good. Calibration was conducted using a series of six standards at concentrations of 0.2, 0.5, 1.0, 2.5, 5.0 and 10 ng/µL. The curves were found to be linear with a correlation coefficient of 0.99 for all compounds on the list; repeatability were routinely better than 10 % RSD.

For matrix spiking studies, three common matrices (soil, sand and glass fibre filter) were chosen to represent typical scenarios in which the samples are presented to the analysts responding to emergency situations. The spiking solution was added to each matrix in the extraction vessel and allowed to stand for 30 min. The surrogate mixture was then added and extraction proceeded as described. Replicates of 5 samples and one blank were conducted; results are summarised in Table 2, showing excellent recoveries for different classes of compounds with reproducibility typically in the 10% RSD range. The only exception being several of the early eluting base-neutral compounds in which the loss could be attributed to any of several steps of the entire process: evaporation loss during matrix spiking, incomplete extraction or post extraction loss from transfer/filtration and concentration of the raw extract. The post-extraction workup loss was addressed by carrying an aliquot of spiking solution in 30 mL hexane/acetone through the filtration/concentration process. The results are presented in the last column of Table 2, in which it can be seen the volatile species in the spiking mixture were recovered at about 80% with reproducibility of 10% RSD. Extraction loss was studied by adding an aliquot of PAH spiking solution into solvent in the extraction vessel and irradiated by microwave. The raw extract was analysed directly without any further sample preparation. Results show there was complete recovery for all PAH compounds. These experiments demonstrate that low recoveries of early eluting compounds are most likely due to evaporation during the spiking step, and not due to the degradation or evaporation loss from the high temperature/pressure microwave-assisted extraction process.

PAH analysis of reference and split samples

Results of MAP extractions of SRS-100 soil, HS sediments and SRM1491 sediment are summarised in Tables 3 to 5. Table 6 presents comparison to the consensus value for the split sample which is contaminated with creosote. Recovery on the whole was satisfactory. The much lower results of naphthalene in the split sample are attributed partly to evaporative loss from this wet sandy matrix, which has been in storage for about 3 years.

PCB analysis of spiked and reference materials

ETC soil fortified with native Aroclor mixtures of 1242/1254/1260 to a 0.6 µg/g level was extracted and analysed by GC/ECD. Recovery was in the 88% range with a reproducibility of 2% RSD. Analytical data of FC 1-3 are plotted in Figure 2. Excellent recovery was noted with 3-7% RSD.

Pesticides and phenol analysis of spiked and split sample materials

ETC soil samples fortified with 0.5 µg/g of each pesticide was evaluated with respect to recovery and degradation loss; results are presented in Table 7. Recoveries were between 85-125%, with reproducibility of about 10% (n=3) with the exception of endrin. The 155% recovery was probably due to interference in the GC/ECD chromatogram. Figure 3 graphically illustrates the comparative data on a split sample. Apart from DDE/dieldrin (only 50% of the consensus value), there is good agreement between the two laboratories.

Methylparathion was analysed in triplicates for 2 split soil samples (FR3-2042 and FR2-2042) : we found 1.08 and 0.72 µg/g of these phosphorus-based pesticides in the soil and are in good agreement with the RFAC laboratory values of 0.97 and 0.68 µg/g respectively.

In the course of studies involving spiked and real samples, degradation of analytes were carefully monitored, especially that of endrin which was known to degrade to endrin epoxide/ endrin ketone and DDT to DDE/DDD when in contact with hot injection ports or subjected to high temperature conditions during sample workup. A study was carried out by adding solutions of DDT and endrin to acetone/hexane in extraction vessels and subjected to the usual 10-min extraction.

another one to a 20-min extraction and as a control, without receiving any irradiation. The resulting TIC chromatograms are illustrated in Figure 4. From the control (no microwave), normal degradation from our GC system was found to be about 11.8% for endrin in the form of endrin ketone and 9% for DDT in the form of DDD. Results for the 10 min microwave treatment were actually less at 8.8% and 4.8% for endrin and DDT; while 20-min irradiation resulted in degradation of 10.9% and 5.6% for the pair. An acceptable level of degradation in the heated inlet of a GC system alone is normally 10%. Considering the data reflected the extent of degradation from the entire process of extraction and analysis, microwave-assisted extraction clearly did not lead to the formation of degradation products.

Table 8 shows recovery of phenol mixture spiked into ETC soil to the equivalent of 2.56 µg/g level. Recoveries were from 85-112%. Due to their relatively polar nature, phenol analysis was usually difficult without derivatisation. In general, we did not experienced any problem of phenol analysis. MRI reported phenol recoveries in the range of 70%, and that of 2,4-dinitrophenol and 2-methyl-4,6-dinitrophenol were very poor. Although we did not use the same phenol compounds in our spiking mixture, we found good recovery of 85% for 2,4-dinitrophenol which means no phenol degradation took place. The low recovery reported by MRI for dinitrophenol may be due to the matrix of the particular soil they used for spiking.

CONCLUSION

A variety of simulated samples as well as real matrix materials have been analysed as an independent evaluation of the MAP extraction process. Recoveries in all cases were satisfactory, problems encountered usually are in the actual instrumental analysis due to the complicated nature of the matrix. Relatively low recoveries are all caused by volatility of particular compounds and likely due to sample workup loss, and not due to the extraction process. Studies carried out using the thermally labile endrin and DDT showed MAP did not cause in more degradation even using more rigorous conditions as prescribed in the proposed method. With a commercially available MAP extractor such as CEM MES-1000, up to 12 samples can be extracted in about one and a half hr (extraction plus cooling of the vessels) while taking up much less space. The rapid sample turn around time is a clear advantage over traditional Soxhlet technique. Other advantages are more precise control over extraction conditions with comparable or better recovery and reduced solvent usage.

ACKNOWLEDGEMENT

The split samples were provided by Mr. Yi-Hua Lin and Vinod Kansal, Roy Weston Laboratory "REAC", Edison, NJ. Maria Llompart conducted some of this work as part of her Ph. D. thesis (Universidad de Santiago de Compostela, Spain).

REFERENCES

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

2. J. R. J. Paré, U.S. Patent 5,338,557, August 1994 (and various international counterparts); US Patent 5,458,557, October 1995 (and various international counterparts).

3. J. R. J. Paré, U.S. Patent 5,377,426, January 1995 (and various international counterparts); U.S. Patent 5,519,947, May 1996 (and various international counterparts).

4. J. R. J. Paré, J. M. R. Bélanger and S. S. Stafford, *Tr. Anal. Chem.* **13** (1994) 176.

5. L. G. Croteau, M. H. Akhtar, J.M. R. Bélanger and J. R. J. Paré, *J. Liquid Chromatogr.* **17** (13) (1994) 2971.

6. K. Ganzler and A. Salgo, *J. Chromatogr.* **371** (1986) 299.

7. F. E. Onuska and K. A.Terry, *Chromatographia* **36** (1993) 191 .

8. F. E. Onuska and K. A.Terry, *J. High Resol. Chromatogr.* **18** (1995) 417.

9. J. R. Fish and R. Revesz, "Microwave Solvent Extraction of Chlorinated Pesticides from Soil" Presented at the Pittsburgh Conference, New Orleans, LA, March, 1995.

10. E. Hasty and R. Revesz. American Laboratory 2 (1995) 66 .

11. T. R. Steinheimer, *J. Agric. Food Chem.* **41** (1993) 588.

12. S. J. Stout, A. R. da Cunha, and D. G. Allardice, *Anal. Chem.* **68** (1996) 653.

13. V. Lopez-Ávila, R. Young, J. Benedicto, P. Ho, R. Kim and W. F. Beckert, *Anal. Chem.* **67** (1995) 2096.

14. V. Lopez-Ávila, R. Young, W. F. Beckert, *Anal. Chem.* **66** (1994) 1097.

15. V. Lopez-Ávila, J. Benedicto, C. Charan, R.Young and W. F. Beckert, *Environ. Sci. Technol.* **29** (1995) 2709.

16. This work is taken in part from an extensive study to be published elsewhere.

Tables

1. Target analytes list
2. Recovery of 41 compounds spiked onto filter, soil and sand; post extraction loss
3. PAH recovery of SRS-103-100 (Fisher soil)
4. PAH recovery of HS marine sediment materials
5. PAH analysis of a real soil contaminated with creosote from REAC
6. PAH recovery of SRM1941 marine sediment
7. Pesticides matrix spike recovery study
8. Phenols matrix spike recovery study

Figures

1. Chromatogram of 41 native, 4 surrogate compounds and d_{14}-terphenyl internal standard.
2. PCB recovery of AS Great Lake sediment materials; EC-2 and EC-3 are provisional values only; RSD from 3-7 % (n=3).
3. Pesticide analysis of a real soil obtained from REAC
4. Pesticide degradation study. Top TIC: Endrin-DDT standard, no microwave; middle TIC: 10 min microwave @ full power; bottom TIC: 20 min microwave @ full power. Peak @ 21.9 min; Endrin; 22.6 min, DDD; 24.1 min, DDT; 25.6 min, Endrin ketone.

Table 1

Base Neutral and Acid	**PAH**		**Organo-chlorines**
Hexachloropentadiene	Acenapthylene		PCB-1
Dimethylphthalate	***d10-Acenaphthene***	Surrogate	PCB-2
Diethylphthalate	Fluorene		Hexachlorobenzene
Di-n-butylphthalate	***d10-Phenanthrene***	Surrogate	Simazine
Butylbenzylphthalate	Phenanthrene		Atrazine
bis(2-Ethylhexyl)adipate	Anthracene		Lindane
bis(2-ethylhexyl)phthalate	Pyrene		PCB-3
	Benzo(a)anthracene		Alachlor
Pentachlorophenol	***d12-Chrysene***	Surrogate	Heptachlor
	Chrysene		PCB-4
	Benzo(b)fluoranthene		Heptachlor epoxide
	Benzo(k)fluoranthene		PCB-5
	Benzo(a)pyrene		gamma-Chlordane
	d12-Perylene	Surrogate	alpha-Chlordane
	Indeno(123-cd)pyrene		trans-Nonachlor
	Dibenzo(ah)anthracene		PCB-6
	Benzo(ghi)perylene		Endrin
			PCB-7
	d14-Terphenyl	Internal standard	Methoxychlor
			PCB-8

Table 2

Order of elution		FILTER		SAND		SOIL		FILTRATION-EVAPORATION LOSSES	
		% Recovery	RSD %	% Recovery	RSD %	% Recovery	RSD %	% Recover	RSD %
1	**hexachloropentadiene**	7	85 7	54	24 0	29	34 0	79	9 8
2	**dimethylphthalate**	76	17 8	81	5 4	11	7 4	85	8 2
3	**acenapthylene**	31	60 0	73	12 5	86	13 4	77	9 1
5	**PCB-1**	46	45 2	89	8 7	99	10 1	81	8 6
6	**diethylphthalate**	87	13 6	37	7 4	119	10 0	97	7 7
7	**fluorene**	65	23 2	88	9 1	109	10 2	79	9 8
8	**PCB-2**	79	12 7	95	8 1	113	9 4	85	8 7
9	**hexachlorobenzene**	85	9 7	93	5 6	108	9 3	87	9 5
10	**simazine**	101	7 5	105	6 8	135	6 7	95	11 1
11	**atrazine**	102	9 3	107	6 7	121	7 6	98	10 9
12	**pentachlorophenol**	68	17 6	77	15 6	56	48 3	82	10 7
13	**lindane**	92	11 2	97	5 4	108	9 0	91	8 9
15	**phenantrene**	82	8 5	88	8 5	115	10 6	81	9 7
16	**anthracene**	83	12 1	93	7 7	108	11 4	87	11 9
17	**PCB-3**	94	8 9	102	5 2	119	7 1	84	8 0
18	**alachlor**	112	8 8	114	4 0	132	8 4	104	8 1
19	**heptachlor**	116	12 9	118	6 6	138	10 0	111	10 5
20	**di-n-butylphthalate**	134	10 5	115	7 2	116	8 7	109	11 5
21	**PCB-4**	106	11 7	112	7 1	114	8 9	105	11 7
22	**hepachlor epoxide**	98	9 7	99	5 3	114	8 1	93	8 4
23	**PCB-5**	106	11 3	112	5 7	127	7 0	105	11 4
24	**gamma-chlordane**	100	11 8	102	7 2	112	6 9	99	11 9
25	**pyrene**	105	9 5	110	7 5	145	8 2	101	11 6
26	**alpha-chlordane**	100	11 8	102	7 2	111	8 4	99	11 9
27	**trans-nonachlor**	103	8 0	103	8 4	112	6 8	99	11 4
29	**PCB-6**	95	8 7	95	4 6	72	3 0	99	5 5
30	**Endrin**	132	10 2	119	8 7	89	4 1	120	6 3
31	**butylbenzylphthalate**	119	9 3	111	5 9	95	2 0	111	5 9
32	**bis(2-ethylhexyl)adipate**	117	7 8	103	12 9	101	1 6	113	3 5
33	**benzo(a)anthracene**	92	10 7	98	12 1	78	2 3	99	4 7
35	**chrysene**	92	10 7	98	12 1	78	2 1	99	4 7
36	**PCB-7**	92	9 4	90	6 8	69	2 3	99	6 1
37	**methoxychlor**	106	10 9	96	7 8	74	5 5	104	4 9
38	**PCB-8**	92	7 9	89	5 9	68	11 1	99	4 2
39	**bis(2-ethylhexyl)phthalate**	122	11 4	110	7 7	91	4 8	118	5 6
40	**benzo(b)fluoranthene**	100	11 8	99	16 5	75	2 6	100	5 7
41	**benzo(k)fluoranthene**	93	8 9	95	17 9	65	4 2	92	3 9
42	**benzo(a)pyrene**	88	11 1	79	14 9	66	5 1	93	6 9
44	**indeno(123-cd)pyrene**	95	6 5	99	10 2	71	15 5	79	16 5
45	**dibenzo(ah)anthracene**	98	15 1	95	18 4	74	7 2	87	5 4
46	**benzo(ghi)perylene**	93	14 2	96	20 2	70	5 2	91	7 7
	SURROGATES								
4	**d10-acenaphthene**	83	12 6	85	4 2	110	15 1	76	12 8
14	**d10-phenanthrene**	93	9 4	94	4 5	135	12 6	84	10 2
34	**d12-chrysene**	90	7 9	96	2 6	81	6 1	93	5 5
43	**d12-perylene**	88	9 9	79	5 3	72	9 4	88	6

Table 3

	certified values ppm	conf interval ppm	recovery %	RSD %
naphthalene	34.8	30.6-39.0	102	16.0
acenaphthylene	16.5		106	7.7
fluorene	443	398-488	94	7.1
pentachlorophenol	1425.4	1109-1741.7	114	5.7
phenanthrene	1924.9	1716.2-2133.6	106	8.7
anthracene	431.1	389.1-473.2	105	8.0
pyrene	1075.1	933.9-1216.3	104	7.1
benzo(a)anthracene	264	240.8-288	82	8.9
chrysene	316.1	286.5-345.8	95	8.3
benzo(b)fluoranthene	114.7		70	13.0
benzo(k)fluoranthene	63.7		111	10.2
benzo(a)pyrene	96.5	84.7-108.3	83	10.1
indeno(123-cd)pyrene	31.9	23.9-40	102	10.3
dibenzo(ah)anthracene	14.2		67	22.1
benzo(ghi)perylene	25.5		90	11.8
Surrogate	spiked level, ppm			
d10-acenaphthene	1		109	15.4
d10-phenanthrene	1		107	16.1
d12-chrysene	1		92	4.3
d12-perylene	1		97	5.0

note: PAH without confidence intervals are not certified

Table 4

	HS 3 marine sediment			HS 4 marine sediment			HS 5 marine sediment		
	Certified value *ppm*	Conf interval *ppm*	Recovery %	Certified value *ppm*	Conf interval *ppm*	Recovery %	Certified value *ppm*	Conf interva *ppm*	Recovery %
naphthalene	9	8 3-9 7	61	0.15	*	54	0.25	0.18-0 32	76
acenapthylene	0.3	0.2-0.4	199	0 15	*	82	0.15	*	107
acenaphthene	4.5	3.0-6.0	80	0.15	*	63	0.23	0.13-0.33	61
fluorene	13.3	10.2-16 4	58	0 15	*	81	0.4	0.3-0.5	63
phenanthrene	85	65-105	87	0 68	0 6-0 76	81	5 2	4.2-6.2	72
anthracene	13.4	12 9-13.9	48	0 14	0 07-0 21	108	0.38	0.23-0.53	84
fluoranthene	60	51-69	91	1 25	1.15-1.35	84	8.4	5.8-10	81
pyrene	39	30-48	86	0 94	0 82-1.06	85	5.8	4-7 6	69
benzo(a)anthracene	14.6	12.6-16.6	78	0 53	0.47-0.58	78	2.9	1.7-4.1	53
chrysene	14.1	12.1-16.1	91	0.65	0.57-0 73	84	2 8	1.9-3.7	76
benzo(b)fluoranthene	7.7	6.5-8.9	101	0.7	0 55-0 85	84	2	1.0-3.0	84
benzo(k)fluoranthene	2.8	0.8-4.8	275	0.36	0.31-0.41	156	1	0.6-1.4	137
benzo(a)pyrene	7 4	3.0-7.0	74	0.65	0.57-0.73	73	1 7	0.9-2.5	52
indeno(123-cd)pyrene	5 4	4.1-6.7	100	0.51	0.36-0.66	88	1 3	0.6-2	63
dibenzo(ah)anthracene	1.3	0.8-1 8	118	0 12	0.07-0 17	117	0 2	0.1-0.3	125
benzo(ghi)perylene	5	3 0-7 0	99	0.58	0 36-0 80	91	1 3	1-1.6	64

* denotes values not certified

Table 5

	PAH values µg/g (n=4)	RSD %	REAC values µg/g
naphthalene	2.17	12.41	710
2-methylnaphthalene	28.71	3.12	
1-methylnaphthalene	33.18	2.42	
biphenyl	13.44	6.03	
2,6-dimethylnaphthalene	52.99	3.78	
acenaphthylene	16.32	3.10	21
acenaphthene	801.21	5.99	1700
fluorene	789.98	3.35	990
phenanthrene	1627.48	0.65	3300
anthracene	346.01	3.99	360
benzo(a)anthracene	300.38	2.73	310
fluoranthene	1331.69	1.63	1600
pyrene	1037.71	2.95	1100
chrysene	293.20	3.35	320
benzo(b)fluoranthene	152.00	3.84	140
benzo(k)fluoranthene	127.74	3.63	130
benzo(e)pyrene	87.61	3.92	
benzo(a)pyrene	128.33	3.89	110
perylene	35.26	4.26	
indeno(123-cd)pyrene	63.90	4.97	25
dibenzo(ah)anthracene	17.29	6.85	
benzo(ghi)perylene	42.72	6.91	20

Table 6

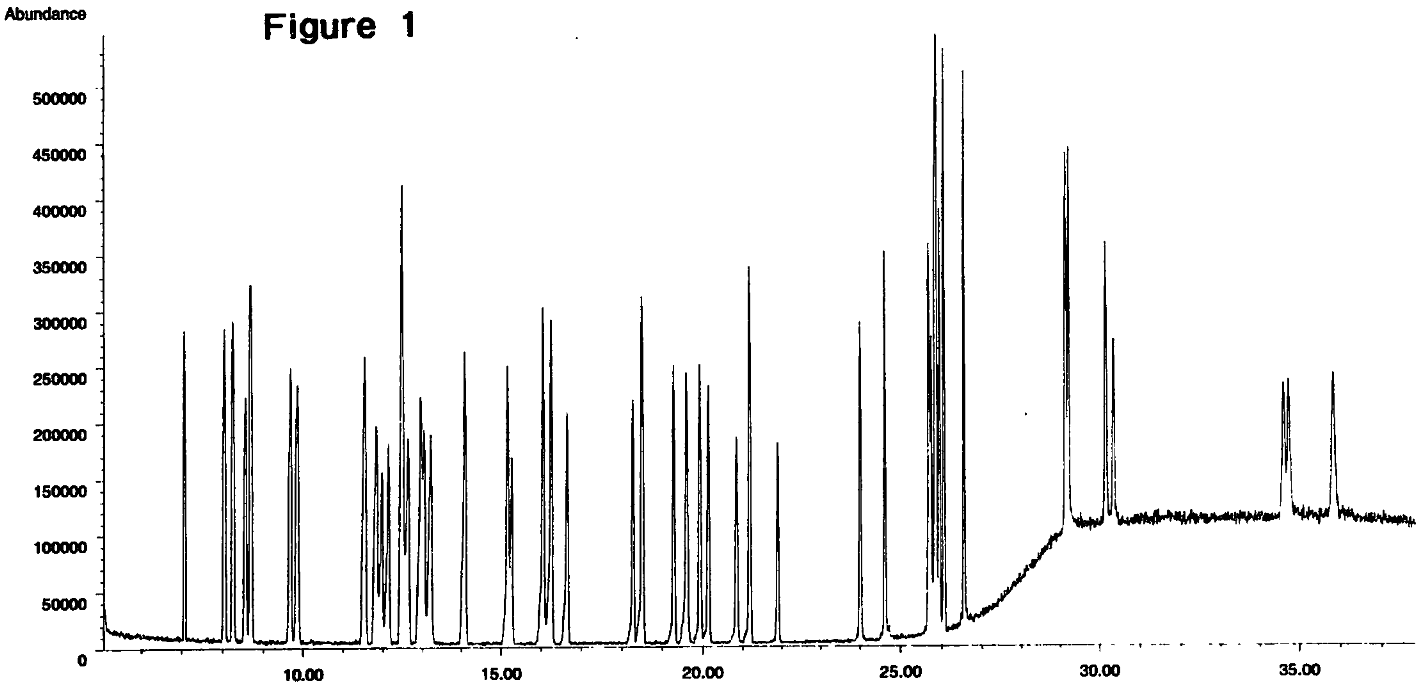
	certified values	% Recovery
Naphthalene	1.01	97.4
Fluorene	0.1	100.0
Phenanthrene	0.49	102.0
Fluoranthene	0.98	116.7
Pyrene	0.81	97.3
Benz(a)anthracene	0.43	89.8
Chrysene	0.38	130.3
Benz(b)fluoranthene	0.74	95.8
Benz(k)fluoranthene	0.36	130.2
Benz(e)pyrene	0.55	81.0
Benzo(a)pyrene	0.63	76.0
Perylene	0.45	72.4
Indeno(123-cd)pyrene	0.5	126.0
Dibenz(ah)anthracene	0.11	78.7
Benz(ghi)perylene	0.53	85.2

Table 7

	% Recovery	RSD %
a-BHC	96	3
b-BHC	126	8
g-BHC	103	4
d-BHC	115	5
Heptachlor	131	5
Aldrin	103	2
Heptachlor epoxide	126	9
Endosulfan 1	122	5
DDE+Dieldrin	118	4
Endrin	155	12
Endosulfan 2	116	5
DDD	95	7
Endosulfan aldehyde	103	9
Endosulfan sulphate	122	5
DDT	118	5
Methoxychlor	119	6

Table 8

	Recovery %	RSD %
2-chlorophenol	101	4.5
m-+*p*-cresol	106	3 1
2,4-dimethylphenol	98	2.9
2,6-dichlorophenol	105	3.9
2,4,5-trichlorophenol	108	3.8
2,4-dinitrophenol	85	13.2
2,3,4,6-tetrachlorophenol	112	4.7
dinoseb	95	12.7



Abundance
Figure 1
500000
450000
400000
350000
300000
250000
200000
150000
100000
50000
0
10.00
15.00
20.00
25.00
30.00
35.00

Figure 2

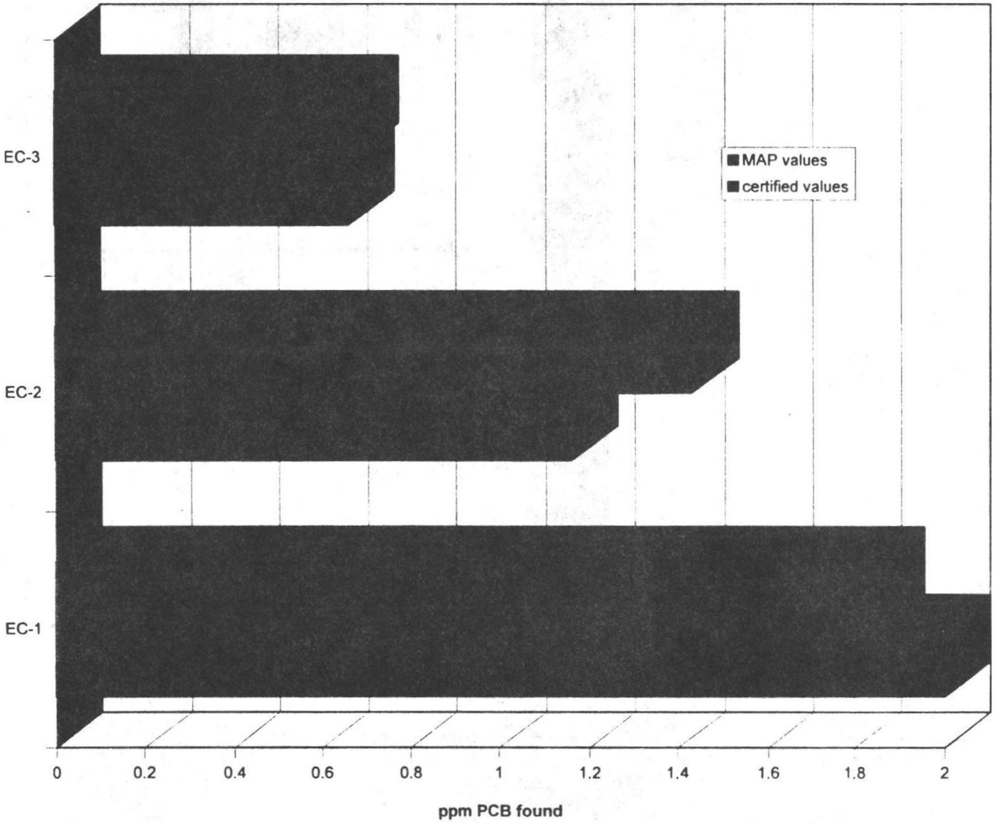

EC-3
EC-2
EC-1
MAP values
certified values
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
ppm PCB found

Figure 3

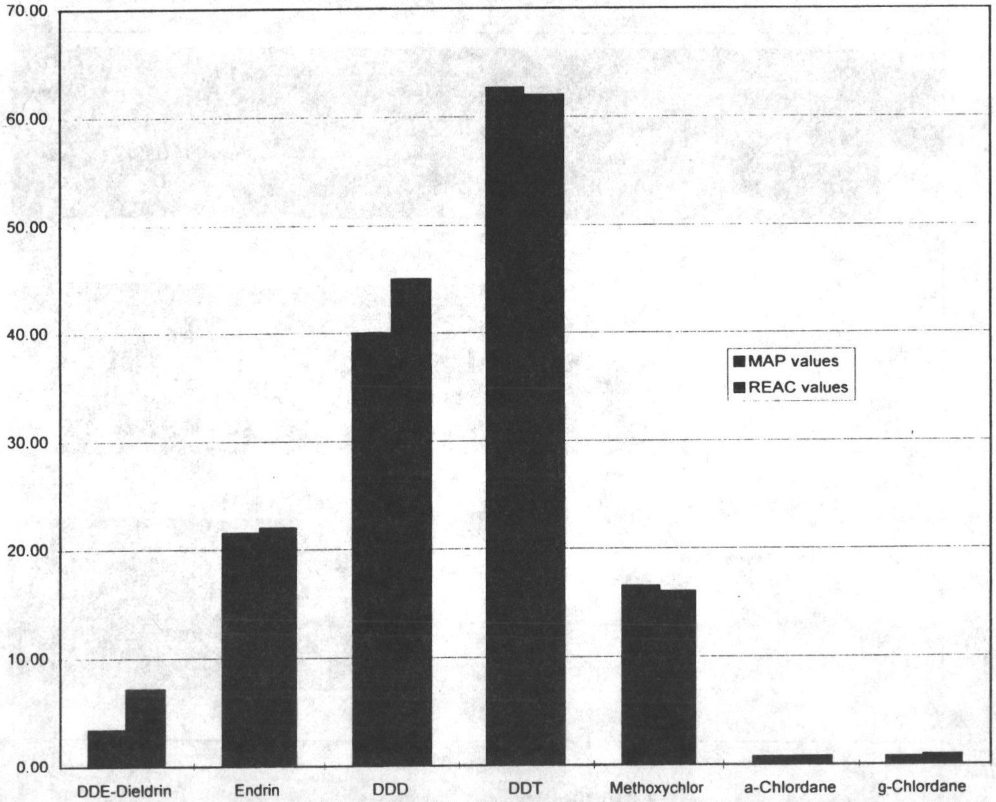
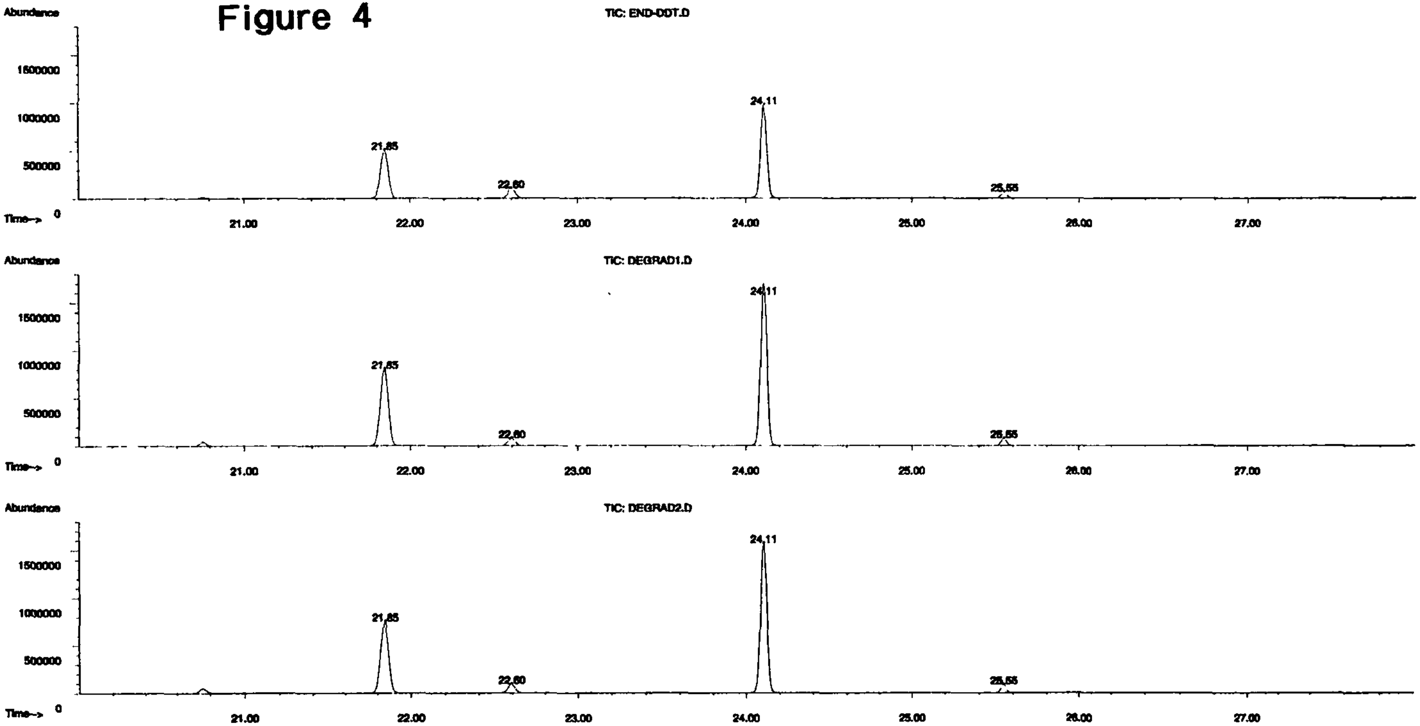

70.00
60.00
50.00
40.00
30.00
20.00
10.00
0.00
DDE-Dieldrin
Endrin
DDD
DDT
Methoxychlor
a-Chlordane
g-Chlordane
■ MAP values
■ REAC values

Figure 4



Abundance
TIC: END-DDT.D
1500000
1000000
500000
0
Time-->
21.00
22.00
23.00
24.00
25.00
26.00
27.00
21.85
22.60
24.11
25.55
Abundance
TIC: DEGRAD1.D
1500000
1000000
500000
0
Time-->
21.00
22.00
23.00
24.00
25.00
26.00
27.00
21.85
22.60
24.11
25.55
Abundance
TIC: DEGRAD2.D
1500000
1000000
500000
0
Time-->
21.00
22.00
23.00
24.00
25.00
26.00
27.00
21.85
22.60
24.11
25.55

A Summary of the Experience Gained from the Emergencies Science Division Role in the Remediation Effort at Canadian Coast Guard Facilities in Newfoundland

P. Lambert [1], M. Goldthorp [2], F. Ackerman [1], M. Fingas [1]

1. Emergencies Science Division, Environmental Technology Centre, Environment Canada, Ottawa, Ontario.
2. Goldthorp Consulting, Nepean, Ontario.

Abstract

The Emergencies Science Division (ESD), of Environment Canada (EC), undertook a project on behalf of the Canadian Coast Guard (CCG), Newfoundland Region, to carry out a number of environmental site investigations at CCG facilities throughout Newfoundland and Labrador.

The project was a comprehensive survey of Lightstations and Marine Navigation Sites for chemical contamination. These included; motor oils, fuels, Polycyclic Aromatic Hydrocarbons (PAH), Polychlorinated Biphenyls (PCB), and metals, most notably lead, zinc and mercury. Each investigation included on-site examination and screening, field testing of the samples, and subsequent laboratory analysis of a portion of the samples. Field screening for fuel and oil contamination was carried out using a portable flame ionization detector. Immunoassay test kits were used in the field to measure PAH, PCB, and total petroleum hydrocarbon (TPH). A portable X-ray fluorescence meter was employed for on-site screening and field measurements of metals. To ensure impartiality, laboratory analysis was performed by an independent contract laboratory employing standard methodologies.

This paper will present an overview of the project with a discussion on the environmental fate of the principle contaminants of concern and a review of the methodologies and instruments selected for the project. With regard to the analytical segment, an emphasis is placed on the performance of the equipment and a comparison of the field results to those results from laboratory analysis.

Objectives

The Canadian Coast Guard Marine Navigation Services, and Rescue and Environmental Response sections have co-ordinated their efforts for the purpose of addressing the environmental concerns at Lightstations and Marine Navigation Sites throughout Newfoundland and Labrador. The Emergencies Science Division of Environment Canada was contracted to work with the Canadian Coast Guard to provide scientific and analytical support. In compliance with the format and terms used in the Canadian Council of Ministers of the Environment (CCME) report, *National Guidelines for*

Decommissioning Industrial Sites (CCME, 1991a), the Emergencies Science Division was charged with the responsibility to carry out, in full or in part, the Phase II - Reconnaissance Testing Program, Phase III - Detailed Testing Program, and Phase IV-Preparation of Decommissioning and Cleanup Plans.

Introduction

Within all sections of the Federal Government, measures have been taken to ensure that government facilities are in compliance with appropriate health and safety guidelines, and environmental legislation. The Canadian Coast Guard, Newfoundland Region has a well established and ongoing program to address these concerns at their Lightstations and Marine Navigation Sites throughout Newfoundland and Labrador. The approach taken by the agency is in accordance with the format outlined in the CCME report, *National Guidelines for Decommissioning Industrial Sites* (CCME, 1991a). The Newfoundland Region of Marine Navigational Services manages the program and, in 1993, carried out preliminary site assessments identifying potential areas and contaminants of concern. In 1994, the Environmental Services Sector of Public Works and Government Services Canada was commissioned to augment and document existing CCG site assessments From this, a report compiling information relating to environmental concerns was completed, taking the form of a Phase I, *Environmental Audit: Baseline Site Assessments* (Public Works and Government Services Canada, 1995a and 1995b).

The Emergencies Science Division of Environment Canada was contracted by the Marine Navigation Services, Newfoundland Region of the Canadian Coast Guard, Department of Fisheries and Oceans to carry out the Phase II and Phase III Testing Programs and assist with the Phase IV- Preparation of Decommissioning and Cleanup Plans of specific CCG facilities identified in the Phase I property assessment.

The project provides a comprehensive survey of Canadian Coast Guard (Newfoundland Region) Lightstations and Marine Navigation Sites for identification and quantification of environmental (chemical) contaminants in the soil and delineation of the extent of the affected regions. These contaminants include: waste oils, assorted types of fuels, Polycyclic Aromatic Hydrocarbons, Polychlorinated Biphenyls, and metals such as mercury, lead, and zinc. In previous work, the CCG carried out an assessment of the risks associated with the most prevalent chemical contaminants, and established a remediation criteria along with developing a technology suitable for soil remediation at CCG facilities. With the intention of expanding on the measures set up by CCG with the Phase IV portion of the program, site-specific recommendations regarding the requirements for further remediation activities were prepared.

Procedures

Project Procedure

A total of 77 sites, including Lightstations and Marine Navigation Sites, were examined. Of these, 56 were Lightstations and 21 were Marine Navigation Sites. The Canadian Coast Guard had previously prepared Phase II/III site investigations and had prepared to carry out remediation activities at ten sites located throughout the province during the spring and summer of 1995. However due to resource limitations, only eight sites were addressed by CCG One of the eight locations was not included in the original plan of ten sites, but was added at,a later date. Clean-up operations, at this site, were based on the investigation by ESD staff. In total, 67 sites required environmental site investigations, and ten required confirmatory investigations for remediation operations. Of the 67 environmental site investigation sites, two had undergone remediation operations the previous year and required confirmatory sampling

Numerous logistical challenges presented themselves with regard to this project as a result of the varied and different objectives to be achieved. The approach taken by ESD was to work on an independent but overlapping time schedule with the CCG group. The geographical locations of sites about the province were loosely divided up into a number of sections, based on their proximity to the locations which were to be dealt with by CCG, and road accessibility. ESD staff, using their own departmental resources, carried out work at the sites in a geographical area until required to coordinate with CCG at a site slated for remediation. Upon completion of the joint work, ESD continued to work independently until the following mobilization date was established and a schedule set for the next joint effort. Arrangements for travel to and from remote sites varied from site to site and included CCG helicopter, commercial airlines, and/or chartered boat.

Field operations began in April 1995 and were completed at the beginning of September 1995 Generally the areas were completed in the following manner: the Burin Peninsula, the northern Avalon Peninsula, Notre Dame Bay sites, the Bonavista Bay and Trinity Bay sites, the southern Avalon Peninsula, sites along the south coast of Newfoundland, west coast locations from Port-aux-Basques to Lobster Cove Head, the Northern Peninsula locations, and finally sites in Labrador and in the Strait of Belle Isle. Table 1 provides a detailed list of the sites summarizing the investigation dates and contaminants addressed over the course of the project. For the purposes of continuity, the areas of concern for each site are listed using an alpha-numeric character, the same format used in the Phase I report.

Table 1: Lightstation and Marine Navigation Sites

Site Location	Date of Investigation (1995)	Areas of Concern	Potential Contaminants
Allan's Island Lightstation	May 22	A - Historical buildings B - Pole mounted transformer	Metals PCB
Argentia Vessel Tracking System	August 1	A - Fuel storage B - Helicopter fuel drum storage	TPH. metals
Bacalhao Island Lightstation	June 27	A - Fuel drum storage B - Equipment building	Petroleum Petroleum
Baccalieu Island Lightstation	April 20	A - West side of generator building E - Stove oil fuel storage H - Drum storage on boardwalk	Petroleum Petroleum Petroleum
Bear Cove Point Lightstation	June 20	A - Historical fuel storage B - Historical buildings C - Pole mounted transformer	Petroleum Metals PCB
Bell Island Lightstation	June 20	A - Historical fuel storage B - Dwelling fuel storage C - Buildings D - Pole mounted transformer	Petroleum Petroleum Metals PCB
Belle Isle (NE) Lightstation	August 23	A - Fuel storage tanks B - Old fog alarm building C - Northwest of generator building, waste oil dump site D - Waste disposal site	Petroleum Petroleum, metals Petroleum. metals Petroleum, metals, general debris
Belle Isle (SW) Lightstation	August 19 to 27	A - Fuel storage B - Old fog alarm building C - Waste disposal site	Petroleum Petroleum. metals Petroleum. metals. general debris
Boar Island Lightstation	July 10	A - Old fuel tank area & fog horn area B - New fuel tank area C - Old drum storage at helicopter pad D - Stain in front of generator building E - Old drum storage trench F - Area south of dwelling G - Area north of dwelling H - Old dwellings	Petroleum, PCB. metals Petroleum Petroleum Petroleum. PCB Petroleum, Petroleum. metals, PCB Petroleum, metals, PCB Metals
Burnt Point Lightstation	June 12	A - Vehicle ramp C - Debris along west side of road	Petroleum Petroleum
Cabot Island Lightstation	June 29	B - Waste batteries west of generator bldg. C - Waste incinerator site D - Fuel storage tanks	Metals Petroleum
Cain's Island Lightstation	July 17	A - Equipment building B - Historical dwelling C - Fuel drum storage area	Petroleum. metals, PCB Metals Petroleum
Camp Island Lightstation	August 16 and 21	A - Old fuel storage tanks B - Old oil and battery dump	Petroleum Petroleum, metals
Cape Anguille Lightstation	July 15	A - Lighthouse B - Old generator building C - Fuel storage D - Pole-mounted transformer	Metals Petroleum. metals, PCB Petroleum PCB
Cape Bauld Lightstation	July 22	A - Former fuel storage area C - Waste disposal site	Petroleum Petroleum, metals, PCB
Cape Bonavista Lightstation	June 13	Light tower	Lead
Cape Bonavista - Old Loran A Site (Abandoned)	June 17	Fuel storage Electrical equipment	TPH, PCB

Site Location	Date of Investigation (1995)	Areas of Concern	Potential Contaminants
Cape Bonavista T & E Remote Site	June 13	Fuel storage for emergency generator Lead based paints	TPH, metals
Cape Norman Lightstation	July 21 and August 30	Area of old foundation	Asbestos, metals, petroleum
Cape Pine Lightstation	June 22	A - Fuel storage B - Fuel storage C - Fuel storage D - Fuel storage E - Fuel storage	Petroleum, metals Petroleum, metals Petroleum Petroleum, metals Petroleum
Cape Pine T & E Remote Site	June 22	Underground fuel storage tank	TPH
Cape Race Lightstation	June 23	Additional sites (A - H) that were not sampled during 1994 Radio station U/G tank, coil hut, coal ash pile, garbage burn, buried transformers, leaky pole mounted transformer, mercury near tower	TPH, metals, PAH, PCB, Mercury Confirmatory sampling of TPH
Cape Race Loran C Site	June 23	Garage drainage Historical fuel storage Waste disposal site	TPH, metals, priority pollutants
Cape Race T & E Remote Site	June 23	Historical fuel storage	Confirmatory sampling of TPH
Cape Ray Lightstation	July 15 and 18	A - Light tower B - Old dwelling & cable station C - Old generator building D - Work shed E - Interim equipment building F - Pole-mounted transformer G - Historical buildings	Mercury, metals Mercury, metals Petroleum, PCB, metals Petroleum, metals Petroleum PCB metals
Cape St Francis Lightstation	May 30	A - Coal ash disposal	TPH, metals, PAH
Cape St Mary's Lightstation	August 2	A - Fuel storage B - Waste disposal C - Light tower D - Pole-mounted transformer	Petroleum Metals, PCB Mercury, metals PCB
Cape Spear Lightstation	May 29	A - Fuel storage B - Fuel storage C - Light tower	Petroleum, metals Petroleum Mercury, metals
Cartwright T & E Radio Station	August 21	Old generator building	TPH
Channel Head Lightstation	July 13	A - Historical fuel storage B - Historical buildings C - Pole-mounted transformer	Petroleum Metals PCB
Comfort Cove Operations T & E Radio Station	June 3	Fuel storage Metal debris and oil staining Pesticide use	TPH, metals, pesticides
Comfort Cove Transmitter T & E Radio Station	June 4	Historical fuel storage Drum storage Pesticide use	TPH, metals, pesticides
Dawson Point Lightstation	July 5	A - Fuel storage tanks B - Storage shed and drum storage C - Dwelling fuel storage D - Battery disposal E - Buildings F - Generator building	Petroleum Petroleum Petroleum Metals, PCB Metals Petroleum, PAH
Ferolle Point Lightstation	July 20 and August 30	Light is mercury bath type	Mercury

Site Location	Date of Investigation (1995)	Areas of Concern	Potential Contaminants
Ferryland Head Lightstation	July 28	A - Light tower	Mercury, metals
Fort Amherst Lightstation	May 29	A - Fuel storage B - Fuel storage C - Fuel storage	Petroleum Petroleum, metals Petroleum, metals, PCB
Fort Point Lightstation	June 14	A - Fuel storage, keepers residence B - Storage shed	Petroleum Petroleum, solvents
Fortune Head Lightstation	May 22	A - Old garage	Petroleum, metals, PCB
Fortune Head T & E Remote Site	May 22	Underground fuel storage tank	TPH
Fox Harbour T & E and Loran C Site	August 21	A - Hazardous materials storage B - Fuel storage and underground piping C - Fuel drainage line	TPH, metals
Francois Point Lightstation	July 1	A - Winch house B - General fuel drum storage C - Dwelling fuel storage D - Generator fuel storage E - Garbage & battery disposal F - Debris disposal G - Old generator building H - Helicopter fuel storage I - Buildings	Petroleum Petroleum Petroleum Petroleum Metals Metals Metals, PAH, PCB Petroleum Metals
Goose Bay - Old Transmitter Site (Abandoned)	August 5	Metal and construction debris Oil staining Disposal areas Historical fuel storage	TPH, metals, PCB
Green Island (Fortune Bay) Lightstation	July 26	1 - Fuel storage platform 2 - Generator building 3 - Helicopter pad and fuel cache site 4 - Dwelling fuel storage 5 - Abandoned fuel tanks 6 - Light tower	Additional site investigation and confirmatory sampling for TPH and metals
Green Island (Trinity Bay) Lightstation	June 16	A - Fuel storage	Petroleum
Gull Island Lightstation	June 5 to 10	A - Fuel storage tanks D - Oil dump - east of duplex E - Fuel drum storage by old well I - Fuel drum storage behind dwelling J - Oil spill at top of tramway L - Winch house P - Waste coal pile	Petroleum Petroleum, metals Petroleum Petroleum Petroleum Petroleum Metals, PAH
Horse Chops Lightstation	June 14	B - Pole-mounted transformer leak	PCB
Kepple Island Lightstation	July 20	A - Former fuel storage area B - Present fuel storage area C - Old generator shed, lead acid batteries D - Fuel tank- keepers dwelling E - Storage shed	Petroleum Petroleum Lead Petroleum Petroleum
Little Burin Island Lightstation	May 24	A - Drum storage B - Fuel storage tank C - Buildings D -Pole-mounted transformer	Petroleum Petroleum Metals PCB
Lobster Cove Head Lightstation	July 19 and August 30	A - Coal ash disposal site B - Garbage disposal site	Metals, petroleum Metals

Site Location	Date of Investigation (1995)	Areas of Concern	Potential Contaminants
Long Point Lightstation	June 4	A - Abandoned fuel tank	Petroleum
		B - Dwelling fuel tank	Petroleum
		C - Helicopter fuel dump	Petroleum
		D - Vehicle repair ramp	Petroleum, oil & grease
		E - Work shed	Solvents
		F - Battery disposal area	Metals
		G - General disposal area	Metals, petroleum, PCB
		H - Disposal site	Metals
		I - Battery disposal	Battery
		J - Pole-mounted transformer	PCB
		K - Light tower	Mercury, metals
		L - Buildings	Metals
Long Point Transmitter T & E Remote Site	June 4	Above-ground fuel storage tank	TPH
Marticot Island Lightstation	May 24	A - Waste oil pit	Petroleum, oil & grease
		B - Fuel storage	Petroleum
		C - Fuel storage	Petroleum
		D - Equipment building	Petroleum
		E - Existing fuel storage	Petroleum
		F - Ravine	Petroleum, metals, PCB
Pass Island Lightstation	June 30	A - Generator fuel storage	Petroleum
		B - Helicopter drum storage	Petroleum
		C - General drum storage	Petroleum
		D - Dwelling oil stain	Petroleum
		E - Buildings	Metals,
		F - Pole-mounted transformer	PCB
Peckford Island Lightstation	June 29	A - Fuel storage tanks	Petroleum
		B - Fuel storage shed	Petroleum
		C - Former fuel drum storage area	Petroleum
		E - Waste coal pile	Metals, PAH
Penguin Island (South Coast) Lightstation	July 8	A - Fuel storage tanks	Petroleum
		B - Helicopter fuel drum storage	Petroleum
		C - Fuel drum storage	Petroleum
		D - Diesel drum	Petroleum
		E - Dwelling fuel storage	Petroleum
		F - Buildings	Metals
		G - Burn pit	Metals, oil & grease
		H - Light tower	Mercury
Point Amour Lightstation	August 8	A - Former fuel storage tank area	Petroleum
Point La Haye Lightstation	June 21	A - Fuel storage	Petroleum, metals
		B - Fuel storage - possibly	Petroleum
		C - Fuel storage	Petroleum, metals, PCB
Point Riche Lightstation	July 20 and August 30	Light was mercury bath type	Mercury
Point Verde Lightstation	August 1	A - Historical dwellings	Metals
Port-aux-Basques - Abandoned Decca Site	July 14	A - Generator building	TPH, metals, PCB
		B - Transmitting building	
		C - Coil hut	
		D - Indiscriminate dumping	
Port-aux-Basques - Abandoned Loran A Site	July 13	A - Loran A operational building	TPH, metals, PCB
		B - Service buildings	
		C - Historical fuel storage	
Port-aux-Basques Vessel Tracking System	July 14	A - Fuel storage	TPH

Site Location	Date of Investigation (1995)	Areas of Concern	Potential Contaminants
Pouch Cove - Abandoned Decca Site	June 18	A - Generator building B - Decca building C - Coil hut	TPH, metals, PCB
Powles Head Lightstation	June 22	A - Fuel storage B - Ruin	Petroleum, metals Petroleum, metals, PCB
Puffin Island Lightstation	June 15	A - Waste disposal sites B - Fuel storage tanks and drums	Petroleum, metals Petroleum
Ramea Island Lightstation	July 7	A - Disposal area in crevice B - Historical fuel storage C - Buildings D - Disposal near old dwelling E - Old winch house	Metals Petroleum, PCB Metals Metals Petroleum
Red Bay Lightstation	August 7	A - Drum fuel storage by dock C - Pole-mounted transformer D - Waste battery dump site, west side of light tower E - Fuel storage tank (keepers residence)	Petroleum PCB Metals Petroleum
Red Head T & E Remote Site	May 30	A - Old receiver building (fuel storage)	TPH, metals, PCB
Robin Hood Bay T & E Remote Site	May 30	A - Historical fuel storage B - Electrical transformers C - Storage yard	TPH, PCB, metals
Sagona Island Lightstation	July 4	A - Fuel storage tanks B - Fuel drum storage on platform C - Fuel drum storage on helicopter pad D - Dwelling stove oil tank E - Buildings F - Generator building exhaust	Petroleum Petroleum Petroleum Petroleum Metals Petroleum, PAH
St. Anthony T & E Radio Station	July 21	A - Fuel storage	TPH
St. Jacques Island Lightstation	May 21	A - Garbage burn area B - Waste disposal over cliff C - Lube oil disposal area D - Fuel storage tanks E - Drum storage F - Buildings	Site investigation and Phase IV sampling for TPH, metals, and PCB.
St. Lawrence Point Lightstation	May 19	A - Old generator building B - Old dwelling	Petroleum Metals, asbestos
St. Shotts Lightstation	June 22	A - Fuel storage B - Equipment building C - Storage building	Petroleum Petroleum, metals, PCB Petroleum, metals
Sopers Crossing Transmitter T & E Remote Site	July 19 and August 31	A - Old equipment building	TPH, metals, PCB
Surgeons Cove Head Lightstation	May 26	A - Waste disposal site B - Waste incineration site D - Dwelling, oil spill E - Lighthouse and surrounding area F - Generator exhaust	Petroleum, metals, mercury Metals and metal debris Petroleum Mercury PAH
Tides Cove Point Lightstation	May 20	A - Existing facility dike valve area B - Old generator building C - Fuel storage	Petroleum Metals, petroleum Petroleum

Environmental Site Investigation Procedure

The initial step in the Environmental Site Investigation was a general inspection of the site, followed by an identification and confirmation of the potential areas of concern as documented in the Phase I reports.

Using the recommendations provided in the Phase I report and the information from the general inspection, the site inspection plan was completed The strategy for the investigation was based on the CCME report, *Guidance Manual on Sampling, Analysis, and Data Management for Contaminated Sites, Volume I: Main Report and Volume II: Analytical Method Summaries* (CCME, 1993a and 1993b). Areas listed in the Liability Audit were examined on an individual basis. The dimensions and extent of a contaminated area were delineated in stages. First, a visual inspection of the surface was employed. Markers were placed at regular intervals around the perimeter of an area and along a trajectory deemed to have a high probability of contamination.

Following the visual examination of the surface, the soil beneath the overlying ground cover, be it gravel or vegetation, was surveyed at each of the markers For all potential hydrocarbon contaminated areas and most areas in general, the physical characteristics of the soil were noted. Physical characteristics of interest included, the presence or absence of a fuel odour or sheen, texture of the soil, and other signs of contamination such as coal, ash, paint chips and metal debris. A portable flame ionization detector (FID) was used to screen the soil for Volatile Organic Compounds (VOC). This class of chemical compounds is commonly found in crude oils and petroleum fuels and products. The screening process provides a reliable means of obtaining information on the age, type, and extent of a fuel contaminant spilled on or in soil.

The information from the on-site investigation and soil screening procedures was used to direct soil sampling. Soil sampling procedures were based on the U.S. EPA, *Standard Operating Procedure #2012, Soil Sampling* (U.S. EPA, 1988). Most samples were collected at a depth of less than 20 cm due to the fact that many sites had soil depths of 20 cm or less. Thus, for the purpose of this report, a surface sample is defined as any sample obtained from a depth of less than 20 cm. The number of samples collected was dependent on the size of the area of interest, with the intention of providing a representation of the source, extent, and distribution of the contaminant.

A hand auger (Hoskins Scientific Limited, Burlington, Ont.) was used to measure the depth of the local soils and/or collect depth samples where required. Steel garden hand tools and spades were used to collect soil samples. A sample-handling protocol was initiated to reduce chances of potential cross-contamination. Sampling equipment was decontaminated on a regular basis using manual cleaning techniques followed by multiple washes with water, followed by methanol, and finally distilled water. In addition, disposable gloves were used by the operators during sampling operations. The samples were stored in new, certified clean, glass bottles with Teflon lined caps (Fisher Scientific, Nepean Ont.; VWR Scientific, London, Ont.) Certification was to U.S. EPA protocols for extractable organics including pesticides and PCB. A temperature-controlled sample cooler (Canadian Coleman Co., Toronto, Ont.) was used to store and transport the samples at a suitably reduced temperature. A chain of custody form was prepared and used to log the progress of samples.

Field screening was carried out concurrently with the on-site investigation while field analysis occurred in a timely manner following the investigation. On-site field screening was limited to hydrocarbon examination. The instrument of choice was the Heath Detecto-Pak IIM portable flame ionization detector (FID; Heath Consultants Canada, London, Ont.). Volatile Organic Compounds from the petroleum products were detected and quantified by the instrument. The instrument is calibrated using methane, and all results are reported in units of parts per million (ppm) of methane equivalence. Prior to operation at each site, steps were taken to ensure the battery power levels for the instrument were satisfactory, and the instrument was set to zero (background reading). These adjustments were done at the background sample collection location, an area clear of any signs of contamination. A regular maintenance schedule for the instrument was established which included battery charging, filter replacement, and hydrogen cylinder changes.

Due to air transportation regulations regarding dangerous goods, a second type of instrumentation was used at one site. A HNU DL101 photo-ionization detector (HNU Canada, Mississauga, Ont.) was employed for on-site screening of hydrocarbons Its operating principle differs somewhat from an FID but it performs a similar function.

The capability existed to analyse each of the primary contaminants of concern in the field. These were Total Petroleum Hydrocarbons, Polychlorinated Biphenyls, Polycyclic Aromatic Hydrocarbons, and metals, namely lead, zinc, and mercury.

Field analysis of TPH, PCB and PAH was performed using immunoassay technology. The commercially available portable field kits (Millipore Canada, Mississauga, Ont.) for each group of compounds are distributed under the trade name Envirogard. Each type of test kit is specific to the contaminant of interest, TPH, PCB, or PAH, however they use similar methodologies. In order to avoid detrimental effects on the sample due to excessive handling, analysis was performed on the sample essentially "as is", with minimal sifting, grinding or drying. Analysis was performed as per the manufacturer's instructions. A background sample was examined in conjunction with the other samples for the purpose of providing information on potential systematic interference in the procedure. The result reported is a total value for the contaminant class analysed, as opposed to analysis of specific chemical compounds. In this manner, the field kits differ from corresponding laboratory analysis. As well, the sample preparation used in the field analysis procedures differs from those of laboratory methodologies. These variations between field and laboratory protocols contributed to discrepancies between corresponding field and laboratory results.

A Spectrace 9000 field portable XRF spectrometer (TN Technologies Canada, Gormley, Ont.) was used for the field measurement of metals. It is capable of detecting 25 metals in soil, including mercury, zinc, and lead The instrument is available from the manufacturer with appropriate pre-programed soil analysis software. Analysis procedures were based on U S EPA *Standard Operating Procedure ≠1713, Spectrace 9000 Field Portable X-Ray Fluorescence Operating Procedure* (U.S. EPA, 1992). A measurement time of 200 seconds for each source was used. To ensure proper operation of the instrument, a daily review of the energy levels and resolution of the instrument was performed Certified metal standards (NBS #1575, NIST, Gaithersburg, MD, U S. EPA CRM003-050, RTC Corp., Laramie, WY) were measured prior to the start of sample analysis, and at regular intervals throughout the course of analysis, for the purpose of checking the accuracy and reproducibility of the apparatus.

For metal analysis, samples were allowed to air dry overnight to lower the water content and reduce possible matrix interferences Detection limits vary with the soil type and are specific to each metal. Detection limits for the portable X-ray spectrometer are affected by age of energy source, soil matrix and moisture content. The soil analysis software developed by the manufacturer employed a group of standards with distinct matrices. Samples analysed over the course of this project have a wide range of matrices which may or may not be significantly different from those used by the manufacturer. Multiple metals, present in the same sample, can cause cross-interference and affect analysis For this reason, field metal analysis may be prone to false positive identification of metals Laboratory results were used to confirm the identification of metals from field analysis.

Laboratory metal analysis was carried out by inductively coupled plasma and atomic absorption methodologies, which differ from XRF spectroscopy. Field and laboratory metal analysis identify two different but overlapping groups of metals As such, samples undergoing both types of analysis do not necessarily have values from both techniques for each metal. Table 2 lists the metals that can be detected by the field instrument and laboratory procedures, along with typical detection limits. The capability of the methodology to detect a specific metal is indicated by the presence of a detection limit value. A blank cell indicates the method was not set up to identify that specific metal.

Table 2: Metals and Detection Limits

Metal	Field XRF Detection Limit (typical) (mg/kg)	Laboratory Detection Limit (mg/kg)
aluminium		1.0
antimony	43	
arsenic	39	
barium	15	0.2
beryllium		0.5
bismuth		2.5
boron		0.5
cadmium	138	0.5
calcium	115	0.5
chromium	138 (Fe-55 source), 404 (Cd-109 source)	0.3
cobalt	158	0.3
copper	69	0.2
iron	173	0.3
lead	23	1.0
magnesium		1.0
manganese	315	0.3
mercury	46	0.01
molybdenum	8	0.5
nickel	96	0.5
phosphorus		3.0
potassium	250	20
rubidium	8	
selenium	27	
silver		0.5
sodium		0.5
strontium	8	0.3
thorium		
tin	77	2.5
titanium	85	0.3
vanadium		0.5
zinc	54	0.3
zirconium	8	

Laboratory analysis was carried out on a minimum of 15% of the samples collected from each site. For sites previously remediated and requiring confirmatory sampling, a higher percentage of the samples were forwarded to the laboratory for analysis. The work was performed by MDS Environmental Services Limited (Mississauga, Ont). A contract laboratory was employed to provide independent and unbiased analysis. Laboratory analysis was carried out using standard U.S. EPA methodologies. A review of quality assurance and quality control criteria showed the data generated by the laboratory to be within acceptable limits.

Recommendations for Remediation Procedure

Decisions on an area with regard to its contamination were based on the CCME report, *Interim Canadian Environmental Quality Criteria for Contaminated Sites* (CCME, 1991b) and Provincial Total Petroleum Hydrocarbon guidelines. Each of these guidelines contain sub-categories based on the use of the land For the CCME guidelines, the three categories are, in order of increasing soil remediation criteria, Agricultural, Residential/Parkland and Commercial/Industrial The Provincial TPH guidelines had two categories, Class A (Sensitive) site and Class B (Non-Sensitive) site. Commercial/Industrial and Class B (Non-Sensitive site) limits were employed for the majority of sites while Residential/Parkland limits and Class A (Sensitive Sites) were referenced when the site was a Federal or Provincial park

In previous work by the Canadian Coast Guard, an assessment of the risk associated with the primary contaminants was carried out. From this, risk assessment criteria were established whereby a specific contaminant concentration was set, above which remediation action was required The criteria established are as follows:

- Polychlorinated Biphenyls - 50 mg/kg,
- Metals - 20x the commercial/industrial value present in CCME Interim Remediation Criteria for Soil (CCME, 1991b);
- Total Petroleum Hydrocarbons - 10,000 mg/kg.

Remediation requirements for PAH contamination were based on the sum of the criteria limits of the individual PAH compounds listed in the CCME guidelines.

The aforementioned Risk Assessment criteria were established partially based on the accessibility of a site and long term potential for hazardous exposure to humans and/or the environment. The majority of Lightstations and Marine Navigation Sites are isolated locations, minimizing the associated risks. A small number of sites, such as those that are presently parklands and have a high tourist interest, do not necessarily have the same low risk levels. These sites require additional due consideration. For these sites, contamination levels and the corresponding remediation action are based on CCME values for residential/parkland guidelines and Provincial TPH guidelines for Class A (Sensitive) sites.

Through discussion with Canadian Coast Guard personnel and ESD personnel, it is clear that remediation of petroleum-contaminated soils by in-situ landfarming techniques is the most appropriate approach, based on geographic and economic considerations. Over time, natural activity by bacteria and other microorganisms in the soil will degrade petroleum hydrocarbons. The effort in landfarming is to accelerate this activity by providing an ideal environment for these organisms.

Excavating the soil, placing it in a drum, and removal of the contaminant off-site is the alternate method of remediation for contaminants such as metals, most notably mercury, and PCBs, which may pose additional risks and are not readily treated on site. From an operational point of view, this is a more difficult and costly method of remediation because of the effort and cost of transporting a container of waste to a disposal facility.

In view of the fact that the topography and location of the sites present unique challenges to the site investigation and the options available for remediation, a baseline set of requirements for the investigation and remediation techniques was established These included the following requirements.

- The investigation would be restricted to chemical contamination of the soil. A significant number of the sites have soil coverage with less than 30 cm depth. Recommendations would be focused on the soil layer down to bedrock with emphasis placed on the upper 30 cm.
- Areas itemized in the Liability Audit dealing with health and safety concerns and/or general debris are not within the scope of this report.
- The remoteness of the sites and difficulties associated with transporting supplies to and from the locations should be considered when determining the volume of soil to be remediated and the level of effort required, without compromising accuracy and accountability.
- In-situ landfarming and soil excavation are the remediation options of choice. Recommendations for remediation should be based on these two processes.

Results

Over the course of this project a significant amount of data was collected. In total, FID field screening generated approximately 2000 data points, there were greater than 560 field metal analyses performed, over 550 field TPH tests, in excess of 100 field PCB results and 17 field PAH analyses. The results listed in this section are a representative sampling taken from various sites with the intent to depict the limitations of the methodologies and instrumentation. The following paragraphs display results as they were generated by each instrument during the project.

The FID was used in petroleum contaminated areas to delineate the extent of the contamination by screening the soils for residual Volatile Organic Compounds (VOC). An example of a typical fuel contaminated area is that of Area 18 at Belle Isle, Southwest. The data recorded during the investigation has been provided in Table 3. A description of the area and Figure 1, a map of the area, provides information helpful in understanding the process used to determine the extent of a contaminated zone's dimensions

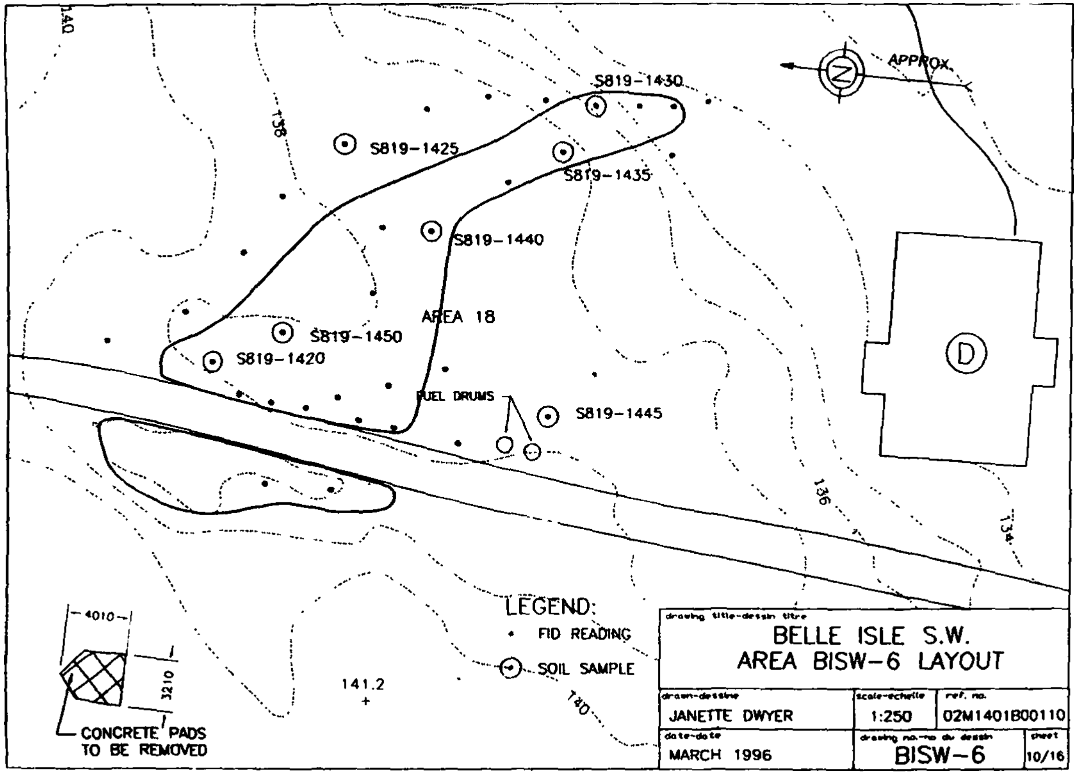
This section of Belle Isle was a large flat area north of the detached dwelling and used to store drums of fuel The area of delineation crosses a gravel road. On the west side of the road, there was a large stain measuring 14 m by 4.5 m in which there was no apparent vegetation. On the east side of the road, only empty drums were stored, however, the drainage from the west side is toward the east. There are several points throughout the area where bedrock protrudes Thirty-three points were selected and screened with the portable FID, most being along the east side of the road and along the perimeter of the natural drainage path A large number were found to have high VOC levels including several "hot spots" as far away as 16 m east of the road. Further south along the east side of the road were two fuel drums in a flat area which would also drain into the delineated area. Seven surface samples were collected in this area.

Table 3: Area 18 - Belle Isle Southwest

Area - Marker	FID Reading	Location	Sample ID Analysis Required	Description
18-1	120	- in stain on west side of road		
18-2	55	- south end of visible stain		
18-3	5	- approx 4 m south of point 18-5	*S819-1420* (TPH, metals)	Sample contained black, moist soil, with few rocks, some clay, and a *slight fuel odour, with a depth of 25* cm Field TPH result. 250<x<1000 ppm Field XRF analysis showed 2 1x cobalt levels
18-4	9	- 2 m SE of point 18-5		
18-5	9	- north end of delineated area, at point where effaced rock is closest to road. approx 1 m from road		
18-6	Background	- 4 m SE of point 18-5		
18-7	Background	- 6 m SE of point 18-5		
18-8	Background	- 8 m SE of point 18-5	S819-1425 (TPH, metals)	Soil was dark and rich, with root mat, and a slight, unfamiliar odour. Depth of 25 cm Field TPH result. 0<x<250 ppm Field XRF analysis showed 1.6x arsenic and 1x cobalt levels
18-9	Background	- 10 m SE of point 18-5		
18-10	18	- 12 m SE of point 18-5		
18-11	6	- 2 m south of point 18-10		
18-12	18	- 4 m south of point 18-10	*S819-1430* (TPH, metals)	Sample contained dark loam with root mat, some blue paint and a *strong fuel odour Soil depth* measured at 20 cm. Field TPH result: 1000 ppm. Field XRF analysis showed 1.5x arsenic levels.
18-13	650	- 2 m NW of point 18-12	S819-1435 (Metals)	Sample contained root mat and was sticky but fairly dry, with some small rocks and a strong fuel odour. Soil depth was 30 cm. Field TPH result. x>1000 ppm Lab. TPH result. 3284 ppm.
18-14	75	- 4 m NW of point 18-12		

Area - Marker	FID Reading	Location	Sample ID/ Analysis Required	Description
18-15	8	- 6 m NW of point 18-12	S819-1440 (Metals)	Soil was sticky, contained root mat, no paint or rocks, and no fuel odour. Depth was 25 cm. Field TPH result. 250<x<1000 ppm
18-16	7	- 2.5 m west of point 18-15.		
18-17	12	- 4.5 m west of point 18-15.		
18-18	25	- 2 m SSE of point 18-12.		
18-19	6	- 4 m SSE of point 18-12.		
18-20	Background	- 6 m SSE of point 18-12		
18-21	11	- 2 m SW of point 18-18.		
18-22	Background	- 3 m SW of point 18-16		
18-23	18	- 2 m SE of point 18-22.		
18-24	50	- Collected from east side of flat, gravelled area where fuel drums were located, approx 3 m SE of point 18-26.	S819-1445 (Metals)	Sample had gravel at surface, mixed rock and soil in sample, and had a strong fuel odour Soil depth was measured at 10 cm with less odour noticeable at depth. Field TPH result: 0<x<250 ppm.
18-25	7	- 2 m SE of point 18-24.		
18-26	10	- along east side of road, north of the flat, gravelled area		
18-27	10	- along road, 2 m north of 18-26.		
18-28	8	- along road, 4 m north of 18-26		
18-29	8	- along road, 6 m north of 18-26.		
18-30	22	- along road, 8 m north of 18-26.		
18-31	30	- along road, 10 m north of 18-26.		
18-32	9	- 2 m east of point 18-30, also approx. 3 m SE of point 18-3	S819-1450 (TPH, metals)	Sample contained lots of peat, root mat, and some dark staining and had a fuel odour. Soil depth measured at 75 cm, with no odour detected at depth. Field TPH result: x>1000 ppm. Field XRF analysis showed 1.3x cobalt levels.
18-33	8	- approx. 2 m north of 18-15		

Figure 1: Delineation of Area 18, Belle Isle Southwest



Immunoassay test kits were used for the field analysis of TPH, PAH and PCBs. Many common trends were observed between the three types of kits regarding their limitations and accuracy. Although the technologies employed by the kits are similar, the form in which the data is presented differs. For this reason, a comparison of the test kit field values and laboratory results have been tabled on an individual basis

Table 4 lists Total Petroleum Hydrocarbon results, for a selected number of samples, for both laboratory and field analysis. Field analysis is reported on an "as is" basis, where as the laboratory data is reported on a dry weight basis. The samples have been grouped by the chemical resemblance of the contaminant. Soil descriptions and moisture content provide information on the potential effect on the results due to soil matrix. Moisture content can also be used to correct field results for water content For reference purposes, the Newfoundland Provincial TPH limit for non-sensitive sites is 1000 ppm.

Table 4 A Comparison of TPH Field Results and Laboratory Results

Site	Field TPH Result (mg/kg)	Laboratory TPH Result (mg/kg)	Chemical Resemblance	Soil Description	Moisture Content
Allen's Is	50<x<250	149	motor oil	- dark, rich earth, some stones	28%
Cabot Is.	0<x<50	867	motor oil	- peat-like earth with significant root material.	39%
Belle Isle SW	>1000	51,200	diesel fuel	- consisted of significant number of small rocks	40%
Bacalhoe Is.	0<x<50	322	diesel fuel	- moist clay-sand mixture	11%
Belle Isle NE	>1250	147,204	diesel fuel and motor oil	- dark clay soil.	52%
Belle Isle SW	0<x<250	3,500	diesel fuel and motor oil	- moist mud-like soil with rocks and root mat .	31%
Gull Is	250<x<1000	288	weathered diesel fuel	- moist soil with significant number of small rocks	47%
Surgeons Cove Head	250<x<1250	22,200	weathered diesel fuel	- moist soil overlying gravel	18%

PAH results from laboratory and field analysis are reported in Table 5. Field analysis techniques generate a single total PAH value, while the laboratory examination produces compound specific data. The sites selected have results which extend over the full range of the results obtained throughout the project, from 0 to 10 µg/g, and their corresponding laboratory results Field results are generally reported as falling within the range of the less concentrated and higher concentrated standard. CCME soil remediation guidelines are not available for all PAH compounds and are limited to those compounds with values provided in the table. As with the previous TPH table, soil description and moisture contents values have been included where measured.

Table 5: A Comparison of PAH Field Results and Laboratory Results

	CCME * guidelines (µg/g)	Red Bay	Fort Point	Francois Point	Surgeons Cove Head
Laboratory Result (µg/g)					
1-chloronaphthalene		not detected	not detected	not detected	not detected
1-methylnaphthalene		not detected	trace	2.24	9.96
2-chloronaphthalene		not detected	not detected	not detected	not detected
2-methylnaphthalene		not detected	0 14	3.20	12 60
acenaphtene		not detected	trace	12 80	1 85
acenaphthylene		not detected	not detected	not detected	8 60
anthracene		not detected	0.32	42.10	10.00
benzo(a) anthracene	10	not detected	0 11	53.60	19 60
benzo(a) pyrene	10	not detected	0.14	47 50	13 40
benzo(b) fluoranthene	10	not detected	0.14	41.90	16 20
benzo(ghi) perylene		not detected	not detected	26 40	9 74
benzo(k) fluoranthene	10	not detected	trace	39 50	17 10
chrysene		not detected	0 17	58 00	23.60
dibenzo(a,h) anthracene	10	not detected	not detected	9.43	3.48
fluoranthene		not detected	0.26	135.00	52 50
fluorene		not detected	0.10	25.60	6.42
indeno(1,2,3-c,d) pyrene	10	not detected	not detected	24 30	14.30
naphthalene	50	not detected	0 60	11 70	11 30
perylene		not detected	trace	11 40	4 03
phenanthrene	50	not detected	0.40	156.00	52 90
pyrene	100	not detected	0.23	105.00	41 00
Field Result (µg/g)		0	0<x<1	1<x<10	10
Soil Description		- background sample contains moist. dark soil with few rock significant root material	- background sample contains root mat and many stones.	- mixture of earth, sand and rock	- moist soil with root material and coal dust.
Moisture Content		29%	not measured	not measured	61%

* CCME guidelines for Commercial Industrial Remediation Criteria for Soil

A comparison of field to laboratory PCB results has been provided in Table 6. The sites chosen have results across a broad range. Both laboratory and field results are given as a single, total value. The field kits are factory calibrated using Aroclor 1248 and produce results relative to that standard. Field calibration standards extend through the concentration range of 0 to 50 ppm, with values 0, 2, 5, 10 and 50. Field results are generally reported as falling within the range of the less concentrated and higher concentrated standard. The total of all the PCB congeners is the value shown by the laboratory.

Table 6: A Comparison of PCB Field Results and Laboratory Results

Site	CCME* guideline (μg/g)	Field PCB Result (μg/g)	Laboratory Total PCB Congegrer Result (μg/g)	Soil Description	Moisture Content
Cain's Is.	50	5	trace	- background sample containing moist peat-like soil. - raw data showed all samples of run had results near 5 ppm standard.	74%
Belle Isle SW	50	0<x<10	0.11	- sample contained roots and wood debris. - raw data showed sample midway between standards responses	63%
Belle Isle SW	50	0	not detected	- peat-like sample contained dark coloured, moist root material. - raw data showed sample having same value as 0 ppm standard.	71%
Surgeons Cove Head	50	2<x<10	180	- root material and gravel. - only sample during run to show positive result above background.	54%
St. Jacques Is.	50	5<x<10	0.33	- recently tilled soil - field result same as background sample	47%

* CCME guidelines for Commercial/Industrial Remediation Criteria for Soil

Field and laboratory methodologies for metals are each capable of measuring 25 metals, however they do not measure the exact same group of metals. In addition, the inorganic parameters listed in the CCME soil remediation constitute a third group of metals. Table 7 lists all of the metals which could potentially be detected. Blank spaces indicated the concentration was below the instruments detection level or the methodology was not capable of detecting the analyte. Method detection limits are provided in Table 2. The primary metals of concern, lead, mercury, and zinc, have been highlighted.

Table 7. A Comparison of Metal Field Results and Laboratory Results

Metals	CCME* guidelines (ppm)	Tides Cove Point Field Results (ppm)	Tides Cove Point Laboratory Results (ppm)	Surgeons Cove Head Field Results (ppm)	Surgeons Cove Head Laboratory Results (ppm)
aluminium			4110		7480
antimony	40				
arsenic	50				
barium	2000	179	179	1009	2450
beryllium	8		not detected		not detected
bismuth			not detected		not detected
boron			12		3
cadmium	20		not detected		not detected
calcium		17120	11000	5610	4140
chromium	800	129 to 210	16	480	33
cobalt	300	416	7	770	5
copper	500	55	47	1349	981
fluoride	2000				
iron		22060	18800	29540	27900
lead	**1000**	**815**	**782**	**2878**	**3840**
magnesium			1910		2090
manganese		850	563		226
mercury	**10**		-	**105**	**130**
molybdenum	40		3		3
nickel	500		13		26
phosphorus			827		4560
potassium		3660	not detected	1050	not detected
rubidium		41		31	
selenium	10				
silver	40		not detected		not detected
sodium			not detected		not detected
strontium		94	45	129	64
sulphur					
thorium					
tin	300		not detected		not detected
titanium		966	166	1048	601
uranium					
vanadium	200		15		30
zinc	**1500**	**613**	**478**	**748**	**666**
zirconium		64		43	

* CCME guidelines for Commercial Industrial Remediation Criteria for Soil

Discussion

Project Summary

In support of efforts by the Canadian Coast Guard to ensure that their facilities are in compliance with environmental and health and safety legislation, the Emergencies Science Division entered into an agreement with CCG to carry out an Environmental Site Investigation as described in CCME report, *National Guidelines for Decommissioning*

Industrial Sites (CCME, 1991a). A total of 77 Lightstations and Marine Navigation Sites were addressed, located throughout the Province of Newfoundland and Labrador and including both road-accessible and remote sites. As well, the sites were a combination of Lightstations, T & E Radio Stations, T & E Remote Sites, VTS Remote Sites, Loran C Sites, VTS Stations, and Abandoned Sites. The project was undertaken during 1995/96 with field work being carried out during the months of April to September, 1995. Each site was investigated individually, findings were summarized, and a report was prepared.

With a project of this size, certain trends become apparent and are common to most sites. The following paragraphs present and discuss some of the general observations noted over the course of the project.

The amount of contamination at a particular site was primarily dependent on the age, size and location of the station. Lightstations, being larger and most often older establishments than the Marine Navigation Sites possessed more areas of concern. Many of the Marine Navigation Sites have been constructed in the past two decades and have been updated regularly to meet environmental standards. As a result, few show signs of chemical contamination. Island lightstations, with their reduced accessibility, appear to have, on average, more soil pollution considerations than road-accessible stations. This trend can be explained by the remoteness of the island sites. They require large volumes of fuel and motor oil for generators, increasing the chances of TPH contamination, and are limited in their waste disposal capabilities.

Environmental Fate of the Contaminants

Fuel contamination of the soil is by far the most common concern. Although there were areas where large spills had occurred, the majority of the affected locations were relatively small. This is especially true at road-accessible sites. Spills were usually located near the drain/fill valves of storage tanks and were a result of inadequate handling practices. These included leaking hoses and clamps, improperly sealed drums, etc. A detailed synopsis on the environmental and health effects of fuels can be found in *Toxicological Profile for Fuel Oils* (U.S. Department of Health and Human Services, 1995a). In general, fuel oils contain a wide range of chemical compounds. There is inconclusive evidence of the effects on the health of humans resulting from physical contact. The lighter aromatic compounds pose the largest inhalation threat. However, studies have shown the vapour pressure of fuel oil, under normal conditions is not high enough to result in a significant buildup of compounds in the air to the point where it would reach levels of concern. Fuel oils will slowly degrade naturally in the environment with time. The rate and extent of the degradation is dependent on the chemical composition of the fuel. The monoaromatic and short chain aliphatic hydrocarbons are more susceptible to degradation, while the long chain and polyaromatic hydrocarbons take longer to degrade and degrade to a lesser extent. Landfarming techniques have been shown to enhance biodegradation of fuel contaminants.

Soils affected by waste motor oil were usually found at island sites. The generators on site require regular maintenance including motor oil changes As disposal methods were not available, a specific dump area was usually present in the vicinity of the generator building. Motor oils contain larger hydrocarbon compounds relative to fuels. In the environment, waste oil is less likely to transport through the soil and usually binds to organic components in the soil. Harmful effects of the oils result primarily from the additives contained in each product, and the addition of materials to the oil from the machinery. Some evidence exists that the PAHs in the oil are carcinogenic

Motor oil is capable of undergoing biodegradation. The rate is slower than that of fuels and sometimes requires a long period of time before any initial significant changes are observed. This is because the larger hydrocarbon molecules have difficulty reacting with the natural bacteria. The report *Toxicological Profile for Mineral-Based Crankcase Oil* (U.S. Department of Health and Human Services, 1994a) provides detailed information on the environmental and health-related aspects of motor oils.

A review of literature dealing with the science of bioremediation and field experience with bioremediation was carried out. The purpose was to collect information from literature on in-situ bioremediation field trials in order to augment the experience acquired during this project. The Environment Canada report titled *Bioremediation of Petroleum Hydrocarbons in Soil Environments* (Rowell *et al.*, 1992) provides a detailed review of the science associated with bioremediation From the collection of data based on field experience, it is concluded that there is agreement on the need to modify and adjust parameters such as soil acidity and moisture, aeration, and the addition of nutrients. However, the nutrient ratios or specific optimal soil conditions varied in most trials Environmental conditions, on a global scale, differ too much for a standard approach to be routinely successful. Experience with regional environmental conditions has proven to be the more successful approach The in-situ landfarming remediation procedure developed by the Canadian Coast Guard, was developed with due consideration to the province's environmental conditions Satisfactory results appear to have been achieved with this method, meeting the remediation objectives set by the Coast Guard.

As mentioned previously, Polycyclic Aromatic Hydrocarbons are a group of chemical compounds suspected of being carcinogenic. They are by-products in the soot from the incomplete combustion of coal used with historic coal-powered generators. In soils, PAH compounds tightly bond to the soil matrix with only low levels of evaporation taking place. They react with sunlight and/or microorganisms to naturally degrade, however, it is a long term process. The biodegradation rate of PAH compounds is dependent on the size of the individual compounds and can range from 20 to hundreds of days (U.S. Department of Health and Human Services, 1995b). Environmental factors such as soil type, pH, temperature, and oxygen concentration can influence the remediation time. At the Lightstation and Marine Navigation Sites, the in-situ landfarming procedure will be employed for areas containing PAH contamination. The desired goal of a reduction in the PAH-in-soil levels will be achieved but over a longer period of time than that required by fuel contaminated zones.

Lead in soil is a distant second in terms of the extent of soil contamination and was predominantly a result of the use of lead as a historic fuel additive, from metal debris, and as a paint additive. Historic fuel spills often had elevated lead levels, however, the concentration only occasionally exceeded CCME soil remediation criteria limits for commercial/industrial sites. High lead levels from debris were seldom observed. Paint chips were present at almost all CCG facilities, near and around painted structures. Most were isolated to an area within 1 m of the wall of the structure. Considering the amount of paint chips on the soil over all of the stations and sites, only a small percentage of samples showed lead levels exceeding the 1000 mg/kg CCME limit.

A detailed synopsis on the environmental and health effects of lead can be found in *Toxicological Profile for Lead* (U.S. Department of Health and Human Services, 1993). In general, elemental lead remains bonded to the soil. Movement to the groundwater occurs only under acidic conditions. Chemicals containing lead can be broken down by sunlight, air, and water to produce other forms of lead. Tetraethyl lead, the most common fuel additive, will degrade into the more toxic compound, primary triethyl lead which ultimately degrades to inorganic lead. Lead has been shown to be absorbed into plants through the roots and made relatively innocuous by the formation of lead/phosphorus compounds. The long term fate and effect of tetraethyl lead is that it will eventually degrade to lead and bioaccumulate in the food chain if these conditions exist (Environment Canada, 1985a).

Mercury contamination was observed at a small number of sites and localized to the area in the vicinity of the light towers. Detailed information on the environmental fate of mercury can be found in *Toxicological Profile for Mercury* (U.S. Department of Health and Human Services 1994b) and the EnviroTIPS series, *Mercury* (Environment Canada, 1984).

Metallic mercury, a liquid at room temperature, will evaporate to the air and can be transported significant distances. In both water and soil, microorganisms can change inorganic mercury to methylmercury. In this form, it attaches itself to particles in the water or soil. In water, mercury usually remains at the bottom in the sediment. In soil, the mercury does not move through the soil and remains predominantly at the surface. The capacity and rate at which mercury absorbs to the soil is dependent on the amount of amorphorus oxides, reducible iron and manganese, and surface area of the soil. Methylmercury does bioaccumulate in aquatic life and can be passed on through the food chain.

Elevated levels of zinc were observed at a very few locations and were due predominantly to the disposal of batteries. Although levels were elevated, they seldom surpassed the CCME commercial/industrial soil remediation criteria In soil, zinc binds with the soil itself and remains relatively immobile unless soil conditions become acidic (U.S Department of Health and Human Services, 1994c). As soil acidity increases (lower pH), the toxicity of the zinc increases because the zinc is more apt to be removed from the soil matrix Clay and peat soils can be exposed to higher zinc levels than sand soils before reaching toxic concentrations. Zinc is known to accumulate in various tissues (Environment Canada, 1985b)

Although metal contaminated soils appear to decrease in concentration with time due to natural interactions with organic compounds and soil, the method selected by CCG for remediation of soils with high metal levels is excavation and removal from the site and suitable disposal. This method achieves the goals for site remediation as required by legislation.

Polychlorinated Biphenyls were used in various transformers, capacitors, and light ballasts. Concern at CCG sites results from historic leaks of these materials Production of PCB ended in 1977. Only a small minority of the sites showed any PCB contamination. PCB is a generic name applied to a group of chemical compounds. On an individual basis the compounds possess different hazard levels. The environmental and health effects of PCBs have undergone a significant amount of research. Some of this is present in *Toxicological Profile for Polychlorinated Biphenyls* (U.S. Department of Health and Human Services, 1995c) PCBs adsorb readily to soils. Decomposition in soil is dependent on the amount of chlorine molecules in the compound. As the number of chlorine molecules increases so does the decomposition time, which may end up requiring years and possibly decades. Although some of the smaller compounds are mobile in soil, PCBs will generally not leach significantly in most aqueous soil systems (U.S. EPA, 1995) The Aroclor 1254 PCB will evaporate with a loss of trace to 50% depending on the soil type. Like metal contaminated soils, excavation and off-site disposal is the remediation method employed by CCG and appears to meet the goals of the program.

Methodology and Analytical Instrumentation

The Heath Detecto-Pak IIM flame ionization detector (FID) was used to delineate hydrocarbon contaminated areas in order to rapidly evaluate the size of an area. The instrument was developed for the oil pipeline industry and was designed to withstand the rigours of field work. It is powered by rechargeable batteries and is fully portable. Because the detector was used for on-site screening, it was subjected to assorted environmental extremes, including near freezing temperatures, snow, rain and strong winds From an operational point of view, the performance of the detector was more than satisfactory. It generates real-time results with a concentration range of 1 ppm to 1,000 ppm. However the instrument is calibrated with methane gas, as such, results are in units equivalent to methane. For the purpose in which it was used, accurate concentration values were not required. Instead, the readings were used on a relative basis to determine the location of "hot spots".

The hydrocarbon contamination was generally from historic spills, thus, there is a high probability that the lighter aromatic compounds had been lost with time, reducing the concentration remaining in the contaminated soil. A FID was employed, as opposed to alternative technologies such as a portable PID or GC/PID, because a FID has lower detection limits for alkane hydrocarbons than a comparable PID. A PID utilizes a ultraviolet light energy source where as the FID uses a flame to ionize a particular gas. A PID instrument is more suited to detect aromatic compounds. One disadvantage of the FID is the requirement of hydrogen as a fuel source for the flame. This can add complications to transporting the detector by air and was the reason a PID instrument was used at one site accessible only by commercial airlines.

From the example of Area 18, Belle Isle SW, given in the results section, it can be seen that the FID was a valuable tool in determining the size of a hydrocarbon contaminated area. The in-situ, real-time results have an advantage over collecting samples and screening them off-site. Time at a site, especially for helicopter accessible sites, was at a premium. With the timely information from the FID, the actual number of samples which had to be collected could be optimized, thereby improving the efficiency of the site investigation. The values from the screening process were used to direct soil sampling and the relative response of the FID provided information on the age of the contamination. More recent fuel spills would have a higher percentage of volatile organic compounds remaining resulting in a higher reading on the FID. As the FID, and most other screening instruments for that matter, measure the amount of VOCs present, their limitations are surpassed when the fuel spill has weathered to the point that a minimal amount of VOCs remain, or when the contamination was a result of motor oil which has few volatile components.

Again, with regard to Area 18, the process used to determine the extent of the contamination is described. The soil in the vicinity of the fuel depot located in Area 18 had been contaminated by fuel. This was apparent by observation. The contamination on the west side of the road was confined by natural barriers from spreading in any direction other than across the road towards the east. Screening for VOCs directed sampling at key locations on the east side of the road to properly delineate the extent of the fuel migration. Analysis of these samples showed no evidence of metals contamination. Three samples contained elevated TPH levels. These were samples taken at points 18-12, 18-13, and 18-32. The laboratory analysis of the sample collected from point 18-13 showed TPH concentration (3284 ppm) to be above Provincial guidelines but below the remediation criteria. The GC trace was indicative of a petroleum hydrocarbon mixture in the diesel/motor oil range. Delineation of the area for the CCG crew was done based on field analysis while the sampling team was on site and was inclusive of all field results with 1000 ppm or greater. Based on the laboratory analysis, this delineated area would have been sufficiently large to include the soil which contained TPH levels above the remediation criteria. Due to results in the vicinity of the fuels drums located at a point further south on the east side of the road, this area was not included in the remediation area. The remediation area, as delineated for the CCG clean-up crew, included the stained area on the west side of the road as well as the plume of contamination east of the road, inclusive of the affected soil to a distance of 19 m from the road, beginning at approx. 14 m wide along the roadway to approx. 2 m wide at the furthest point.

Results from field analysis methodologies and those from laboratory analysis are seldom numerically equivalent. This is a result of the fact that each technique employs different sample preparation procedures and each type of instrument has its own unique limitations Field TPH, PAH, and PCB analysis showed similar trends to laboratory analysis, however the numerical values were not similar. The kits are marketed as a semi-quantitative tool. Some general trends were noted which were common to all of the immunoassay based test kits Although they did not always produce results which were numerically equivalent to laboratory analysis, they were capable of detecting the presence of the contaminant and did not generate false negative results. The detection limit of the kits was dependent of the soil matrix and calibration standards employed but was on the order of the low ppm range The advantage of these kits is that they can significantly reduce the time and cost of analysis and this technology is one of the few commercially available as a complete portable kit.

A comparison of field TPH analysis to laboratory analysis data was presented in Table 4. For each type of fuel contaminant, as identified by laboratory analysis, two representative sites were shown. One shows similar results between the field and laboratory data while the second shows a discrepancy exists. The common link between the data with discrepancies is the soil type. Both moist clay and high organic content samples generated low field screening results. This is likely due to effects on the extraction of the contaminant from these types of soil. Field results for Belle Isle SW (diesel fuel) and Belle Isle NE (diesel fuel and motor oil) show greater than (>) standard (1000 or 1250 μg/g) results. This is a satisfactory data value and is due to the fact that this is the upper detection limit of the field kits and results in excess of the limit are reported in this manner. The standards included in the kit are home heating fuel. TPH results for the field kits are reported in terms of "equivalent" to home heating fuel.

With regard to the PAH results shown in Table 5, a direct comparison on a compound by compound basis is not possible as the field tests produce a "total" value and the laboratory results are compound specific. Like the TPH results, the numeric values are not equivalent. What is noteworthy is the relative relationship The sample having a zero (0) value in the field analysis had "not detected" concentrations in laboratory analysis. As the range in which the sample result was detected increased for field analysis, the number and quantity of PAH compounds present, as detected in laboratory analysis, increased proportionally. This trend was common to all of the different immunoassay procedures. It was noted that when field analysis gave results greater than 1 ppm there was a high probability the sample contained elevated PAH concentrations.

The results in Table 6 highlight a concern more commonly found with the PCB field tests This was the generation of false positive results. There was no information to support the theory that an interfering chlorinated compound was responsible for the positive bias For this reason, the importance of the measures instituted to ensure analytical accuracy cannot be understated. They provided a means to evaluate and interpret the data. These measures are outlined in a following paragraph. An example of the evaluation process can be seen by reviewing the field result for Surgeons Cove Head and St. Jacques Is. Surgeons Cove Head was numerically below action levels, but it was the only sample during the run to generate a positive response. On the other hand, the result for St. Jacques Is., although numerically higher than the Surgeons Cove Head sample, was the same as most of the samples analysed during that run including a background sample.

The effect of the sample matrix can be seen in the correlation between field and laboratory for all of the immunoassay test kits. Water content, the make up of soil, and type of contaminant will influence the performance of the immunoassay kits. Methanol is the solvent used in the procedure to extract the contaminant from the soil. It is used for two reasons; its chemical composition differs enough from the contaminant of interest so that it will not compete for, or interfere with, the reaction and it is not toxic to the antibody. However, the extraction capability of methanol is low for samples containing motor oil or weathered fuel. Extraction of a chemical from soil is affected by soil type. Soils with a high organic content contain naturally occurring oils which are somewhat similar in structure to motor oil and contaminants often bind strongly to the organic compounds. Clay based soils tend to absorb the solvent, reducing the recovery. Sand and gravel soils generally have the best extraction efficiencies. Water contents above 30% may influence the results. As methanol is water soluble, when diluted, its ability to remove the chemical from the soil is reduced. This being said, several samples with high water contents were tested in the field with good correlation between laboratory and field results. Soil matrix and the solubility of the contaminant in methanol were the principle influences on field results.

Field and laboratory analysis for metal content were numerically comparable, however, each technique does not detect the same 25 metals and the laboratory analysis has lower detection limits. The correlation between the field and laboratory results for the three primary metals of concern, lead, mercury, and zinc was excellent, as seen in the examples shown in Table 7. Concern was noted over results for mercury analysis as the typical detection limit of the instrument was above CCME limits. It was found that when metal contamination was observed, it was at levels well above the detection limits of the instrument. Additional steps, such as laboratory analysis on questionable samples, was performed to address concerns. Shown in the examples as well, was the trend of falsely identifying cobalt in field analysis. This finding was never confirmed by laboratory data and is likely a result of the effects caused by multiple metals, present in a single sample, interfering with the specific detection of metals.

In-situ examination of the soil for metal content, using the XRF unit, was possible but not utilized. The sacrifices to detection limit and the potential of damaging the instrument outweighed the benefits. An added asset discovered during the project was the ability of the Spectrace 9000 to be used to delineated historic fuel contaminated areas. Since lead was once used as a fuel additive, many historic fuel spill areas possess elevated lead levels. The low detection level for lead and the minimal sample preparation required, concluded in a rapid turn around time for results. The disadvantages of the portable XRF unit are that, it requires some training, the detection limits for certain metals is above the CCME guidelines, and the price of the unit of approximately $80,000 Considering that the capabilities of the Spectrace 9000 far surpass alternative technologies, the disadvantages listed are not unreasonable

Sub-sampling, for the purposes of field analysis, may have played a part in the outcome of the results as well An aliquot of the 250 mL soil sample collected was analysed. A potential existed that the aliquot was not representative of the sample as a whole. Results do not support this, however. Although there was a variation between laboratory and field data for the immunoassay kits, this was not the case for metal analysis. If systematic errors were present due to sub-sampling, there would have been an observable trend where field and laboratory metal results did not correlate

The measures taken to minimize the possibility of errors with field analysis entailed instituting proper quality control and assurance measures. These included the use of standard methodologies, where available, regular maintenance and calibration of the instruments, duplicate analysis, and a sampling/analysis log system. As well, a background sample was collected at each site and was included during analysis. The purpose of which was to obtain results which could be compared to those from samples collected in identified areas of concern Any naturally occurring chemical compounds, which may skew results, would be noted and compensated for in the results for the contaminated samples. In addition, it provides a valuable tool for comparison to false positive sample results, as often the same positive value appears in the background sample.

Conclusion

A comprehensive survey for chemical contamination of CCG facilities in Newfoundland and Labrador was carried out

A combination of in-situ field screening, onsite analysis and subsequent laboratory testing was incorporated into the program to obtain an accurate depiction of the contamination present. The methodologies and instrumentation employed were used under extreme environmental conditions and, from an operational point of view, performance met or surpassed expectations. Field screening data is not universally numerically equivalent to laboratory analysis but can be used by experienced and trained personnel to interpret the level of contamination and make recommendations regarding the need for further action.

The advantages realized, by using a combination of analysis techniques, was a reduction in the overall time and cost to carry out the project. By employing on-site field screening and analysis procedures, the cost of analysis was approximately 30% to that of the option of sending all samples for laboratory analysis.

Acknowledgments

The author would like to thank the staff and contractors at the Emergencies Science Division for their assistance throughout this project and to Mr. R. Turpin and Mr. P. Campagna, of the U.S. Environmental Protection Agency, for their technical assistance.

References

CCME (Canadian Council of Ministers of the Environment), *Guidance Manual on Sampling, Analysis, and Data Management for Contaminated Sites, Volume I: Main Report*, Report CCME-EPC-NCS62E, Winnipeg, Manitoba, 79 p., 1993a.

CCME (Canadian Council of Ministers of the Environment), *Guidance Manual on Sampling, Analysis, and Data Management for Contaminated Sites, Volume II: Analytical Method Summaries*, Report CCME-EPC-NCS66E, Winnipeg, Manitoba, 163 p., 1993b.

CCME (Canadian Council of Ministers of the Environment), *National Guidelines for Decommissioning Industrial Sites*, Report CCME-TS/WM-TRE013E, Winnipeg, Manitoba, 98 p., 1991a.

CCME (Canadian Council of Ministers of the Environment), *Interim Canadian Environmental Quality Criteria for Contaminated Sites*, Report CCME EPC-CS34, Winnipeg, Manitoba, 20 p., 1991b.

Environment Canada, *Environmental and Technical Information for Problem Spills Manual, Tetraethyl Lead*, Environmental Protection Service, Ottawa, Ontario, 86 p., 1985a.

Environment Canada, *Environmental and Technical Information for Problem Spills Manual, Zinc Sulphate*, Environmental Protection Service, Ottawa, Ontario, 84 p., 1985b

Environment Canada, *Environmental and Technical Information for Problem Spills Manual, Mercury*, Environmental Protection Service, Ottawa, Ontario, 119 p., 1984.

Public Works and Government Services Canada, *Environmental Audit/Baseline Site Assessments, Marine Navigation Sites*, Volume 1 and 2, Canadian Coast Guard, St. John's, Newfoundland, 144 p., 1995a.

Public Works and Government Services Canada, *Environmental Audit/Baseline Site Assessments, Lightstations*, Volume 1, 2 and 3, Canadian Coast Guard, St. John's, Newfoundland, 286 p., 1995b.

Rowell, M.J., J Ashworth, A.A Qureshi, *Bioremediation of Petroleum Hydrocarbons in Soil Environments*, Environment Canada Manuscript report Number EE-141, Ottawa, Ontario, 94 p., 1992

U.S Department of Health and Human Services, *Toxicological Profile for Fuel Oils*, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, 203 p., 1995a.

U.S. Department of Health and Human Services, *Toxicological Profile for Polycyclic Aromatic Hydrocarbons (PAH)*, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, 457 p., 1995b

U S. Department of Health and Human Services, *Toxicological Profile for Polychlorinated Biphenyls*, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, 363 p , 1995c.

U S. Department of Health and Human Services, *Toxicological Profile for Mineral-Based Crankcase Oil*, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, 117 p., 1994a

U.S Department of Health and Human Services, *Toxicological Profile for Mercury*, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, 357 p , 1994b.

U S Department of Health and Human Services, *Toxicological Profile for Zinc*, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, 229 p., 1994c.

U S. Department of Health and Human Services, *Toxicological Profile for Lead*, Agency for Toxic Substances and Disease Registry, Atlanta, Georgia, 307 p., 1993.

U S EPA (U.S. Environmental Protection Agency), *WinSPIRS™ Database*, SilverPlatter Information, Inc., Norwood, Massachusetts, 1995.

U S EPA (U S Environmental Protection Agency), *Standard Operating Procedure #1713, Spectrace 9000 Field Portable X-Ray Fluorescence Operating Procedure*, U.S. EPA Environmental Response Team, Edison, New Jersey, 33 p., 1992.

U.S. EPA (U.S. Environmental Protection Agency), *Standard Operating Procedure #2012, Soil Sampling*, U.S EPA Environmental Response Team, Edison, New Jersey, 17 p., 1988.

Chemistry and Health and Safety Aspects of Powell Duffryn Spill

Jim Farr, Nir Barnea,
National Oceanic and Atmospheric Administration

Charles Henry,
Louisiana State University

INTRODUCTION

On April 11, 1995, there was an explosion and fire at the Powell Duffryn facility on the Savannah River near Savannah, Georgia. This incident posed a very real public health threat to the community and it is appropriate that the response community try to establish a factual sequence of incident events. Most of the health issues pertained to the initial explosion and fire and the resultant production of toxic gases generated by the incompatible chemicals. Hopefully the lessons learned here will enable responders to more quickly and effectively deal with future accidents involving these types of chemical substances.

This paper reflects the NOAA on-scene chemist's observations, interpretations, and resulting conclusions about many of the chemistry issues that were continually being addressed during the weeks that followed the initial explosion. There was an inordinate amount of misinformation and confusion generated early into the incident. Initially, even the identities and amounts of the chemicals were inaccurately reported. Many safety issues arose as the conditions at the site and the resulting chemistry changed. There may be other interpretations of the observations than are presented here; we encourage all of those involved to read and comment on this report, as again, the goal is to learn and prepare for future incidents of this type.

Facility and Incident Location

Powell Duffryn is an international company operating tank facilities and repackaging chemicals for clients. The tank farm is about 3 miles east of the City of Savannah, Georgia. The facility is on the southern shore of the Savannah River and about half a mile upriver from Fort Jackson (Figure 1). The facility is only 50 meters (m) from the Oak Tree Apartment complex and 150 m from East Presidents Street. On the other side of East Presidents Street is a large residential area and an elementary school, located only 200 meters from the site.

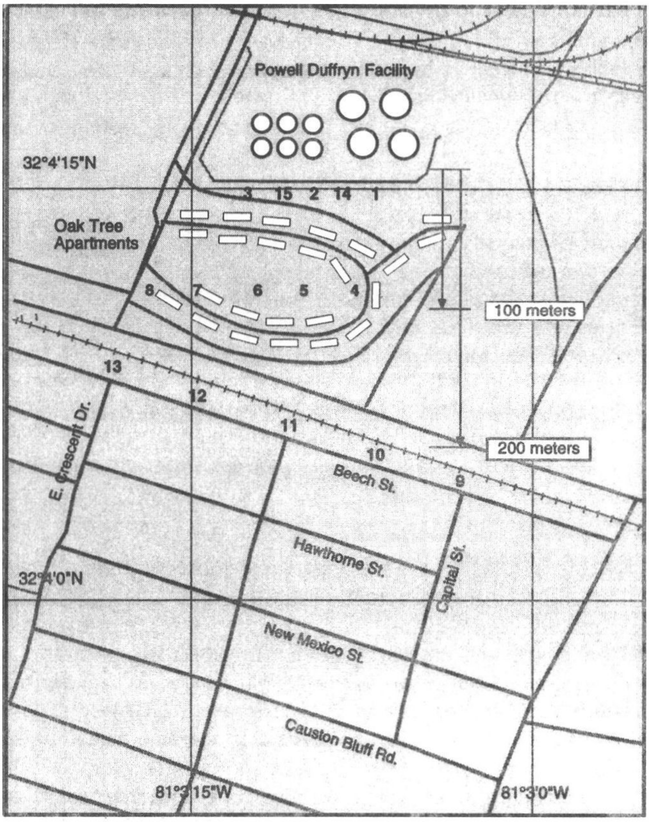


Figure 1. Overview of the Powell Duffryn storage facility in Savannah, Georgia.

Materials Involved in the incident

About 1,200,000 gallons of chemicals in six tanks were involved. The tanks shared a common berm wall 5 feet tall and 200 by 150 feet in length. The chemicals involved in the incident are listed in Table 1 below. An estimated 400,000 gallons were consumed in the initial explosion and fire and the remaining mixture drained into a ditch that led into a marsh and then into the Savannah River. The records of the contents and amounts stored in the tanks were lost in the fire, but it is believed that the tanks were full. The capacity of each tank was between 220,000 to 400,000 gallons. Complete Material Safety Data Sheets (MSDS) of each product were provided by the manufacturers.

Table 1. Chemicals involved in the Powell-Duffryn incident.:

- crude sulfate turpentine (CAS# 8006-64-2)
- a mixture of pinenes
- limonene
- beta phellandrene
- pine oil resins
- sodium hydrosulfide (NaSH), 45% solution in water)
- Antiblaze 80, tris (1-chloro-2-propyl) phosphate
- Briquest, a mixture of
  - hydrochloric acid
  - phosphoric acid,
  - (2-hydroxyethyl imino)
  - bismethylene bisphosphonic acid (CAS# 5995-42-6)
  - tetrahydro-2-hydroxy-4h-1,4,2-oxazaphosphorin-4-yl)methyl)-
  - (-phosphonic 0),a tank cleaning solution with pH=2)

INCIDENT OVERVIEW (Fire and Explosion)

Early Tuesday morning April 11, 1995, there was an explosion and fire at the Powell Duffryn facility on the Savannah River in Georgia. The cause of the initial explosion was investigated by The Bureau of Alcohol, Tobacco, and Firearms. ATF has not released information to explain the cause of the explosion. The three tanks of crude turpentine, a highly flammable liquid, had a combined volume of more than 600,000 gallons. Turpentine has a flash point of 95°F, an autoignition point of 488°F, and a lower explosive limit of 0.8 percent.

The fire that followed the explosion was not completely extinguished until the early morning of April 13. Except for the residue left in the tanks and that which was lost to the marsh, the fire caused the near complete combustion of all the turpentine product. During the fire, the 5-foot berm wall, along the western edge, was destroyed. A great deal of firefighting water, aqueous film forming foam, and product was lost over or through that berm wall.

Turpentine, primarily a combination of pinene, limonene, and pine oil resins, was the primary fuel for the fire. Combustion products and possible chemical incompatibilities of the materials in the tanks were identified early on (Table 2).

The flames from the fire were said to be 300 feet high and could be seen in Savannah nearly three miles away. Clouds of black smoke containing soot and turpentine residues were generated and the prevailing winds blew the

Table 2. Combustion products and possible chemical incompatibilities of chemicals.

CHEMICAL	REACTION NO FIRE	 FIRE
Crude sulfate turpentine and Antiblaze	None	Crude sulfate turpentine easily burns and produces incomplete combustion products: smoke, carbon monoxide (CO), and carbon dioxide (CO_2). Antiblaze doesn't easily burn, but if involved in a fire, it may burn and produce incomplete combustion products including phosphorous oxides, CO, CO_2, hydrochloric acid (HCl), phosgene ($COCl_2$), and phosphine gas (PH_3), the later only generated under highly reducing conditions
Crude sulfate turpentine and Briquest	Briquest may react to cause ignition of the crude sulfate turpentine. (ignition risk is very low).	Crude sulfate turpentine easily burns and produces incomplete combustion products: smoke, CO, and CO_2. Briquest will not burn, but if involved in a fire could decompose and produce HCl, $COCl_2$, and PH_3, the later only generated under highly reducing conditions
Crude sulfate turpentine and NaSH (pH>10)	NaSH solution when spilled in contact with the crude sulfate turpentine may generate enough heat to ignite the flammable liquid. When heated, NaSH will decompose and generate hydrogen sulfide gas (H_2S), a toxic, flammable gas.	Crude sulfate turpentine easily burns and produces incomplete combustion products: smoke, (CO, and CO_2. NaSH will not easily burn, but if involved in a fire will produce H_2S and sulfur oxides (SOx). Hydrogen sulfide burns to produce SOx. If H_2S is being produced, it is best to let the fire continue to burn.
NaSH (pH>10) and Briquest	If mixed, a chemical reaction will occur producing toxic (H_2S). H_2S may be generated in sufficient quantity to produce an explosive mixture.	Neither chemical is flammable, but both will decompose when heated. H_2S will burn to produce SOx. If H_2S is being produced, it is best to let the fire continue to burn.
NaSH and Antiblaze	Incompatible with production of heat, H_2S, and HCl.	Will not easily burn. (See 4 above if involved in a fire.)
Briquest and Antiblaze	Incompatible with possible production of heat and HCl and toxic fumes, such as phosphine, the later only generated under highly reducing conditions. In the case of this particular site and conditions it was thought that the risk of generation of phosphine was extremely low. There were no known, strong reducing agents at the site and it was difficult to conceive of a set of conditions that could produce reduced phosphorus from phosphate ion.	Will not easily burn.

smoke to the northwest and up the river. Smoke was observed over the city of Savannah.

Effect on the Marshland

One of the results of the intensely hot fire was destruction of the west side of the berm wall. At first, much of the material that was spilled was thought to be turpentine because it looked like the crude turpentine material. However, on further inspection, odor, and pH testing, the dark liquid was identified as NaSH. The pH of this diluted NaSH solution was in the range of 10 to 13. Much of that material was flowing into a canal that ran along the north edge of the facility. into a large marshland area to the east of Powell Duffryn's facility. The area had a strong odor of rotten eggs, as expected for H_2S. The NaSH in water reacts with carbonic acid (formed from dissolved CO_2 from the atmosphere) or any acid species present in solution to generate H_2S.

$$2NaSH + CO_2 + H_2O \rightarrow Na_2CO_3 + 2H_2S$$

Stabilization of the marsh rapidly became an important cleanup issue. H_2S and pH measurements were taken on a regular basis. Nearly all the contamination on- and off-site was from releases of NaSH. This product was stored as a 45-percent solution, with a pH of 14 and a specific gravity of about 1.3. NaSH is highly water soluble; it readily mixed with the fire-fighting water, and by April 15 had spread over an estimated 40 acres of marsh. Assuming an average water depth of 0.3 m over the areal spread of the contaminated water, it was estimated that there were 12 million gallons of contaminated water in the wetlands. This contaminated water remained a problem because of the residual reactive sulfide present. Released fugitive hydrogen sulfide gas, the toxicity of the dissolved sulfide, and high pH to the aquatic wildlife in the marshlands contributed to this hazard.

Berm Stabilization

After the fire was extinguished, a day of no action was required to allow the area around the berm to cool sufficiently to allow entry teams into the berm area to survey damage to the tanks. It was discovered that the tanks had been compromised by the heat of the fire and were leaking product into the berm. The most troubling observation was that the acidic Briquest solution was also leaking into the berm. It was determined that 50,000 gallons of the Briquest were unaccounted for and the acid had leaked and was reacting with the NaSH already present within the berm. Air monitoring around the berm for H_2S showed extremely high levels of the poisonous gas. The Briquest acid mixture could convert the NaSH sludge into H_2S. The conversion of the hydrosulfide ion (essentially only SH^- is present in aqueous solution) to H_2S takes place according to the equations on page 6.

$$SH^- + H^+ \rightarrow H_2S$$

and

$$S^{2-} + H_2O \rightarrow SH^- + OH^-$$

$$SH^- + H^+ \rightarrow H_2S$$

are accelerated at low pH.

Generation of a percent concentration of H_2S released versus pH curve showed that as pH decreases from 8.0 to 7.0, the amount of H_2S increased by 40 percent (Figure 2). At a pH of 5.0 the hydrosulfide ion is nearly 100 percent converted; therefore, at a pH slightly more acidic than natural fresh water, you would expect complete conversion to H_2S vapor.

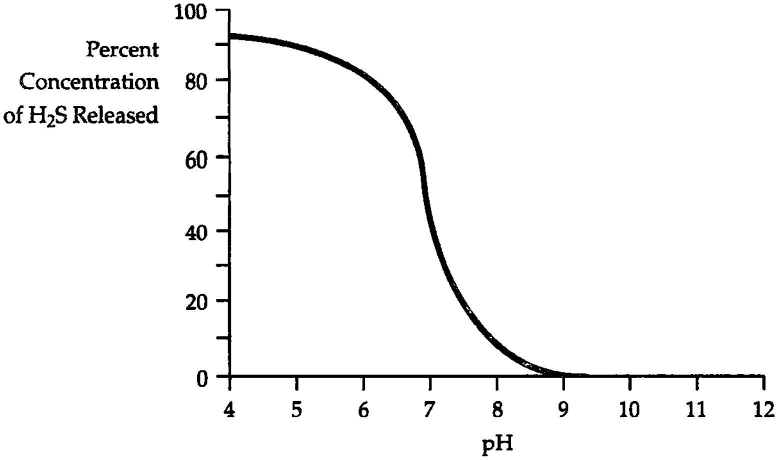


Figure 2. Percent H2S released versus pH.

Other poisonous gases such as PH_3, CO, $COCl_2$, and SO_2)were likely generated during the fire. These are combustion by-products and are normal consequences of combustion of materials of this type; however, after the fire was extinguished there was no plausible mechanism by which any of these gases could be generated in sufficient concentration to be considered a health threat especially in comparison with the active and potential health risk posed by the H_2S.

What was the magnitude of the potential health threat to the community posed by the H_2S? About 200,000 gallons of 44 percent NaSH had leaked within the berm (an unknown amount of this material leaked out by way of the western berm wall). The potential quantity of H_2S generated was about 300,000 pounds. There was a good possibility that the acid, if released into the berm, could yield an instantaneous production of H_2S because of the large amount of NaSH. On-scene personnel could not fully assess the structural integrity of the Briquest acid tank causing local officials and the OSC to evacuate the elementary school and the surrounding neighborhood on April 14, four days after the initial explosion and fire.

Increased concern for the identity and reactivity of the characteristically different materials observed within the facility's containment system resulted in a decision to conduct systematic sampling. During three Level A entries the USCG Strike Team conducted, eight solid samples and six liquid/solid samples were collected. The samples were returned to a staging area for characterization by NOAA and the Strike Team. All the liquid samples were producing H_2S gas as measured by meter above the liquid. The pH of each was measured and simple solubility tests were conducted to assess possible cleanup and response options. Here is a brief summary of the results of these tests:

1. Liquid, dark green—pH >12, NaSH/water.

2. Liquid, milky white/ gray—pH 3-5, probably residual Briquest acid mixed with additional chemical byproducts.

3. Liquid, clear—pH paper measured a 7 but this should be interpreted as no measurable pH, this liquid was initially thought to be Antiblaze-80, but never confirmed

4. Solid, yellow—soluble in water with the evolution of gas and increase in pH, this was solid NaS, and sodium sulfide (Na_2S).

5. Solid, white—soluble in water with no change in pH, probably an oxidation product such as Na_2S_2O or Na_2SO_4 and products of the acid/base reaction including sodium salts of phosphate (i.e., dibasic sodium phosphate).

6. Solid, yellow/green—mostly NaSH, and Na_2S.

7. Solid, gray—mostly soluble in water with increase in pH, this material is a mixture of solid NaSH, oxidation products such as Na_2S_2O or $Na_2SO_4^-$ and a black soot and insoluble metalsulfide complex .

8. Solid, black/green—mostly NaSH and a black soot and metalsulfide complex.

Overall, the berm was essentially a giant reactor, with an observable vigorous reaction with frothing boiling liquids, especially between tanks 18 and 21. A salt dome was visible near tank 21 and liquids were dark to milky white around the acid areas. The appearance of a white precipitate followed the dark green solution. The white precipitation formed a top crust along the surface. Workers in Level A, while breaking through the crust ,noticed the green solution under the white-crust layer. Breaking this crust was often accompanied by a vigorous exothermic reaction that seemed to indicated that different materials were present in separate layers and when allowed to mix, began reacting.

Fugitive emissions of H_2S continued to be a major concern, especially during the early morning hours of the second week of the spill response. The OSC and health officials urged more aggressive operations to stabilize the situation at the berm. Whatever was to be done had to be finished without further evacuation of the community. The emptying of the Briquest tank allowed response personnel to focus their attention on the sludge in the berm. This significantly reduced the risk of release of a large cloud of H_2S gas.

Continued pH sampling of the berm allowed responders a better idea of the nature of the sludge and all of its inhomogeneities. Contractors pumped more than 60,000 gallons of sludge from the low pH area between tanks 19 and 21 into three frac tanks. As a result, the next day's sampling gave pH readings that were uniformly high (>10) meaning that the risk of generating a large release of H_2S had been considerably reduced, although the homogeneity of the sludge material could still not be determined.

As an additional precaution against producing H_2S, it was suggested that NaOH be added to the berm at the surface and allowed to cover the sludge as a blanket. Since the acid had been partially removed, this could be done without a strong acid-base reaction occurring and causing any unpredictable consequences. Review of the chemistry of the mixture of NaSH and caustic is as follows:

$$NaSH + NaOH \rightarrow Na_2S + S^0 + H_2O \text{ (primary reaction)}$$

$$2Na_2S + 202 + H_2O \rightarrow Na_2S_2O_2 + NaOH$$

$$\mathrm{Na_2S_2O_2 + O_2 + H_2O \rightarrow Na_2SO_4 + NaOH}$$

Exposure of sodium sulfide (Na_2S) to air gives the following:

$$Na_2S + CO_2 + H_2O \rightarrow Na_2CO_3 + H_2S$$

and $$NaOH + H_2S \rightarrow NaHS + H_2O$$

The reaction of hydrosulfide with added NaOH produces elemental sulfur and Na_2S is slowly oxidizes to sulfate through the intermediate sulfite form. This reaction was confirmed by using the USCG Strike Team's field chemical-testing equipment. Sulfide and sulfates were confirmed by appropriate test procedures. Over time (a day or two) yellow sulfides/sulfites were slowly converted to the white sulfate precipitate. It is important to remember that

H_2S in the sludge was quickly converted back into hydrosulfide ion and not released into the atmosphere by the addition of caustic soda.

In conjunction with the addition of the caustic, cleanup contractors wanted to begin aggressive pumping of the sludge to the Marine Spill Response Corporation (MSRC) barge on the Savannah River, but there were two major concerns that had to be resolved:

> First, any kind of aggressive pumping would mix large quantities of the sludge. Concerns about the homogeneity of the sludge and, given the restraints of producing no fugitive gas into the surrounding community, precautions had to be considered.
>
> Second, the weather forecast was unfavorable for the next couple of days, light winds blowing toward the residential area, with nighttime inversion.

Because of these considerations, USCG personnel were advised that a small-scale pumping experiment be attempted and that off-gas concentrations of H_2S be monitored to determine concentration gradients that could be expected downwind.

The experiment was carried out the evening of April 24 when 2,000 gallons of the sludge was pumped into a stainless-steel vacuum truck. H_2S gases were measured at the exhaust and found to not exceed 38 ppm. Given this concentration and a predicted D Stability Class (light and variable winds) for April 25, dilution of the gases below odor thresholds was expected before entering any of the neighborhoods across East Presidents Street. Use of NOAA's air dispersion model, ALOHA (NOAA 1992), allowed responders to get a sense of the dilution pattern that would be expected. Dilutions of 1 to 10,000 in 200 m where the odor threshold was in the range of 10 ppb was expected. The nearest populated area was 300 m from the berm wall.

Because of the test results, a planned pump test of the berm was scheduled for the afternoon of April 25. To guard against a major release, 15 monitors were stationed downwind (Figure 3) of the site. Each monitor reported by radio every 2 minutes to the USCG command post. The OSC was listening and could call an end to the test at any moment if levels began to exceed 10 ppm at the 100-ppm line. Also H_2S monitoring began 15 minutes before pumping began to ascertain whether there was any measurable difference between pumping and non-pumping emissions. Pumping went on for 2 hours without incident. The pump test gave confidence that there was no significant difference in the amount of generated H_2S or rate of H_2S generation before or after the pumping activities; nothing was detected at 100 m except odors that seemed no worse than before pumping. It was concluded that the sludge could be pumped from the berm without affecting the community. Pumping the sludge was becoming more important as the berm had greatly deteriorated and was beginning to show signs of failure at several locations.

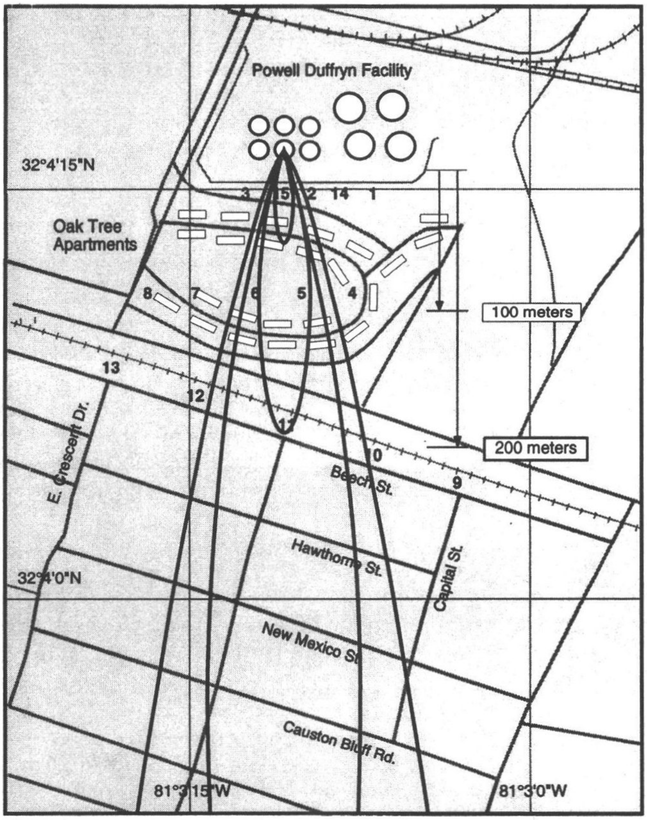


Figure 3. H_2S dilution contours at the Powell Duffryn storage facility. Each contour represents these dilutions: first = 1:1,000, second = 1:10,000, third = 1: 100,000, and fourth = 1:1,000,000.

As pumping began, caustic was added as a blanket over the sludge and pH and H_2S monitoring occurred around the edge of the berm on a nearly hourly basis. Results showed the pH was stabilized and H_2S levels were extremely low (<5 ppm).

Another problem at the berm area was the four feet of sludge remaining in the bottom of the NaSH tank. It was feared that over time the headspace in the tank would fill with H_2S generated from the sludge. If the headspace contained pure H_2S, it would yield a mass of 2,000 pounds of the gas; a very real threat of explosion. Because of this concern, a hose was dropped into the tank and the gas pumped into a NaOH tank. The H_2S/NaOH mixture becomes what is known as "White Liquor" and is stable in this form. This operation was discontinued when popping sounds were heard coming from the caustic tank. It was hypothesized that water vapor was being pumped into the concentrated caustic, generating heat that caused the NaOH to boil. The final solution of the headspace gas problem was to pump the vapors from the bottom of the tank through a charcoal-filter system.

Fractionization Tanks

A variety of types of storage tanks were used to store liquids from different on-site operations. They came in various sizes and shapes. Because of the large number of these storage tanks on-site, it became increasingly important to have some kind of status reporting system in place because of several safety issues raised while working around some of these tanks.

Probably the most serious problem concerning the frac tanks occurred on April 27. Tanks holding sludge from the vacuum pumping of the berm where the low pHs were identified, began emitting a burning-rubber-like odor. An inspection of the tank showed that material on the surface was an acidic dark viscous material. Unfortunately the frac tanks were not air-tight and the gases being generated were escaping from cracks in the metal on top. Samples were collected and sent for chemical analysis. Results of those analyses have not been received. One hypothesis for the source of the burnt-rubber smells was that disulfides and mercaptans were being created in the acidic environment. Reactive sulfide may have been added across olefinic bonds from the turpentine pinenes and other cyclic alkenes. in addition, residual material from the cleaned frac tanks may have reacted with the acids/bases. The disposition of these reactions are unknown.

HEALTH AND SAFETY

The health and safety problems introduced by this spill were substantial, and most were directly affected by the chemistry of the spilled materials in the berm. Therefore, they are discussed in some length below.

Initial Evacuation

The Powell Duffryn incident started at 1:00 a.m., April 11, 1995, with an explosion that shattered windows in the nearby Oak Tree Apartment complex. A fire ensued, which engulfed three turpentine storage tanks. Approximately 200 residents were evacuated from their homes shortly after the explosion.

At the initial stage of the incident, burning turpentine and other spilled products generated a large amount of smoke which drifted at times over populated areas. A level of concern (LOC) was developed by the Agency for Toxic Substances and Disease Registry (ATSDR) in consultation with NOAA and EPA. The LOC was developed for potentially exposed population downwind of the fire, both for particulates and for SO_2. If public exposure to the smoke was to exceed the LOC, further steps (including evacuation) would have been considered. Since synergism may occur between particulates and SO_2, LOC were developed as follows:

Particulates: 3.5 mg/m^3 if SO_2 is not present. 0.35 mg/m^3 if SO_2 is present

SO_2: 3 ppm if particulates are not present. 1 ppm if particulates are present

H_2S: 1 ppm if particulates are not present. 0.1 if particulates are present.

Monitoring

Monitoring was initiated at the request of the USCG FOSC. The EPA was in charge of the initial monitoring activities. Most of the air sampling conducted used real-time instruments so the sampling results could be read immediately and conveyed to the FOSC. The real-time methods were occasionally backed up by grab samples that were sent to the lab for analysis. Early in the response while the fire burned, the primary concern was the concentration of particulate emissions, primarily PM-10. Once the fire was extinguished, the monitoring shifted to H_2S emissions around the spill site and in adjacent neighborhoods. Initially, limited monitoring resources were available; therefore, a roving team approach was used. Eventually, the monitoring responsibility shifted to the USCG and the task was assigned to the National Strike Force (Gulf Strike Team) with additional technical assistance from NOAA. The number of monitoring instruments increased during the incident and the role of the monitoring team was rather dynamic; the monitoring locations and number of teams responded to changes during the incident. Overall, the monitoring was effective in providing the FOSC near real-time information to assess threats to both responders and the surrounding community.

Individuals suffering from respiratory or cardio-vascular illness may be more sensitive to the presence of SO_2 or particulate. It was recognized that for these individuals the LOC developed for particulates and SO_2 may be too high. Therefore, a voluntary evacuation option was presented to residents who wished to leave their homes because of exposure to the smoke.

Exposure to hydrogen sulfide

The hazard from the toxic constituents of the smoke diminished as the fire subsided. However, the level of H_2S, a toxic and foul smelling gas, became increasingly higher. The source of the gas was the spilled NaSH, which released H_2S upon contact with the spilled acidic Briquest and even upon contact with water from the fire fighting activity. It became apparent that these levels of H_2S present a risk not only to response personnel but to the nearby population. An air-sampling program was implemented to measure the level of H_2S both at the spill site and in nearby neighborhoods. The levels measured varied with wind direction and speed. At the berm the maximum concentration measured was about 200 ppm. At the nearby Oak Tree neighborhood and adjacent unevacuated neighborhoodthe levels varied between 0 and 10 ppm with occasional excursions. The maximum concentration of H_2S measured there was about 50 ppm for a very short time. The high level of H_2S necessitated response personnel use Level A and B when working near or within the berm.

Evacuation

Driven by concerns for the health and safety of nearby residents, the potential risk posed by a massive H_2S release was assessed. Four main factors were considered:

1. Structural integrity of the tanks: Both the Briquest and the NaSH tanks were exposed to high temperatures during the turpentine fire. The extent of the structural damage to the tank was not known. The leak from the NaSH tank increased and the Briquest leak was bigger than originally thought. The possibility of the leak increasing further or the tank totally failing and releasing the remaining Briquest was a major concern.

2. Large amount of spilled NaSH: Most of the berm area was covered with spilled NaSH, creating a large surface area of NaSH that could have readily reacted with Briquest. Had a large Briquest spill occurred, a massive amount of H_2S could have been generated over a short period of time.

3. Atmospheric conditions: On the night of April 14, atmospheric conditions were forecast to be stable, little or no wind, and possible inversion. These conditions could have greatly contributed to high concentrations of H_2S near the spill site.

4. Uncertainty: The level of uncertainty regarding possible H_2S exposure was high. Wind direction was unknown; (wind was expected to be "light and variable"); the structural integrity of both the NASH and Briquest tank was uncertain, and, based on the erratic H_2S concentrations measured that day, the magnitude of reaction taking place in the berm and the generation of H_2S were also uncertain. The high level of uncertainty contributed to the recommendation to evacuate.

The possibility of a massive H_2S release (worst-case scenario calculated the H_2S released at 300,000 pounds) and the forecast atmospheric conditions combined to form a serious threat. This threat was discussed with the local county emergency management authorities. Considering the options, they imposed a mandatory evacuation a half-mile radius from the spill site.

That night the measured H_2S concentrations around the berm area were as high as 300 ppm. The wind was light and variable, but fortunately the general wind direction carried the H_2S over the river rather than toward the nearby neighborhoods.

After the NaSH and Briquest tanks were emptied and the threat for a massive H_2S release diminished, an air sampling protocol was developed to assess the levels of H_2S at homes near the facility. ATSDR, in cooperation with other agencies, recommended a LOC of 0.05 ppm of H_2S, below which residents were allowed to return to their homes. At this level of concern some people could still detect the H_2S odor, but its health threat even to sensitive people, was negligable. Homes adjacent to the spill sites were sampled for H_2S, and when the level dropped below the LOC, residents were allowed to return to their homes.

Other concerns

Several issues were raised and addressed during the response. Among them was the possible generation of SO_2 and PH_3.

$\underline{SO_2 \text{ or } H_2S?}$

At some point when the generation of H_2S became a serious problem, the question was raised whether the gas generated by the reaction of NaSH and Briquest is H_2S or SO_2, and whether the air sampling conducted really measures H_2S or perhaps the monitors are cross sensitive to SO_2 and this is the gas that was being measured. Although careful examination of this issue was done earlier in order to assess the possible products of the NaSH and Briquest reaction, extensive communication was conducted between NOAA scientist and chemists and technical support personnel at the EPA, ATSDR, and several monitoring equipment manufacturers in order to put this issue rest.

Examination of the possible reactions of NaSH with the acidic Briquest concluded that during the fire, SO_2 was probably generated since it is a combustion or oxidation product of H_2S. A concern was raised that production of SO_2 could occur via a photochemical mechanism (absorption of ultraviolet light, followed by some photochemical oxidative process). However, there is no evidence that this occurs in a time frame that would make it a reasonable concern. In the absence of strong oxidizing conditions such as fire, or contact with strong chemical oxidizers, H_2S in the air will only slowly oxidize to SO_2, and the SO_2 in-turn will eventually become sulfuric acid in water droplets. The speed of that reaction depends on many factors, mostly humidity and temperature. That process is measured in hours and days rather than seconds. Besides, most of the biggest releases off site were measured in the darkness of early morning when there was very little wind and extremely stable air around the site. There seemed to be no mechanism for the generation of large quantities of SO_2 under the conditions of this spill.

The instruments used to sample H_2S have a sensor that oxidizes sulfur compounds to sulfates. These sensors vary somewhat among manufacturers. Usually instruments' cross sensitivity to SO_2 does not exceed 15 to 20 percent If only SO_2 is present in the air at a concentration of 10 ppm, the meter measuring H_2S will indicate 1.5 to 2 ppm

Considering this information, it seems that SO_2 was not generated in significant amount after the fire was extinguished, and that the monitoring for H_2S was conducted correctly.

Phosphine gas

Concern for another possible chemical hazard was raised late in the response. It was suggested that phosphine gas may be generated in open air in the berm and the frac tanks. The reduction of the phosphonic acid in the Briquest to form PH_3 was the only source of the gas. The mechanism for phosphate reduction could not be conceived given the conditions at the site.

The response was slowed by worries of PH_3 generation. Under such conditions, a professionally conducted air sampling could have proved or disproved the existence of PH_3. Unfortunately, H_2S, which was present in high concentration where PH_3 presence was suggested, interfered with the measurements of PH_3, giving a false-positive indication. Not until time-weighted-average sampling was done using sorbent tube (NIOSH method 6002) and the results came back negative was the issue put to rest.

CONCLUSIONS AND LESSONS LEARNED

This incident was unique in that it involved large amounts of incompatible chemicals that were brought together as a result of explosions and fire. Each part of the incident posed different hazards responders had to deal with. Because of its proximity to the community, public health issues immediately became the primary driving force in the response. Careful planning and execution of response options allowed for a successful conclusion without serious injury to responders or the public.

Chemical Assessment

It was clear during the incident, that accurate pH information was essential for predicting the behavior of toxic gas generation in the berm and the frac tanks. Initially pH measurements were taken with paper of unknown quality.and pH meters were giving readings that differed as much as three pH units. Given the sensitivity of the reaction mixture to pH the response team should have had adequate instrumentation to accomplish this type of basic chemical analysis.

Since there were unknown chemical species involved in this incident, it has been suggested that a mobile laboratory be present on-site. It is unclear if an on-site laboratory could have identified some of the unknown chemicals being generated in the mixture in the berm and frac tanks. Specialized sampling and analysis techniques would have had to be employed to successfully identify such compounds as phosphine and many of the disulfide species that were probably being generated by the combination of Briquest and reactive sulfide species. In addition, the cost of setting up and maintaining a functional laboratory is extremely high. Using, a fixed-site laboratory could be contracted to do rapid turnaround and non-standard analyses. Samples could be sent overnight and results returned the next day. Analyses would be run that fit the specific questions being raised at the site that often required specialized attention to a specific analyte or detection limit, which often requires the laboratory to use non-standard techniques to reach a beneficial conclusion

The use of draeger tubes is a well-established front-line method for emergency responders. The use of such methods has rather severe limitations as the tubes themselves cannot serve as a positive identification for the presence of a compound. In the case of Powell Duffryn, the presence of phosphine gas could neither be confirmed nor denied, because of the ever-present high concentration of H_2S gas,. Unfortunately, as a result of having no chemical analytical backup system for confirmation, the issue was never resolved. Its non-resolution caused much concern and use of project resources.

Health and Safety

The Powell Duffryn fire and spill created health and safety problems to response personnel working the general public.

The use of air sampling during this spill provided essential feedback to the FOSC. It also provided the information needed to determine whether residents could return to their homes. The lack of an effective real-time air sampling method for determining phosphine levels in the presence of high concentrations of H_2S exemplified the importance of specific and discriminating air sampling.

Evacuation of the general public during spill response happens infrequently, and when it does the decision to evacuate is debated and executed quickly. Time was at a premium. In this spill however, there was more time to examine the information available in a scientific and methodical way. The conditions on the site were carefully considered, and the pros and cons of evacuation (which carries its own risks) were debated. The evacuation option was brought to local officials, who, after being informed of the factors involved, made the decision to evacuate.

During an emergency response all the hazards endangering the responders and the public at large should be considered and carefully evaluated. We need to remember, however, that a rapid reduction or elimination of the factors endangering the responders or public health is often the safest way to reduce the hazard posed by an emergency or a spill. A response should slow down or stop if reasons exist to justify it. The reasons for such moves should be considered carefully, as conditions on site are constantly changing.

References

American Conference Of Governmental Industrial Hygienist, 1995-1996. *Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices.* ACGIH Technical Affairs Office, Cincinnati OH.

American Industrial Hygiene Association, 1991. *Emergency Response Planning Guidelines: Hydrogen Sulfide.* AIHA Publications, Akron, OH.

Klaasen, C. D., Amdur, M. O., Doull, J., Third Edition, 1986. *Toxicology, the Basic Science of Poison.* Macmillan Publishing Co. NY, NY.

Environment Canada, 1984. *Technical Information for Problem Spills: Hydrogen Sulfide.* Technical Services Branch, Ottawa, Ontario.

Agency for Toxic Substances and Disease Registry, 1996. ATSDR Record of Activity (unpublished).

NOAA, Hazardous Material Response and Assessment Division, 1995. First Class Hot Line, Incident # 177, Savannah River Explosion.

NOAA. 1992 *The ALOHA™ 5.1 Manual for the Apple Macintosh and IBM Compatibles*. Washington, D.C.: National Safety Council. 350 pp.

ENVIRONMENTAL IMPACT OF PENTACHLOROPHENOL (PCP)

Richard Lawuyi and Merv Fingas
Emergencies Science Division
Environmental Technology Centre
Environment Canada.
Ottawa, Ontario
K1A OH3

ABSTRACT

Pentachlorophenol (PCP) and its salts are purely anthropogenic, ubiquitous substances that have been widely identified with wood protection and preservation by virtue of their broad spectrum of antimicrobial characteristics. Industrially, their applications as fungicides, bacteriacides, herbicides, insecticides, ovicides, algicides and molluscicides are well known.

These substances enter the environment and work their way into the soil, surface water, ground water, food, air, mostly from treated utility poles and fences, during production, treatment facilities, hazardous waste sites, accidental spills, and its use as a pesticide.The major contaminants in commercial pentachlorophenol could be very toxic and include polychlorodibenzodioxins, polychlorodibenzofurans, polychlorodiphenyl ethers, chlorophenols, etc.

Many toxicologists have reported that short-term, high-level exposure that often occur during accidental spills can cause damage to the liver, kidneys, nervous system, blood and death in humans. Other researchers have shown they cause decrease in the number of offspring in animals. The use of PCP is now restricted both in Canada and the United States.

INTRODUCTION

For many years PCP and its salts were one of the most heavily-used substances in North America, having been introduced into commerce in 1936. They were mainly used as a timber preservative for the control of molds, wood-boring insects, termites and a variety of fungal rots (Bevenue and Beckman, 1967; Rao, 1978; Eisler,1989) . Their widespread use was due to their solubility in both aqueous and organic solvents. They were so successful that their use was extended to other applications such as in petrochemical drilling fluids, paints, oils, leather, masonry, paper mill systems, agricultural seeds, rope, and cooling tower water.

Unfortunately, PCP often contains impurities that are not only toxic to fungi and bacteria but lethal to other living organisms as well (ATSDR, 1992; Choudhry et al., 1986; Eisler, 1989). Its environmental impact includes not only human health but also the effects on plants and other environmental organisms, for example, aquatic species and wildlife. The impurities include the less chlorinated phenols, polychlorinated phenoxy phenols, polychlorinated dibenzo-p-dioxins and polychlorinated furans (Bevenue and Beckman, 1967). By the late 1980s pentachlorophenol and its impurities have become so ubiquitous in the environment that its use has now been restricted.

SPILL PROFILE

PCP and its salt enter the environment through a variety of sources such as mostly during wood treatment, spills, discharge at dump sites, other disinfecting uses, and also during manufacture. A vast majority of the spills were due to one or more of the following causes.

1. overflow
2. container leak
3. pipe leak
4. underground tank leak
5. intentional discharge
6. process upset
7. valve and fitting leak
8. unknown

Figure 1 shows the annual spill frequency of PCPs from 1982-92 (NATES 1996). There are very few spills, a total of 31 in eleven years. The frequency of spills has been decreasing since 1987 when major concerns were being raised and some restrictions considered.

FIGURE 1: SPILL PROFILE OF PCP 1982-92. ANNUAL SPILL FREQUENCY

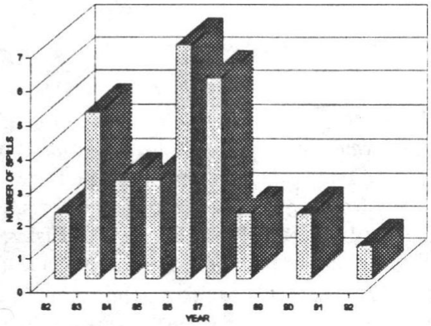


Figure 2 shows the annual spill quantity of PCP. The only major spill occurred in 1983 in Delson, Quebec. Others are in very small quantities.

FIGURE 2: SPILL PROFILE OF PCP 1982-92. ANNUAL SPILL QUANTITY.

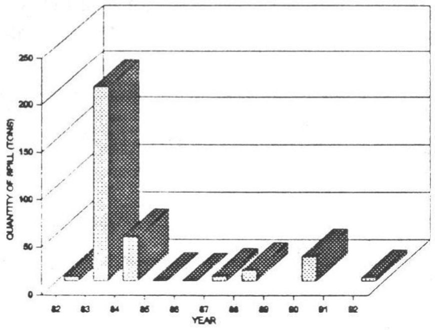


Figure 3 shows how the spill frequency of PCP compares with those of other commonly spilled commercial chemicals. Clearly, it is the least spilled substance in the group.

FIGURE 3: SPILL PROFILE OF PCP 1988-93. TOP 5 PRIORITY CHEMICALS COMPARED.

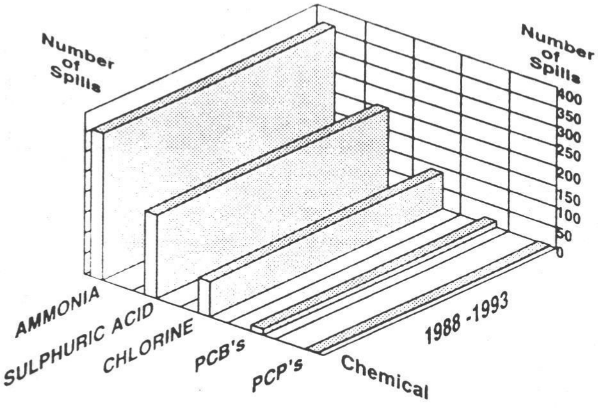


Table 1 shows how PCP is placed in a research study in our branch about five years ago, in which all hazardous chemicals were ranked according to their degree of hazard (Fingas et al., 1991). One of our goals then was to determine the minimum number of hazardous substances that were most frequently spilled. The list was developed by a simple ranking of: a) reported spill frequency, b) supply volumes, c) historical spill volumes and d) toxicity data, stability, accumulation, and persistence. Pentachlorophenol was placed tenth in the study.

TABLE 1: PRIORITY LIST RANKING OF HAZARDOUS CHEMICALS

CHEMICAL	RANKING	SPILL NUMBER	SPILL Quantity(t)	SUPPLY Quantity(Kt)
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

2. BEHAVIOUR AND ENVIRONMENTAL FATE DURING SPILLS.

There is little doubt that spills and discharges of PCP and its salts in the environment could disrupt many stable, ecological systems especially in localized populations. This may result in shifts of the abundant and predominant species be it microbes, plants or animals.

There are four possible sources of PCP in the environment:

1. Anthropogenic sources such as, wood treatment (Ahlborg and Thunberg, 1980), pesticides, chlorine bleaching of pulp and paper (Suntio et al., 1988), water chlorination (Detrick, 1977) etc.
2. Metabolic by-product of some microbial reactions e.g. hydrolysis of hexa- and pentachlorobenzene.
3. Natural sources such as in forest fires or during burning of fresh wood (Paasivirta et al., 1990).
4. Other biological origins have been suggested but are not conclusive (McDowell and Waladde, 1986).

Once introduced into the environment, PCP transport is very rapid. Transport often occurs through run-off waters, wood-treatment plant effluents, leaching, snowmelts, manufacturing plants sewage and evaporation (Bevenue and Beckman, 1967).

The behaviour of PCP and its salts in the environment is mostly determined by their physical and chemical properties. The most important ones are:

1. Solubility in aqueous and organic solvents
2. Sorption
3. Volatilization
4. Biodegradation and Persistence
5. Photodegradation

Solubility in aqueous and organic solvents

The solubilities of PCP and its salts tend to complement each other. While PCP is readily soluble in most organic solvents such as, oils, hydrocarbons, ethers, alcohols (ethanol 470-520 g/L), esters etc. it is only slightly soluble in water (14 mg/L at 20°C). On the other hand, sodium pentachlorophenate, its salt, is very soluble in water (330 g/L at 25°C) and only slightly in organic solvents. The solubilities of PCP and its salts are pH dependent. For example, the solubility of sodium or potassium pentachlorophenate in water increases from 79 mg/L at pH 5 to > 4 g/L at pH 8.0. High concentrations of these salts would, of course, have profound and adverse effects during exposure at high pHs. Differences in lipid solubilities also reflect different bioaccumulation potentials. Clearly, the highly lipophilic pentachlorophenol will be more prone to bioaccumulate than the salts. The toxic contaminants such as, tri-, tetra- and other chlorophenols isomers, dibenzofurans, dioxins, hexachlorobenzene, phenoxyphenols etc. that are often present in the technical grades are also lipophilic.

In terms of transport, during precipitation the readily soluble pentachlorophenate salts will most likely be dissolved and washed away in run-offs from spill and wood-treatment sites to rivers, lakes and streams or leached through the soil to groundwater while the lipophilic PCP will easily adsorb to soil material and sediments (Wan, 1992).

Sorption

The adsorption of pentachlorophenol by soils strongly depends on the chemical and physical properties of the soil, pH of the soil-water systems, the chemical species and their affinity for the soil surface (Callahan, 1979). Soil properties that can affect adsorption are grain size, soil pH, clay and organic carbon content. The organic matter includes mostly biodegradation products, humic and fulvic acids that usually cover the surface of soil particles. Large organic matter content tends to increase adsorption. Clay soil consists of fine particles with large surface area and large solid-water interfaces on which PCP molecules can adhere. The measured adsorption coeffient (K_{oc}) is 3,000-4,000.

The type of chemical species present will also influence adsorption. Pentachlorophenol behaves like a weak organic acid (pK_a=4.74, same as acetic acid). It ionizes in solution according to the following equilibrium:

$$C_6Cl_5OH \rightleftharpoons C_6Cl_5O^- + H^+$$

The equilibrium constant for the reaction increases with temperature and pH. A plot of the log of species concentrations (pC) with pH shows the relative amounts of dissociated and undissociated forms that are present as shown below (Figure 4). At low pHs the undissociated form of PCP is the predominant species, while at high pHs the reverse exists, the pentachlorophenate being the predominant species. Hence at low pHs the adsorption coefficient is high because the undissociated PCP is strongly adsorbed onto the soil particles by virtue of its affinity. On the other hand, at high pHs above the pK_a the pentachlorophenate ions (PCP^-) that have little affinity for the soil surface predominate and adsorption is greatly reduced. Another reason is that pentachlorophenate is more soluble at high pHs than lower pHs.

When PCP in solution is added to the soil, the PCP molecules adsorb on to the of the soil particles until an equilibrium is reached at the liquid and soil particle interface. The model that is often used for solid-liquid systems is the Freundlich equation:

$$q = K_f C^{1/n}$$

where

q is the amount chemical adsorbed per unit weight of adsorbent

K_f and 1/n are contants

C is the equilibrium concentration in the liquid phase

Figure 5 shows adsorption isotherms for PCP in the soil at pHs of 7 and 10. These adsorption isotherms seem to follow the Freundlich behaviour. It could be seen that solute sorption at pH 7 is much than at pH 10. Figure 6 shows the adsorption isotherms for four different types of soils. The adsorption capacity in medium sand seems to be the least while that of loam the highest.

FIGURE 4: SPECIES DISTRIBUTION FOR PENTACHLOROPHENOL IONIZATION

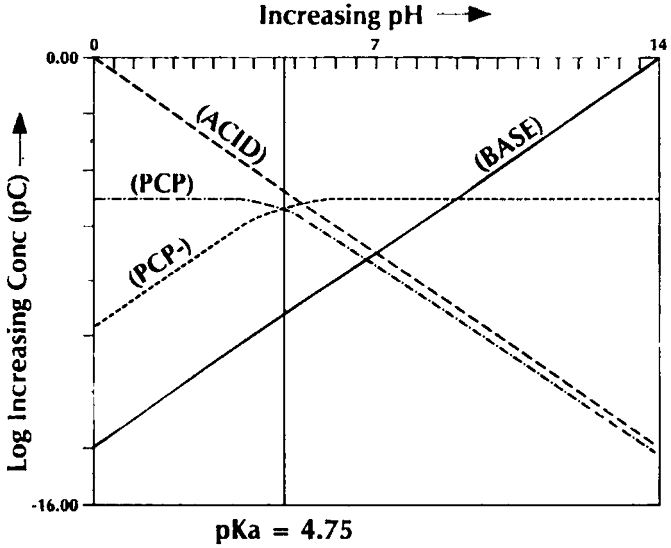


FIGURE 5: ADSORPTION ISOTHERMS OF PCP IN SOIL AT pH 7 AND 10

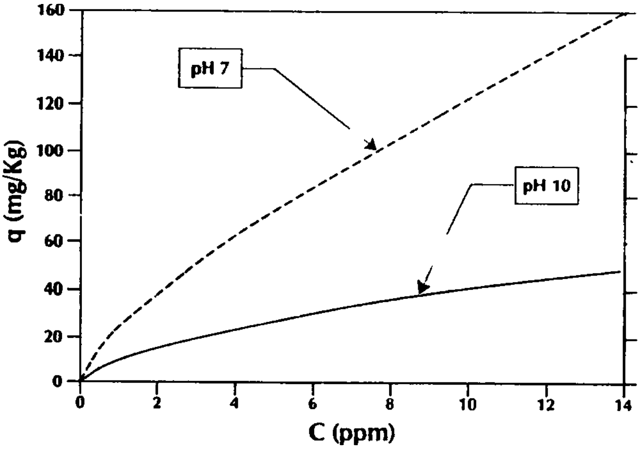
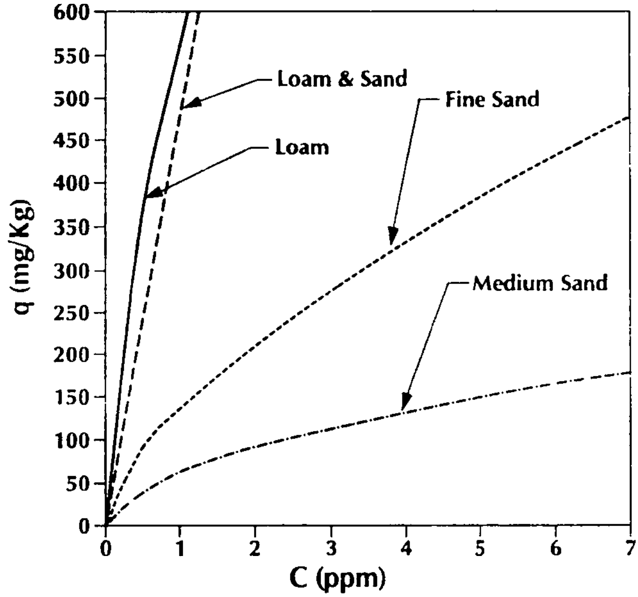


FIGURE 6: ADSORPTION ISOTHERMS OF PCP FOR FOUR SOILS



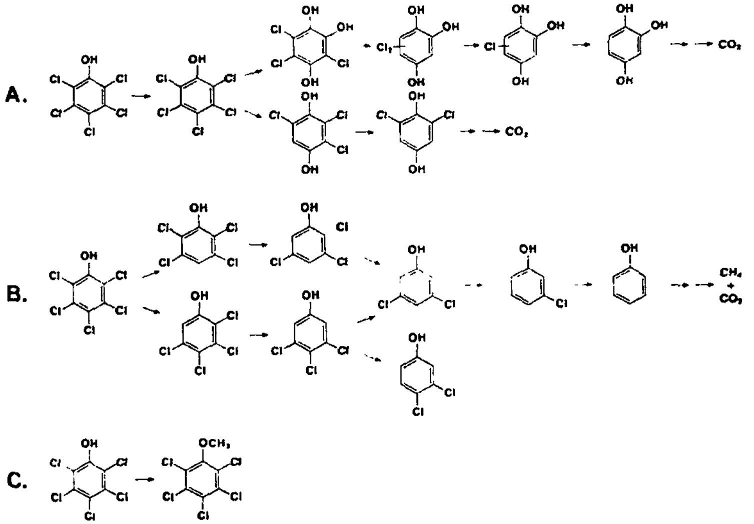
Volatilization

PCP is not a volatile substance even though it is easy to detect in the air where ever it is being used (the vapour pressure is 0.00011 mm at 20°C; methanol is 92 mm at 20°C). One reason is that most aqueous solutions are at pH 7 when PCP is already in ionized form. Transport by evaporation is therefore not an important process (Callahan et al., 1979). However, it has been shown to volatilize in special pesticide formulations as aerosols or mists. Significant quantities have been detected in air and precipitation (Boyd, 1989; Weiss et al., 1982). PCP has been found to evaporate at high temperatures and humidity and volatilization is a probable means of transference into the air (Kozak et al., 1979).

Biodegradation and persistence

The microbial degradation of pentachlorophenol has been well studied and the pathways determined (Boyd, 1989, Haggblom and Valo, 1995). The concensus is that although it is rather persistent in the soil and groundwater it is degradable either by photochemical, microbiological, or chemical processes. PCP has been biodegraded by different strains of bacteria and fungi to produce differing products and a number of these bacteria have been isolated. The degradation pathways seem to differ with different microbial groups (Tabak et al., 1981). A number of these are aerobic, while others are obligately anaerobic. Polychlorinated phenols are in the main degraded by initial dechlorination, followed by hydroxylation and reductive dechlorinations. Ring cleavage often occurs after most of the chlorines have been removed. As shown in Figure 7 chlorinated catechols, quinones, and hydroquinones are the central intermediates in the biodegradation of PCP. Methylation of PCP produces anisoles which are more hydrophobic, more resistant to degradation and may bioaccumulate. In many organisms PCP is rapidly bioaccumulated and excreted, biomagnification does not occur in the food chain. Biodegradation is the most predominant process for PCP removal from the environment. PCP has been known to persist in soils for 15 to more than 60 days depending on the type of soils. In warm, moist soils PCP was still detectable after 12 months. The half-life of PCP in water ranged from 0.15 to 15 days; in the presence of bacteria alone it was 5-12 hours.

FIGURE 7: BIODEGRADATION AND BIOTRANSFORMATION PATHWAYS OF PCP (A) ANAEROBIC (B) AEROBIC AND (C) O-METHYLATION



Photodegradation

PCP readily absorbs sunlight in the UV region (wavelength=320 nm). Irradiation of dilute aqueous solution of PCP with sunlight or UV light has been found to be an effective means of degradation, yielding chlorinated phenols, trichlorobenzoquinones, non-aromatic fragments such as dichloromaleic acid (Callahan et al., 1979; Weiss et al., 1982; Ghoshal et al., 1992). Octachlorodibenzo-p-dioxin and furans have also been detected when PCP and sodium pentachlorophenate were irradiated. Photodegradation is definitely significant in PCP removal from the environment.

FIGURE 8: PHOTOLYSIS OF PENTACHLOROPHENOL

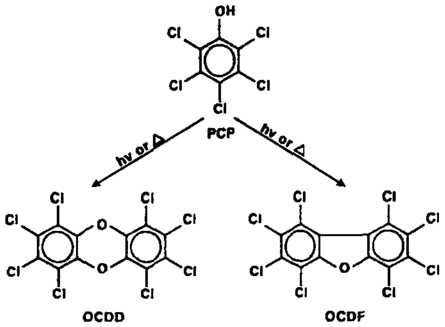
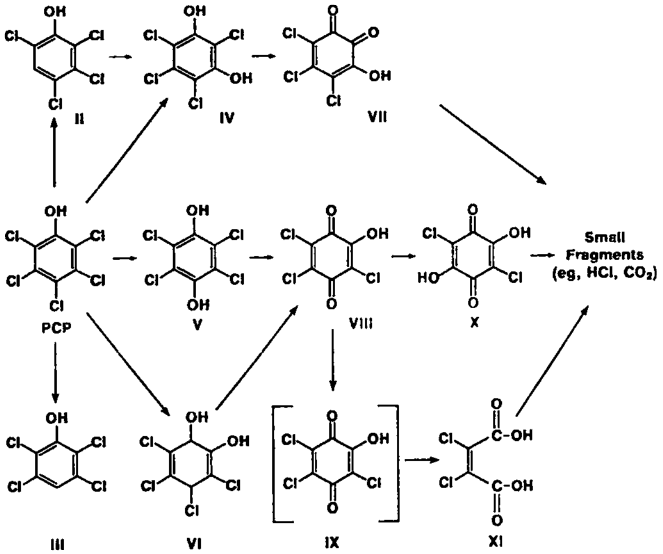


FIGURE 9: PROPOSED PATHWAY FOR PCP PHOTODEGRADATION



Spill on Land

When pentachlorophenol solution in oil or the aqueous solution of the sodium salt is spilled on land, after initial settling, some overland flow will occcur depending on the quantity spilled. The pentachlorophenol oil solution will mostly be adsorbed to the soil while the aqueous solution will be much less adsorbed. Leaching to groundwater can occur in both cases. Little evaporation will occur but some biodegradation and photodegradation will, depending on the moisture content, pH, organic matter content and the bacteria strains. Some of the spill will, however, be washed off in run-offs during precipitation to rivers and streams. One incident involving a PCP spill occurred when telephone poles were resprayed. In 1975, a company sprayed the base of a number of telephone poles to prevent rot. In one month 15 fish kills were reported. The fish kills were all found to be caused by the wash-off from the sprayed poles. The poles were all close to the stream where the kill occurred, heavy rains having washed the solution some distance to the stream.

Spill on Water

When released into water bodies, PCP will readily dissociate at ordinary pHs (for PCP, pKa =4.74) to produce the pentachlorophenate, sodium, and hydrogen ions in the water. Any undissolved PCP will eventually end up in the sediments. Some photolysis and biodegradation will occur. Evaporation will be negligible. An incident of PCP pollution occurred after a four inch rainfall at a lumber treatment site. The treatment tank containing 10,000 ppm penta- and tetrachlorophenol, overflowed into a stream killing 5,000 adult coho salmon.

3. CHEMISTRY

Manufacture

The most common method for the manufacture of pentachlorophenol is the progressive chlorination of phenols in the presence of catalysts. Another method specific for 2,4,5-trichlorophenol and pentachlorophenol is by hydrolysis of chlorobenzenes such as penta- and hexachlorobenzene. In general, the hydrolysis method always produces more impurities. The final product is a horrendous mixture often containing a couple or more of the following compounds:

Dichlorophenol
Trichlorophenol
Tetrachlorophenol
Hexachlorobenzene
Tetrachlorodibenzodioxin
Hexachlorodibenzodioxin
Heptachlorodibenzodioxin
Octachlorodibenzodioxin
Pentachlorodibenzofuran
Hexachlorodibenzofuran
Heptachlorodibenzofuran
Octachlorodibenzofuran
Heptachlorohydroxydiphenyl ether
Octachlorohydroxydiphenyl ether.

Reactions

Pentachlorophenol while essentially an aromatic alcohol is a rather acidic substance. This is because the pentachlorophenate anion is resonance stabilized by the aromatic ring resulting in increased stability for this anion. The electron-withdrawing chlorines also delocalizes the negative charge (electrons) on the oxygen thus making the proton easily removable and hence much more acidic ($pK_a=4.7$).

1. Acid-Base Reactions

Pentachlorophenols will react with bases to produce a salt, sodium pentachlorophenate, and water.

FIGURE 10: MANUFACTURE OF PCP

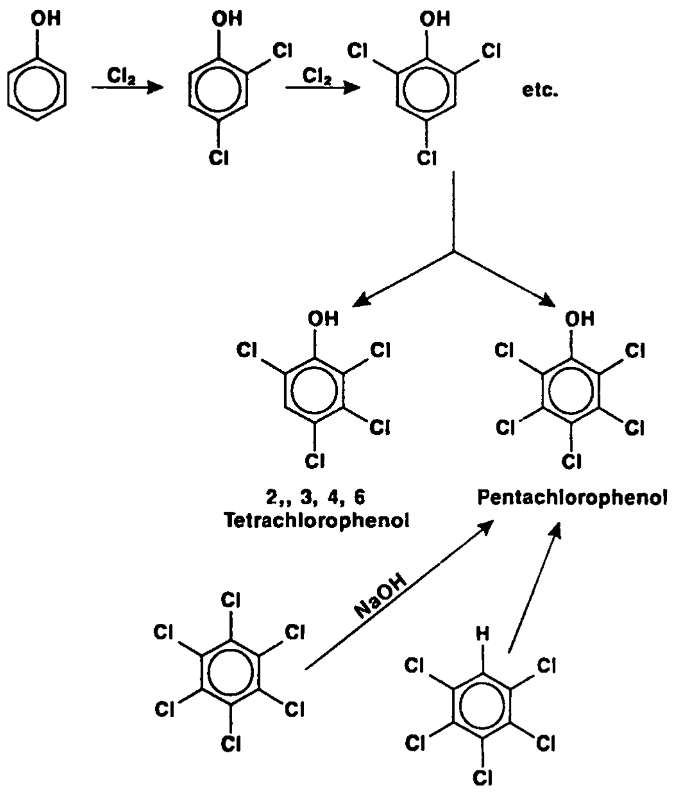
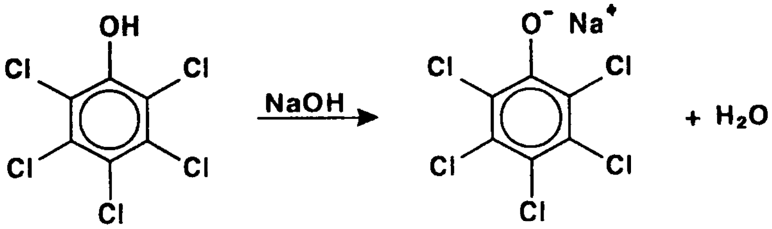


FIGURE 11: ACID-BASE REACTION OF PCP

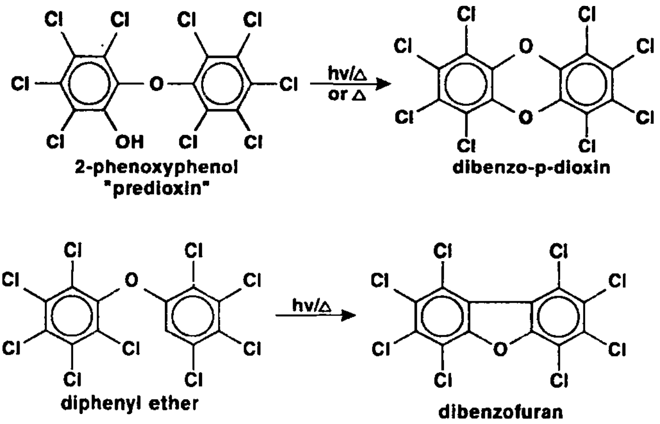


Pentachlorophenol

2. Formation of Dioxins and Furans.

When heated PCP will form chlorinated diphenyl ethers which can further react to produce chlorinated dioxins and furans. This is why wood treated with PCP should only be burned at controlled temperatures.

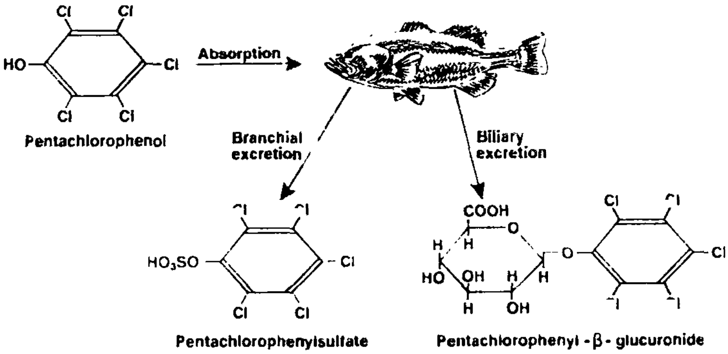
FIGURE 12: FORMATION OF DIOXINS AND FURANS



3. Formation of other Ethers

PCP will also take part in nucleophilic displacement reactions to produce the non toxic conjugates such as sulphates, glucoronides and anisoles. This is the principal process for the elimination of PCP in fish and many mammals (Kobayashi et al., 1977; Glickman et al., 1977).

FIGURE 13: DETOXIFICATION PATHWAY FOR PCP



TOXICOLOGICAL PROFILE

The toxic effects of PCP are not only due to the undissociated PCP but other impurities such as the polychlorinated dioxins, furans and ethers. PCP formulations in oil are therefore more toxic than in aqueous media.

Acute Effects During Spills.

PCP causes severe irritation of the eyes, skin and upper respiratory tract. Even at moderate concentrations coughing, violent sneezing, pain in the nose and throat, dizziness, convulsions and unconsciousness can develop and in extreme cases, fatal. Acute toxicity is the result of uncoupling of mitochondrial oxidative phosphorylation (Eisler, 1989; ATSDR, 1992). The eventual stimulation of cell activities can produce heat stress. Other acute effects include increase in alkaline phosphatase, blood urea nitrogen and serum creatinine. Excessive exposure can cause damage to the liver, kidneys, skin, blood, gastrointestinal tract, nervous and immune system and death. Many deaths have been reported as a result of unnecessary exposure and improper handling of treated lumber and sawdust. Some of symptoms of poisoning are general weakness, vomiting, nausea, abdominal pain, headache, anorexia, intense thirst, pain in the extremeties, tachycardia (rapid heartbeat), tachypnea (rapid breathing), hypertension and fevers (Wood, 1983).

Chronic Exposure

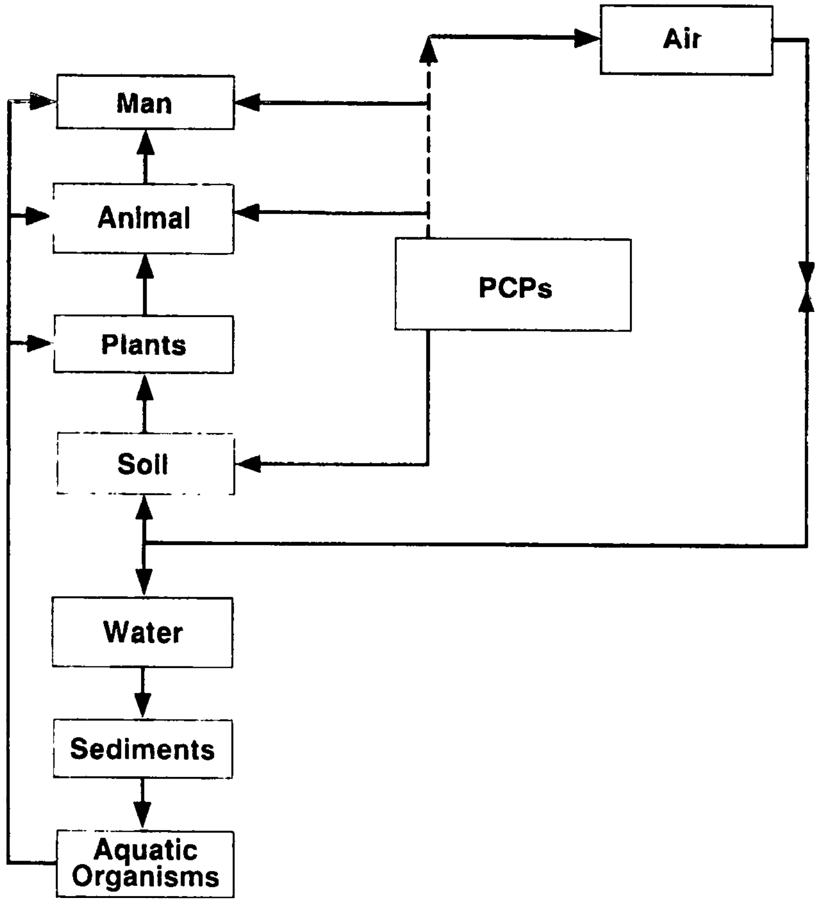
Acute effects are often pronounced during chronic exposure as in occupational setting. These include: conjunctivitis, chronic sinusitis, bronchitis, dermatitis and polyneuritis. Presence of impurities such as dioxins and furans can cause chloracne (ATSDR, 1992). Many animal studies have shown that the immune system is adversely affected on prolonged exposure (Bevenue and Beckman, 1967; Roszell and Anderson, 1994). Increased susceptibility to tumors growth was observed in mice fed diets containing 50-500 ppm PCP. Exposure of newborn guppies to the toxicant caused decreased growth, increased mortality and delayed sexual maturity (Crandall and Goodnight, 1962). When administered to pregnant rats in doses of 5-50 mg/kg bw/d, symptoms of fetotoxicity were observed (Schwetz et al., 1974); these include dilated ureters, resorptions, subcutaneous edema and anomalies in the bones structure. Evidence of carcinogenicity has also been found in mice for some PCP mixtures. Mice fed diets with 100-200 ppm technical grade PCP showed increased incidences of heamangiosarcomas and hepatocellular neoplasms. Another group of male and female mice given up to 600 ppm PCP, showed increased incidences of adrenal medullary and hepatocellular neoplasms. However, no concensus on its carcinogenicity has been reached. So far the weight of evidence supports its being negative.

CONCLUSION

There is no doubt that the persistence of PCP and its impurities has been of concern since the late seventies. Like many chlorinated organics, the long-term effects of this substance and its contaminants have not been clearly defined. It is now known that though PCP is readily metabolized in animal tissues and in the environment, many of its metabolites such as the anisoles, and impurities such as dioxins, furans and diphenyl ethers are even more toxic or persistent. Not much is known about the toxicity of the tetra-, tri- and dichlorophenol precursors. PCP use as a pesticide is now restricted.

With PCP, environmentalists are presented with a dilema. The use of PCP in wood preservation definitely increases the life of timber which means less tree cutting with the attendant environmental degradation. One solution is finding a wood substitute without the attendant environmental pollutants. A restricted use of PCP is therefore in order.

FIGURE 14: PCP IMPACT SUMMARY



References:

Ahlborg, U.G. and T.M. Thunberg, "Chlorinated Phenols: Occurrence, Toxicity, Metabolism and Environmental Impact", *CRC Crit. Rev. Toxicol.* 7: 1-35 (1980)

ATSDR. *Toxicological Profile for Pentachlorophenol,* U.S. Department of Health and Human Services, 1992

Bevenue, A. and H. Beckman, "Pentachlorophenol: A Discussion of its Properties and its Occurrence as a Residue in Human and Animal Tissues". *Residue Reviews,* 19: 83-134 (1967) .

Boyd, S.A.(Author). Sawhney, B.L., and K. Brown (eds.), "Chlorophenols in Soils" *in: Reactions and Movement of Organic Chemicals in Soils,* Soil Sci. Society, 209-228 (1989).

Callahan, M.A. et al., *Water-Related Environmental Fate of 129 Priority Pollutants,* p87-94, EPA-440/4-79-029b, 1979.

Choudhry, H., J. Coleman, L.T. De Rosa and J.F. Stara, "Pentachlorophenol: Health and Environmental Effects Profile", *Toxicology and Industrial Health,* 2 483-571 (1986).

Crandall, C.A. and C.J. Goodnight, "Effects of Sublethal Concentrations of Several Toxicants on the Growth of the Common Guppy, *Lebistes reticulatus", Limnol. Oceanogr.,*7:233-239 (1962).

Detrick, R.S., "Pentachlorophenol, Possible Sources of Human Exposure", *Forest Products,* 27:13-16 (1977).

Eisler, R., "Pentachlorophenol Hazards to Fish, Wildlife and Invertebrates: A Synoptic Review", *Contaminants Hazard Review-17,* pp. 83, NTIS. (1989).

Fingas, M., 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, 1991.

Ghoshal, S., S.K. Banerji and R.K. Bajpai, "Role of Photodegradation in Pentachlorophenol Decontamination in Soils", *Annals of the New York Academy of Sci,.* 665, VII, 412-422 (1992).

Glickman, A.H., C.N. Statham, A.Wu, and J.J. Lech, "Studies on the Uptake, Metabolism and Disposition of Pentachlorophenol and Pentachloroanisole in Rainbow Trout", *Toxicol. Appl. Pharmacol.,* 41:649 (1977)

Haggblom, M.M. and R.J. Valo., "Bioremediation of Chlorophenols Wastes", in: *Microbial Transformation and Degradation of Toxic Organic chemicals*, p389-434, Wiley-Liss Inc. 1995.

Kobayashi, K., S. Kimura, and E. Shimizu, "Studies on the Metabolism of Chlorophenols in Fish - IX. Isolation and Identification of Pentachlorophenols-B-glucuronide Accumulated in Bile of Goldfish", *Bull. Japan Sci. Fish.*, 43:601-607 (1977)

Kozak, V.P., G.V. Simsiman, G. Chesters, D. Stensby, J. Harkin, *Reviews of the Environmental Effects of Pollutants: XI Chlorophenols*,US EPA Health Effects Research Laboratory, EPA-600/1-79-012, Cincinnati, Ohio. 1979.

McDowell, P.G., and S.M. Waladde, "2,6-Dichlorophenol in the Tick, *Rhicephalus appendiculatus* Neumann. A Reappraisal", *J. Chem. Ecol*, 12:69-81 (1986).

NATES, *National Analysis of Trends in Emergencies System*, Environment Canada, 1996.

Paasivirta, J., H. Hakala, J. Knuutinen, T. Otollinen, J. Sarkka, L. Welling, R. Paukku, and R. Lammi, "Organic Chlorine Compounds in Lake Sediments. III. Chlorohydrocarbons, free and Chemically Bound Chlorophenols", *Chemosphere*, 21:1355-1370 (1990)

Rao, K.R.(ed.)., *Pentachlorophenol Chemistry, Pharmacology, and Environmental Toxicology*, Plenum Press, New York, 1978.

Roszell, L.E. and R.S. Anderson, "Inhibition of Phagocytosis and Superoxide Production by Pentachlorophenol in Two Leukocyte Subpopulations from *Fundulus heteroclitus* ", *Marine Environ. Res.*, 38:195-206 (1994)

Schwetz, B.A. et al., "The Effect of Purified and Commercial Grade Pentachlorophenol on Rat Embryonal and Fetal Development", *Toxicol. Appl. Pharmacol.*, 28:151-161 (1974).

Suntio, L.R., W.Y. Shiu, and D. Mackay, "A Review of the Nature and Properties of Chemicals Present in PulP Mill Effluents", *Chemosphere*, 17: 1249-1290 (1988).

Tabak, H.H., *J Water Pollut Control Fed* ,53: 1503-18 /(1981).

Wan, M.T., "Utility and Railway Right-of-Way Contaminants in British Columbia: Chlorophenols", *J. Environ. Q.*, 21:225-231 (1992).

Weiss, U., P. Moza, I. Scheunert, A.Hague and F.Korte, "Fate of pentachlorophenol-^{14}C in rice plants under controlled conditions", *J. Agric. Food Chem.* 30:1186-1190(1982a).

Weiss, U., I. Scheunert, W. Klein, and F. Korte, "Fate of pentachlorophenol-^{14}C under controlled conditions", *J. Agric. Food Chem.* 30:1191-1194(1982b).

Wood, S.et al., "Pentachlorophenol Poisoning", *J. Occup Med.*, 25:527-530 (1983)

LPG TANK FAILURE: Ste. Élisabeth de Warwick, Quebec, June 27, 1993; The Lessons to be Learned.

Y. Xiong, Jian Xu and J.E.S. Venart
Fire Science Centre and Department of Mechanical Engineering
The University of New Brunswick
P.O. Box 4400, Fredericton, N.B., E3B 5A3
(506) 453-4513 Ph.; (506) 453-5025 Fx.

ABSTRACT

A 1000 US gallon, horizontal propane tank suddenly circumferentially separated at its central section while under fire attack near Ste. Élisabeth de Warwick on June 27, 1993. The vessel was exposed on one side, one end and its top to fire burning on the walls of a barn and its attached milk house. An analysis has been made of the possible thermal loading on the tank and its consequent thermal stress state. This, along with an examination of some of the tank remnants, photographic, eyewitness and metallurgical evidence, coupled with cone calorimeter testing of the paint coatings on the vessel and reviews of the official report on the incident permits conclusions to be made relative to the possible reasons for the failure of the tank. Recommendations are made in order to prevent similar accidents in the future.

1. INTRODUCTION

On June 27, 1993, at Ste. Élisabeth de Warwick, Quebec, a 3785 l (1000 US gallon) horizontal propane tank suddenly circumferentially separated at its central section. The vessel was exposed on one side, one end and its top to fire burning on the walls of a barn and its attached milk house (Fig. 1).

The tank was 4.915 m (16'-1 1/2") overall length and 1.029 m (40.5") inside diameter with hemispherical ends. One side of the tank was located 3.436 m (11.272') from the milk room wall. One end of the vessel was only 2.713 m (8.9') from the barn wall and was thus placed approximately 10 percent less than the separation distance required,(3 m), by Canadian Gas Association (CGA) recommendations [1].

The tank was stated to have been designed and approved for a maximum allowable working pressure (MAWP) of 1.824 MPa (250 psig) at 51.7°C (125°F) under ASME Section VIII code requirements. The bronze pressure relief valve was located at the far cold end of the cylinder barrel (Fig. 1). The valve orifice was 2.286 cm^2 (1.25 in^2) and had an ASME capacity of 4640 SCFM, air (4406 SCFM(UL))[2].

There were also the other usual fittings suitable for a two-stage bulk tank system. These consisted, in part, of a fill line and valve with over-fill protection, a high pressure first stage regulator and a vertically mounted liquid level gauge. These last two items were located under the protection of a light gauge pressed sheet steel dome hinged on one side located on top near the center of the vessel.

In the course of the incident, a fire, which had developed in the milking parlor and attached barn, caused flames to radiate upon one end, side and top of the tank causing the metal to heat, along with its contents, so that with time the PRV opened and vented (reportedly ∿3 times of 10 to 15 s duration [2]). The tank was stated to be 55 % full at the time of its failure [3].

Firemen, who had arrived some 12 minutes after the alarm and some 30 minutes into the event noted, as they commenced their setup, that the dome cover was in place and that flame appeared to be encircling the tank at its midpoint in addition to the extensive radiant loading from the fires burning on the walls of the building.

While setting up to attack the fire the firemen heard a "pop" and "whoosh" with the establishment of a near vertical jet flame, about 10 m high, from the top of the central tank region [2]. Firemen commenced an approach to the barn in an attempt to lessen the radiant load on the vessel by applying water through a 38 mm (1 1/2") diameter nozzle in the space between the wall of the milking room and the tank. Water application had only just begun (∿1 min.) when the tank suddenly circumferentially separated. The two halves of the vessel were projected ∿ 109 m (for the cold end) and 122 m (for the hot end). There were four fatalities and 5 injuries [3].

The major question to answer is why the vessel failed circumferentially and in such an abrupt manner; another is why there were so many fatalities?

The material which follows deals with the transient and steady state thermal condition of the tank and its contents and their influence on the stress state of the vessel. In addition our visual and physical examination of the tank and some of its components, available photographs [4] and eyewitness accounts [2], a review of the official report into the incident [5] as well as our metallographic and other evaluations of some portions of the tank and its joints [6] permit a detailed assessment of the event and determination of possible causes. The paper concludes with some recommendations to prevent similar failures and loss of life in the future.

2. THERMAL STATE OF THE VESSEL AND ITS CONTENTS

In order to estimate the temperature of the walls of the tank and the time dependent pressure behaviour of its contents both a PLGS_4 [7] thermohydraulic and an ANSYS [8] finite element thermal model of the vessel, its contents and surroundings were made.

2.1 The PLGS_4 Thermohydraulic Model

The PLGS_4 program [7] simulates the full or partial fire engulfment of horizontal and vertical cylindrical tanks as well as spherical vessels of a pressure liquefied gas (PLG) fitted with a pressure relief valve (PRD). The program has been checked and verified. Validation of the program simulations have been carried out against small scale (40 l) R 11 laboratory experiments conducted at UNB and medium scale (1- 5 tonne) pool fire exposure trials against horizontal cylindrical propane vessels experiments carried out by the Health and Safety Laboratory, (HSL), of the United Kingdom Health and Safety Executive, (HSE). The program, in a modified form, has been utilized in the evaluation of recommendations to the IMO for the safe filling limits of marine PLG vessels (SIGTTO).

The results of these simulations are discussed relative to the ANSYS analyses which follow.

2.2 The Transient ANSYS Thermal Model

The thermal problem is a complex transient combined convection and radiation problem. In the ANSYS model radiation view factors are required between each shell element and its surroundings; these include the inside fluids - vapour and liquid, the fires developing on the walls of the barn and milk house, the air and gases surrounding the tank element, the surface of the ground and the atmospheric surrounds. This model must employ both radiation and convection links between element nodes and a space node utilized to absorb any radiant energy not incident upon the model. The convection requires a film coefficient that was estimated from correlations based upon whether the element was being heated or cooled by free convection and its orientation [9].

In the ANSYS model the liquid propane, which is heated by radiation to its surface and by convection and boiling from the liquid wetted walls, was modeled as five horizontal layers each isothermal and of the same volume. The liquid wetted wall temperatures were taken as the temperature of the liquid since with boiling temperature differences are small. Vertical heat transfer between each volume element, aside from the top of the first, was by conduction using an enhanced thermal conductivity ten times the molecular value in order to consider the slight influence of convection in this very stable configuration. In order to model the behaviour of the PRV and its ability to maintain the propane, once heated, at a constant pressure, the temperature development in these elements was fixed, as a maximum, to the saturation temperature corresponding to the set pressure of the valve; thus as each layer increased in temperature with time to this value it became fixed at 52°C.

The radiation and convective heat transfers to and from each node of the model are governed by the following expressions:

$$q_r=\sigma\epsilon_i F_{ij} A(T_i^4-T_j^4)$$

$$q_c=h_f A(T_i-T_j)$$

where q_r is the radiation heat flow rate, q_c is the convection heat rate, σ is the Stefan-Boltzmann constant, ϵ_i is the surface emissivity (0.9 assumed), A is the area associated with a node, T_i and T_j are the higher and lower temperatures respectively, h_f is the convection film coefficient and F_{ij} is the view factor from surface i to surface j.

The view factor, F_{ij}, is defined as the fraction of total radiant energy that leaves surface i which arrives directly on surface j; it can be determined from [6]:

$$F_{ij} = \frac{1}{A_i} \int_{A_i} \int_{A_j} \frac{\cos\theta_i \cos\theta_j}{\pi r^2} \, d(A_j) d(A_i)$$

where A_i, A_j are the area of surface i and j, r is the distance between surfaces i and j, Θ_i is the angle between N_i and the radius line to surface $d(A_j)$, Θ_j is the angle between N_j and the radius line to surface $d(A_i)$ and N_i, N_j are the surface normals of the elemental areas $d(A_i)$ and $d(A_j)$.

Two-node nonlinear line elements were used to evaluate the radiant heat transfer between points along with a generalized radiation matrix generator. The generation of the matrix of view factors utilized a hidden-line algorithm to determine which surfaces were visible to the others [8].

The thermal boundary conditions utilized the assumption that the wall fires were at clear flame temperatures of 1000°C. The air and temperature of the surroundings, not involved in the fire, was assumed to be 20°C. Several thermal load cases were considered for the tank in its position with both 50 and 40 % volume fills and wall fires that were only partially and then fully engaged and then again with the tank nearly at the CGA specified distance from its hottest end. The initial conditions took the tank and its contents at ambient temperature.

The load cases considered were: i) the barn and milk house walls engaged as a 8.5 m long(L) by 6 m high(H) area at 1000°C (to represent the barn wall) and two sections 2.4 m H, one intersecting the barn at 1000 °C 6 m L and its neighbor 300°C 3 m L (to represent the milk-house wall), ii) the barn fire now 11.5 m L, and iii) as in ii) but with the height of the milk house fires increased to 4.8 m.

The transient thermal ANSYS model employed a total of 640 elements; 491 shell elements were used to model the tank shell and the size of these elements was approximately 0.254 by 0.254 m square. The detailed results are given in [10].

2.2.1 Temperature Development and Distribution

For the ANSYS model Figs. 2(a) and (b) illustrate the temperature development of the liquid, two elements near the top centre of the vessel and the hottest end element on the tank for the partially and fully developed fires respectively. Both figures illustrate that the valve could have operated within 10 to 13 minutes and that the contents could have been fully saturated within 27 to 30 minutes. They further show that the top elements of the vessel could have reached temperatures of between 410 - 480°C in 15 to 18 minutes with the hot end possibly attaining 710-765°C in 9-12 minutes. Within 30 minutes steady state thermal conditions would likely have been established. Similar, though less detailed, results were obtained with the PLGS_4 model.

The ANSYS temperature distributions shown in Fig. 3 for Case ii) (top(a), hot(b) and cold sides(c)) clearly show that the side of the vessel adjacent to the milk house is much hotter than the other and that the two ends of the tank differ in temperature by upwards of 670 C°. The figures should be compared to Photographs 3(a) and (b) of the tank, presented later, particularly relative to the amounts and location of paint residue.

The total heat gain by the propane was determined to be approximately 75 kW. This would have only generated about 980 kg/hr of vapour to be relieved by the PRV, well below the capacity of the valve and approximately consistent with the number of valve cycles reported; similar results were obtained with the PLGS_4 model.

2.3 The ANSYS Stress Model

Linear elastic as well as non-linear and temperature dependent, elastic-plastic and creep deformation ANSYS finite element stress analyses [8] were also carried out. The elastic model employed 491 shell elements. Each element was about 0.245 m square and 8 mm thick except in the region of the central circumferential join where the elements were increased in thickness ($\sim$20 mm) and reduced in width to represent the increased stiffness of the circumferential backing spigot and its weld.

The non-linear and creep models also employed a similar geometric model but in addition utilized a refined sub-model wherein the extra thickness of both the longitudinal and circumferential welds were depicted. The steady-state temperature distribution determined earlier was input to evaluate the thermal expansion, plastic deformation, creep and cooling strains relative to its original state and these were added to those of pressure and gravity in order to determine the final stress state of the vessel.

Four cases were considered; two with fill levels of 50 percent and two with a fill level of 40 percent for each of the thermal situations depicted followed by simulated cooling due to the wetting by the application of water during the hose deluge. The detailed results are available as a separate document[10] and only the developed stresses at the liquid vapour interface and in the vicinity of pre-existing weld defects [5] located on the cold side of the tank at the junction of the longitudinal and circumferential welds as well as those around the heat affected zone, (HAZ), of the circumferential weld for the case of the 50% fill and the most extreme fire will be considered further here.

Due to the complex three dimensional nature of the thermal loading and its contents the vessel was under considerable axial and radial thermal strain. On the hot side this tended to be primarily compressive; on the cold-side, however, and particularly in the region of the weld intersections, this could be highly tensile. Its magnitude was further augmented by bending stresses imposed by the increased stiffness of the spigot join and its circumferential weld.

The maximum principal, axial, stress intensity and Von-Mises stresses are given in Table 1 for nodes in the interface region and at the weld intersection. Axial stresses on the interface inside surface in particular can be high but are not over yield. Sub-model results for the stresses at the weld intersection are only slightly compressive; stress intensity and Von-Mises stresses are significantly below yield.

These results illustrate how complex and sensitive the stress state in the vessel is to its presumed fill level. A 50% filled tank with only partial heating results in tensile axial stresses at the interface nodes; with the fully developed fire this becomes compressive. The 40% fill vessel shows an increase in the axial tensile stress as the fire model develops from partial to full exposure.

3. THE STEELS AND THEIR WELDS

The steel (ASTM A 455) cylinder was ∿8 mm (0.318") and its hemispherical ends (ASTM A 285-C) ∿ 5.8 mm (0.230") in thickness. The tank cylinder was formed of two sheets each welded longitudinally with one sheet having two male rolled spigots and the other only one spigot in order to provide weld backing for the circumferential join welds to each other and the hemispherical ends. The longitudinal welds were interior/exterior butt welds which were located on opposite sides of the bottom quadrants of the tank. The central and end circumferential joins were two pass exterior butt welds [2].

3.1 The Fracture

Post accident and photographic evidence examination of the tank failure indicated a plane stress shear type (45 degree shear lip with little plastic contraction) circumferential fracture surface very near the weld on the female cold side and PRV end of the vessel (Photograph 1. [4]). The failure appeared to have been initiated near the intersections of the longitudinal and circumferential welds at a point where there was reported a small (∿2.5 mm) defect as well as a portion lacking in penetration in the first pass weld [2]. In the longitudinal weld, ∿ 3 mm from the fracture initiating defect, was a further weld defect consisting of a lack of penetration (due to weld misalignment) 1 mm in size along with a nearly 2 mm long shrinkage crack formed in the outer shell weld.

In the Photograph a region, (∿25 mm total length), of what appears to be an inter-granular or trans-granular cleavage fracture (the bright region marked (a) in the photograph) on the inside surface of the shell appears to have initiated the failure. This feature was located on the unheated side of the vessel, (i.e. away from the fire), some 438 mm circumferentialy below the presumed liquid level at a point coincident with the intersection of the two welds. The fracture proceeded circumferentially in both directions from this point to meet on the heated side ∿ 180° from initiation in the top heated vapour space. The fracture deviated only slightly from the HAZ of the weld towards the end of its path. As the vessel halves separated they hinged about this end point, then parted, with each spinning and rocketing off propelled by the depressurized explosively evapourating superheated propane liquid.

It is difficult to be certain in our diagnosis the influence such defects would have had without having made a through visual and metallographic (macro and micro) evaluation of the fracture surface; this was however conducted for the CSST [5]. Direct examination of the region in a similar join between the cylinder and a hemispherical end was, however, made at UNB. This study determined similar sized defects and lack of penetration from a series of metallographic macro sections made along the weld. These indicated that such faults were to be expected and that approximately 50% of the joint length (250 mm) could be involved.

3.2 The Welds

Using the samples, made above, detailed micro-hardness and micro-metallographic surveys were also conducted across the deposited metal, coarsened, refined and transition metal zones into the parent unaffected cylinder steel. In coarsened metal zone of the HAZ a Widmanstätten type structure was observed with lines of ferrite breaking up the pearlite areas. This structure is common in low-carbon steels in which transformation occurs from large austenite grains during a medium fast rate of cooling[11]. The ferrite grain size in this region was estimated to be approximately 55 µm; the Vicker's microhardness values determined through the region (using a Leitz Mini-Load Tester in 100 µm steps) ranged from VH 125 to VH 223 from the lower carbon A 285_C steel to the 0.33% C A 455 steel respectively.

3.3 The Strength of the Plate and its Welds

Tensile strength can be estimated from an empirical relationship between hardness and strength[12];

$$\sigma_{ts}(\text{MPa}) \approx 3.2(\text{VH})$$

The values thus determined are consistent with the tensile specification for the A 285_C steel (380-515 MPa[13]) but are somewhat higher than to be expected (515-655 MPa[13])for the cylinder material, perhaps due to the prior forming required to make the spigot in the cylinder material. The parent metal in the failed female join would not have had any such strengthening. Hardness in the Widmanstätten type structure (VH ∿180) could not be used to determine the strength of the ferrite grains, since these are very thin compared to the size of the indenter.

The tensile strength of the ferrite can, however, be estimated from the Hall-Petch equation [14] which empirically relates the influence of alloying elements and grain size. Based on the stated maximum amounts of effective alloying constituents (Mn 1.05% and Si 0.13 % max. [13]) and the measured ferrite grain size:

$$\sigma_y=15.4(3.5+2.1(1.05)+5.4(0.13)+1.13(0.055)^{-1/2})$$

$$=180 \text{ MPa } (25 \text{ ksi})$$

and

$$\sigma_{ts}=15.4(19.1+1.8(1.05)+5.4(0.13)+0.5(0.55)^{-1/2})$$

$$=370 \text{ MPa } (53 \text{ ksi})$$

The fracture stress in the HAZ region may be taken as the tensile strength in a low work hardening material such as ferrite [15].

3.4 The Stress State

The two cylindrical sections of the vessel are kept together at the welded spigot joint by shearing forces and bending moments per unit length of the circumference at the mid-point of the join. These forces produce bending of adjacent parts of the tank and since the spigot end is "stiffer" its deflection will be less than the thinner welded end of the shell. The discontinuity stresses due to the stiffness of the spigot and weld material must now be added to the membrane stresses due to thermal expansion, pressure and gravity. As was seen earlier from the ANSYS stress analysis axial stresses in a region near the weld defect are much less than yield. If, however, residual stresses at the level of the fracture stress were present (as they must have been as is evident from the presence of the shrinkage crack) the stress state at the initiating defect becomes important.

The stress concentration factor for a small round hole imbedded in an infinite plate is $K_t=3.0$ [12]. The local stress around the hole, including the residual stress field from the shrinkage crack could now be greater than the tensile strength of the material, 515-655 MPa (75-95 ksi), and the material will locally fracture on the outside surface. As the crack grows a leak will develop causing, as the propane expands, a local severe temperature gradient in the material going from the containment temperature, 52°C, to the normal boiling point of propane, -42°C. This will further increase the local axial tensile stress state by some 300 MPa. The lower temperature will also decrease the fracture toughness. The stress intensity factor now becomes important in determining whether a crack can still continue to propagate; obviously, as judged from Photograph 1, the crack did extend towards the circumferential join some 15 mm in each direction at 45° to the horizontal weld as an overload fracture before it entered the HAZ of the circumferential weld. This crack would now take on the appearance of a part-through thumbnail crack.

The stress intensity factor for a part-through thumbnail crack in a plate subjected to a uniform tensile stress can be calculated from [16] to be:

$$K_1=1.12\sigma(\pi a/Q)^{1/2}*M_k=39.7 \text{ MPa}\sqrt{\text{m}}(36 \text{ ksi}\sqrt{\text{in}})$$

In the expression for stress intensity factor, (K_1), Q is a flaw shape parameter which is a function of both the shape of the crack and the ratio of the stress to yield stress ratio (taken as 1),a the depth of the crack (2.5 mm), and M_k a back free surface correction factor which is nearly 1 in this case. The stress, σ, utilized above was the maximum on the inside shell surface and thus should, in an approximate manner, take into account the influence of bending.

If the initial rupture is to progress from this original cleavage type fracture to a final plane-stress fibrous or shear failure depends upon the local stress and strength states. In this case the final fracture surface, (Photograph 1.), appears to be much more in the nature of shear cracking than internal necking between voids. As cavities form the final fracture will then be a marked softening effect in the shear band and the whole region can "unzip" catastrophically, [17], if the stress intensity factor is sufficiently high.

3.5 The Stress Intensity Factors

Critical plane-strain stress intensity factors for the A 455 parent plate should have been well in excess of the value determined above. Defects in the first longitudinal join may be so severely "hot-strained" when welding the second circumferential joint to effectively raise the ductile-brittle transition temperature (NDT) at the defect tip by some 60° C [18]. Large grain size also adversely influences the NDT.

The fracture toughness of weldments is complicated by their heterogeneous microstructure and composition as well as cleanliness. Coarse-grain regions adjacent to the weld interface generally exhibit the poorest toughness [17]. Low temperatures also favour lower toughness. The actual stress intensity conditions prevailing when failure occurred can be estimated from the depth of the shear lip formed on the fracture surface [12]. Shear lips form on ± 45° bands to the sheet thickness and thus correspond approximately to the inclination of the HAZ.

The depth D of the shear lips can be approximated by the plane stress plastic zone radius. Hence [12];

$$D \approx r_y \approx 1/2\pi(K/\sigma_{ys})^2$$

If the thickness of the shell is taken as the shear lip depth (Photograph 1.) and the yield strength that of the ferrite grains in the HAZ a critical stress intensity factor of 39.2 MPa$\sqrt{m}$ (35.5 ksi$\sqrt{in}$) results. This value agrees with that existing at the termination of the cleavage type fracture and thus failure could have proceeded in the manner assumed.

4. THE TANK FITTINGS

At the colder end of the tank, near the circumferential join, was located the fill line and valves, a level indicator and the high pressure regulator in addition to overfill protection. There was a hinged pressed steel dome cover over these fittings. The valves were bronze and the fittings copper pipe (∿ 10 mm) with brass fittings.

The high pressure first stage regulator is designed to handle vaporization of tanks and reduce tank pressure to intermediate pressures suitable for entry to a low pressure regulator. Its body and bonnet was die cast zinc with internals of steel, brass, rubber and a fabric rubber composite.

The vertical fill indicator consisted of a zinc alloy die cast head (1" NTP), an intermediate seal plate over a cavity enclosing a magnet affixed to the top of a drive shaft and a top cover encasing a plexiglass crystal over a magnetic indicator. The head seals are a synthetic rubber O ring and a gasket. The indicator is driven by an aluminum alloy drive-shaft within a tube housing (∿13 mm ID) approximately 0.6 m long. The shaft is connected to a gear, counterweight and float system. The tube is press fitted into the head and either staked or pinned to it. The arrangement is such that if the end of the tube was below the liquid level and the head were damaged, such to breach the integrity of its seals, liquid could be driven out of the vessel under pressure up the support tube. For this to happen would require that approximately 20 g of molten zinc fall inside the tube into the liquid propane; this could generate an internal pressure (∿ 4 MPa(600 psig) which could blow out the bottom bearing and allow the liquid propane to be discharged.

The melting point of most zinc die casting alloys is between 390-430°C[19] and as is evident from the residue of splattering in the space beneath the dome cover and the top of the level indicator shown in Photograph 2 both items had melted.

Removal of the level indicator body showed that it had initially commenced melting over a small region of its 1" NTP thread while obviously under pressure and that, perhaps later, the top may have melted such to permit liquid discharge under vapour pressure.

Photograph 2 also illustrates the sooting resulting from ignition and burning of an under dome discharge of propane vapours from the high pressure regulator tank connection and that of the small melt-through in the level indicator boss prior to what could have been the later very violent two-phase flashing discharge up through the top of the breached indicator thus accounting for the observations of the firemen.

5. THE PAINTS

The tank exterior appeared to have been painted with a white enamel type coating over a zinc chromate covering on a base coat of red lead. Photographs 3(a) and (b) illustrate the hot and cold sides of the vessel after the incident. On the hot side and end there is a distinct separation between the remnants of the white enamel coating and the other coverings; this was used as evidence of a 55 percent volumetric fill at failure.

The patchy removal of the silver zinc chromate paint evident in the photographs could have been caused by mechanical abrasion during flight and impact of the tank pieces or by the limited water exposure from the fireman's hose which could have dissolved the oxides formed during its combustion. Since the tank thermal analysis indicated vapour space metal temperatures well in excess of the "wetting" or minimum film boiling or Liedenfrost temperature, T_f (∿290°C [20]) and the water application had only been applied approximately one to two minutes it is possible that the removal of the silver paint, remote to the circumfrential join, was primarily due to water removal of the oxide since there was sufficient time to quench surface temperatures to below T_f (the time constant for cooling to say ∿ 98% in the original temperature difference would be approximately 20 s for the shell and 80 s for the join. Cooling due to the water-fog application may thus have caused cooling of the vapour space walls though quenching strains in the vessel for the time frame considered would perhaps not have resulted.

Steel samples (100*100 mm) cut from the tank and provided by CSST were radiantly heated using the UNB Cone Calorimeter[21] at heat fluxes from 15 to 110 kW/m2. The standard test and samples were modified so that temperatures could be recorded. A central 1.2 mm diameter chromel-almuel thermocouple was mounted in a hole drilled into the thickness of the material. These results indicated that at low exposures, e.g. 15 kW/m2 an equilibrium temperature of 200 C was reached in about 12 minutes; the white paint commenced smoking at around 6 minutes but was still adherent at the end, though slightly discolored with a brown tinge. At higher heat fluxes, say 50 kW/m2 the white paint blistered at a temperature of 100 C (70 s), ignited at 140 C (100 s) with combustion complete at 130 C (130 s) with the paint becoming detached as flakes which could be easily brushed off. As heating continued the silver zinc chromate surface started smoking at 300 C(320 s), stopped smoking at 380 C(480 s) and blistered slightly at 500 C(1000 s). The coating even while hot was still adherent as well as later when cold. The zinc chromate coating only became susceptible to mechanical or water removal upon heating to temperatures in excess of 500 C. Equilibrium temperatures attained were 200 C(15 kW/m2), 400 C(25 kW/m2) and 500 C(50 kW/m2). The sample that was heated in step increments from 75 to 100 and then 110 kW/m2 attained temperatures of 600+ C, 750 C and 800 C respectively. An exposure of 110 kW/m2 is similar to that for a PLG vessel directly immersed in a hydrocarbon pool fire [22].

Under steady-state thermal conditions then, the paint level could be taken as indicative of the liquid level since the fin effect, [6] - that is the influence of the circumferential conduction down the wall to the boiling liquid - is small ≤15 mm.

6. THE VOLUMETRIC FILL AT FAILURE

The volumetric fill at failure was originally estimated to be 55 percent. This was determined from the level of the white enamel remaining on the sides of the tank [2]; Photograph 3 [4]. As seen above the white paint is, however, capable of remaining intact and adherent even at temperatures of 200 C for periods of up to 1-2 minutes even at exposures to 100 kW/m2 when its temperature is less than approximately 130 C. The inference of liquid level from this evidence is therefore suspect and another means of estimating the amount of propane in the vessel at failure must be utilized that will take into account not only the temperature but also the time and level of exposure.

It was previously indicated that the top of the level indicator could have melted and thus may have permitted the discharge of liquid propane under the saturated vapour pressure if sufficient pressure were generated to blow out the bottom bearing seal. It was also shown that the thermal state of the tank and its contents had developed over approximately one-half hour and thus the paint level might be taken as indicative of the fill just prior to the melt-out of the level indicator; the amount of paint remaining after this would now depend upon if there was a liquid discharge, how long it could have taken to vent and the time to actual failure of the vessel. The determination of this will require a transient analysis of the choked two-phase discharge up the aluminium level indicator drive shaft support tube.

An evaluation of the two-phase choked flow from this opening can utilize several different models. The homogeneous equilibrium model(HEM) provides the best estimate for the pressure ratio; while the homogeneous frozen flow(HFM) the best estimate of the mass flow-rate[20]. Here the HEM model was utilized to determine the exit condition (T=316 K, p=1.46 MPa and x(quality)=0.098) and the HFM model, for these conditions, the critical mass flow-rate (G_c = 20,000 kg/m2 s)[1]. Next taking the initial level as between 50% and 55% and the bottom of the level indicator tube at approximately 40% fill it would take some 100-150 s for this material (∿300-400 kg) to be discharged.

The question now to resolve is what would happen to the white paint in this time period? Initially the metal temperature would be only slightly above the saturation temperature since the liquid would be boiling(∿52 C). The cone

---

[1] The thermodynamic and transport properties required in these analyses were obtained using the NIST STRAPP program [23].

calorimeter tests earlier discussed showed, for a more severe condition (i.e. the plate insulated on its back), that starting from ∿ 50 C the painted surface temperature would only just be approaching 150-200 C and that the paint could still be intact for heat-fluxes as large as 100 kW/m2 during this time period. It can be concluded then that the white paint could thus still be adherent at nearly its original level if as was stated the hose deluge had only just commenced after cessation of the presumed two-phase jet discharge [3].

From the above the fill level at failure may thus have been approximately 40 % and not the 55 % estimated originally. Photographic evidence for this could be seen as a witness line separating the liquid from the vapour which could be faintly distinguished in some of the photographs [4]. It is estimated[2] that the line was some 100 mm below the tank centreline; a distance that approximately corresponds to what must have been the bottom of the level indicator driveshaft support tube (Figure 5). In Photograph 3(a), point A, there is also confirmatory evidence of a rapid change in liquid level since there appears to be small regions of paint removal just below and parallel to the upper white paint boundary line particularly at the central hot section; the hot end paint line is also very indistinct indicative of its very severe exposure while not protected internally by the boiling liquid propane.

A further consideration relative to level determination and the positioning of fracture initiation is the fact that the start of the failure was determined by presuming the level to be indicated by the paint and then measuring down to the longitudinal weld on the cold end of the vessel. This process would have been satisfactory had heating on the tank been uniform; it was not however. The radiant load would have affected the paint on the side away from the milk-room fire less than on the other as can be seen in Photograph 3(a) and (b) and thus the level would have been less than 55%, just prior to the melt-out of the level indicator, and the positioning of the point of failure somewhat higher relative to the tank centerline than was originally supposed.

7. AN INTERPRETATION OF EVENTS

The correct determination of the cause of the incident is only possible after a careful assessment of all the evidence. Not all of this was available to the authors, however, and so our explanation must be based upon what information was accessible, the analyses that were undertaken, the available report and reasonable engineering interpretations.

It is clear from the statements of the surviving firemen that, as they were setting up to attack the fire, the high pressure regulator and perhaps a portion of the level indicator boss had melted sufficiently to release propane vapour under the dome of the tank; this was what was responsible for the observed 'encircling' flames at the mid-section. Shortly thereafter the topmost seal of the level indicator could have melted out and tank pressure was able to discharge liquid propane as a vertical two-phase flashing jet which would have immediately ignited. This torching flame would have persisted for some 100-150 seconds before the liquid level would have dropped to a point where only vapour could be vented.

This rapid change in level from approximately 50% to 40% volume fill and the consequent changes in thermal exposure and stress state of the tank caused by the application of water deluge may then have caused a previously stable small weld defect to become critical, fracture and transfer load to the heat affected zone of the

---

[2] By direct measurement from Photograph 4 and scaling to tank dimensions.

circumferential weld triggering the catastrophic unzipping of the vessel. Such a failure, in our view, would have also occurred had this particular vessel been located within the specified setbacks required by the CGA and even if there had not been the application of water to the tank wall. The spacing recommended by the CGA is inadequate for rural fire brigade response times.

A failure like this might not have been possible had the level indicator support tube been provided with a hole, just before its junction with the boss, that would have permitted a vapour only discharge. It might also have helped to have had the high pressure indicator and the level indicator head made of bronze since then there would have been little possibility of even a vapor discharge near the critical central section of the tank. Both the vapour hole and bronze fittings could possibly have provided sufficient time for definitive fire attack and control and thus avoided the tragedy.

Welded pressure vessels constructed using a rolled spigot to provide weld backing do not allow visual inspection to determine if there are faults such as existed in the first pass weld of this vessel. If vessel sizes constructed with a central circumferential weld are to be allowed by regulations only two pass inside and outside butt joins should be permitted or X-ray inspection of the weld intersections should be required. In this manner then there can be adequate inspection of the first pass weld root prior to completion of the second and final exterior or interior pass weld. An additional benefit of this would be to lessen the level of discontinuity stresses due to the join.

Molten zinc contamination of hot stressed steel surfaces can also lead to very rapid and unexpected failures; this is what is called Liquid Metal Induced Embrittlement, (LMIE). LMIE failures result in severe reductions in ductility, usually indicated by small or zero reduction in cross sectional area at failure and significantly reduced fracture toughness. Crack growth is usually very fast with crack initiation at the solid liquid interface. Fracture surfaces are covered by a layer of liquid metal that may only be a few atoms in thickness and therefore extremely difficult to detect. Zinc, which may be present either in the form of a galvanized coating or zinc based primer paints may also provide a source of contamination of steels and their welded joints, [24]. It is not clear that zinc contamination played a role in this failure.

8. CONCLUSION AND RECOMMENDATIONS

The analyses given and considerations of the available evidence permit the conclusion that the tank failed due to the existence of a small weld fault that became critical due to the combination of thermal load and possible rapid loss of volumetric fill caused by the melting of the top of the zinc alloy level indicator.

In order to prevent similar occurrences in the future, tank fittings should all be made of bronze and vertical level indicators should be modified by the provision of a vapour vent hole in the drive shaft support tube.

Zinc alloy fittings and zinc based paints on all steel pressure vessels should be avoided due to the possibility of melting, zinc surface contamination and liquid metal induced embrittlement.

If tanks with central cylindrical joins are to be permitted within existing setback allowances then only two pass (interior/exterior) butt welds, with adequate provision for inspection, should be allowed or fully X-ray inspected circumferential/longitudinal joins should be required.

Fire attack on vessels with complex thermal strains, such as in this case, should only be carried out by firemen from the unheated side of the vessel and not from either of its ends or the heated side.

ACKNOWLEDGMENT

Claude Cazes, Fire Chief of Loretteville, Andre Marchand and Norman Lambert, Inspectors of the Commission de la Sante et de la Securite du Travail(CSST), Trois-Rivieres (Quebec) provided background information, eyewitness reports, photographs, samples and the opportunity for the senior author to inspect the tank and some of its fittings. The Transportation Development Centre of Transport Canada, the Natural Science and Engineering Research Council and the University of New Brunswick provided financial support.

REFERENCES

1. **Canadian Compressed Gas Association Standard**, (1991), **CAN/CGA B149.2_M9**, Section 10.10.
2. Cazes, Claude, **Private Communications** (1993 and 1994).
3. Lambert, N.,(1993), Nov. 17; CSST Private Communication, **Sommaire du Dossier**, 4 pp.
4. CSST Photographs provided the authors by CSST (N. Lambert, Nov. 1993).
5. Lambert, N., Marchand, A., Drolet, R. and Paulin, N., (1995), **Accident Mortel Survenu a Quatre Pompiers Volontaires de la Ville de Warwick le 27 Juin 1993 au 491 Rang 6, a Sainte-Élisabeth de Warwick**, Rapport R704867(Dossier d'Intervention 2171213), Commission de la Sante et de la Securite du Travail du Quebec(CSST), Direction Regionale Maurice-Bois-Francs.
6. Venart, J.E.S. & Xu, J., **Ste. Élisabeth de Warwick LPG Tank Failure; Report & Supplement**, UNB FSC Reports prepared for CSST, 10/95, 48 p; 04/95, 39 p.
7. Yu, C.M., Venart, J.E.S. & Cogswell, S., **Pressure Liquified Gas Simulator; PLGS_5**, UNB Fire Science Centre (1995).
8. ANSYS, Swanson Analysis Systems Inc., (1994), Houston, PA.
9. Mills, A.F., Heat Transfer, (1992), Richard D Irwin Inc., Homewood, IN.
10 Xu, Jian, MScE Thesis, UNB (1995), **Failure Analysis of Some LPG Vessels.**
11. Clark, D.S. and Varney, W.R., Physical Metallurgy for Engineers, (1962), Ed., D. van Nostrand, New York.
12. Jones, D.R.H., Engineering Materials 3: Materials failure analysis - case studies and design implications, (1993), Pergamon Press, Oxford.
13 Annual Book of ASTM Standards, Vol **01.04** (1992): i) **ASTM Designation A 285/A 285M-82**; Standard Specifications for Pressure Vessel Plates, Carbon Steel, Low- and Intermediate-Tensile Strength, p 186-187; ii) **ASTM Designation A 455/A 455M-82**; Standard Specifications for Pressure Vessel Plates, Carbon Steel, High-Strength Manganese, p 275-276.
14. Pickering, F.B., Physical Metallurgy and the Design of Steels, (1978), Applied Science Publishers Ltd., London.
15. Barsom, J.M. and Rolfe, S.T., Fracture and Fatigue Control in Structures: Applications of Fracture Mechanics, (1987), 2nd Ed., Prentice Hall, Englewood Cliff, N.J.
16. Duffy, A.R. et al, Fracture Design Practices for Pressure Piping, Fracture, V. 5, Fracture Design of Structures, Academic Press, New York and London, Ed.: H. Liebowitz, (1969), pp. 159-232.
17. Nibbering, J.J.W., Fracture Mechanics and Ships, **Proc. Int. Conf. on Prospects of Fracture Mechanics, Ed.: G.C. Shih, H.C. van Elst, D. Broek, Delft Univ. Tech., The Netherlands, (1974), June 24-28, pp. 353-366.**

18. Hertzberg, R.W., Deformation and Fracture Mechanics of Engineering Materials, (1989), John Wiley and Sons, New York.
19. American Society of Metals Handbook, Vol. 1, 8th Ed. (1961).
20. Whalley, P.B., Boiling, Condensation and Gas-liquid Flow, Oxford Eng. Sci. Series 21, Ed.: A. Acrivos, J.M. Brady, F.W. Crawford, A.L. Cullen, L.C.V. Woods and C.P. Wroth, Oxford, (1987), 291 p.
21. Ma, S., MScE, Thesis, UNB (1994), **Development of a Cone Calorimeter for the Measurement of Ignition and Fire Properties.**
22. Griffiths, J.R., Beckett, H., Collis, N.J. & Willoughby, D.B., **Total Pool Fire Engulfment Trials on a 5 Tonne LPG Tank**, Parts 1-8, Project No. 04.12, File No. SMR841/270/01 RPG 1805, June 1987, HSE(SRLD) Buxton, UK.
23. Ely, J.F. and Huber, M.L., NIST Thermophysical Properties of Hydrocarbon Mixtures Database (SUPERTRAPP), Version 1.0, Users' Guide, NIST Standard Reference Database 4, U.S. Department of Commerce, Gaithersburg, MD, July 1992.
24. Fernandes, P.J.L., Clegg, R.E., and Jones, D.R.H., (1994), **Failure by Liquid Metal Induced Embrittlement**, Eng. Failure Analysis, Vol. 1, No. 1, p. 51-63.

Table 1: Stresses in the vicinity of the liquid vapour interface and the weld defects; ksi.

Tank with 55% fill, submodel, stress at interface (node 235) (ksi)(53°C)

	σ_z	σ_{int}	σ_{eqv}
Internal surface	25845	26416	22877
external surface	25032	25193	23176

Tank with 55% fill, submodel, stress at longitudinal weld (node 205)(ksi) (53°C)

	σ_z	σ_{int}	σ_{eqv}
Internal surface	146.48	19401	19349
external surface	-4629.4	16902	15137

Tank with 45% fill, submodel, stress at interface (node 256) (ksi) (53°C)

	σ_z	σ_{int}	σ_{eqv}
Internal surface	26245	26655	23148
external surface	29100	29356	25427

Tank with 45% fill, submodel, stress at longitudinal weld (node 226)(ksi) (53°C)

	σ_z	σ_{int}	σ_{eqv}
Internal surface	-8016.3	21968	19233
external surface	-3504.7	17273	15878

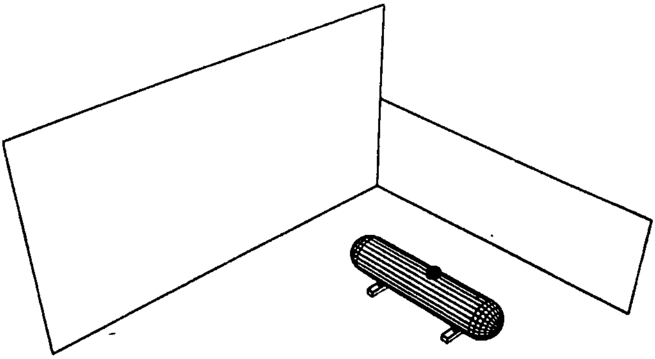


Figure 1. Ste. Élisabeth de Warwick Tank Site Layout.

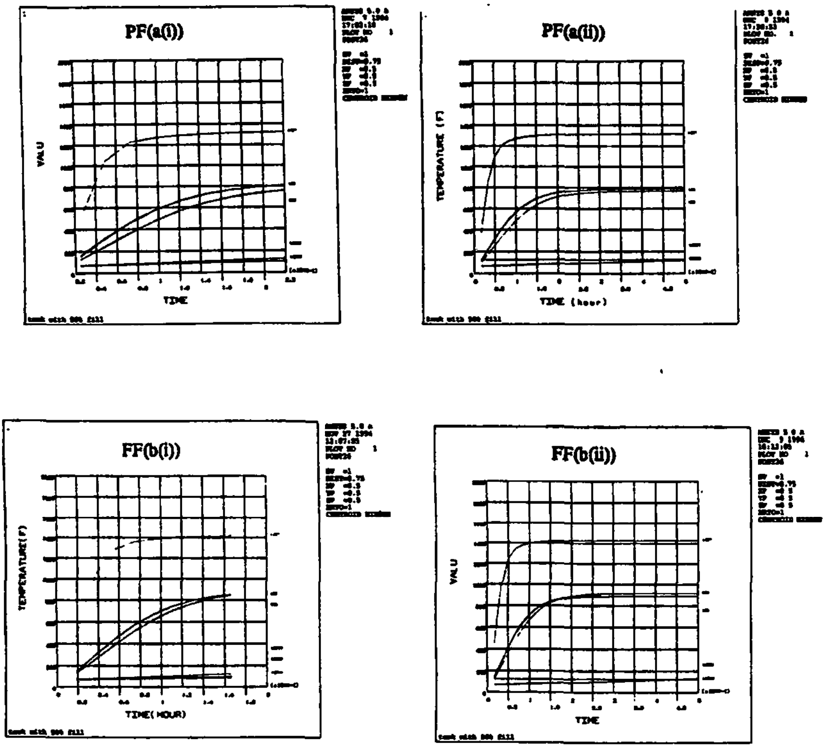


Figure 2. Transient Temperature Development; (a) Partial Fire Exposure, and (b) Full Fire Exposure, ANSYS Thermal Model at 50% Volume Fill.

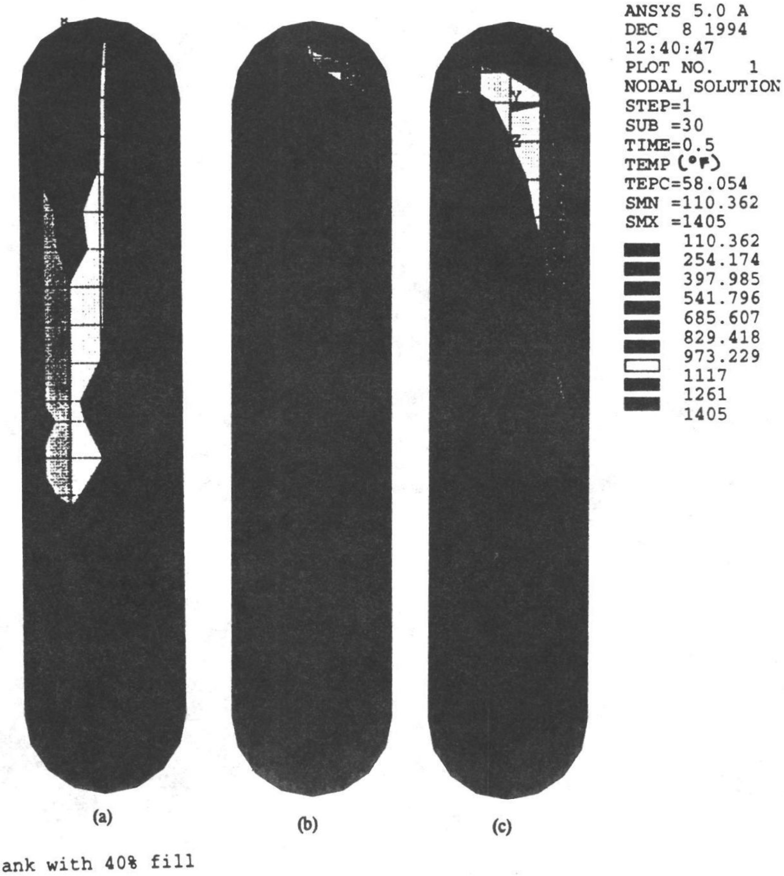
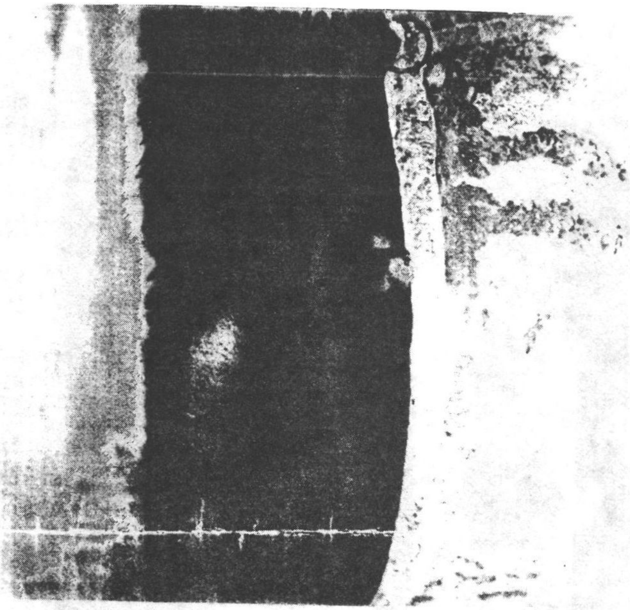
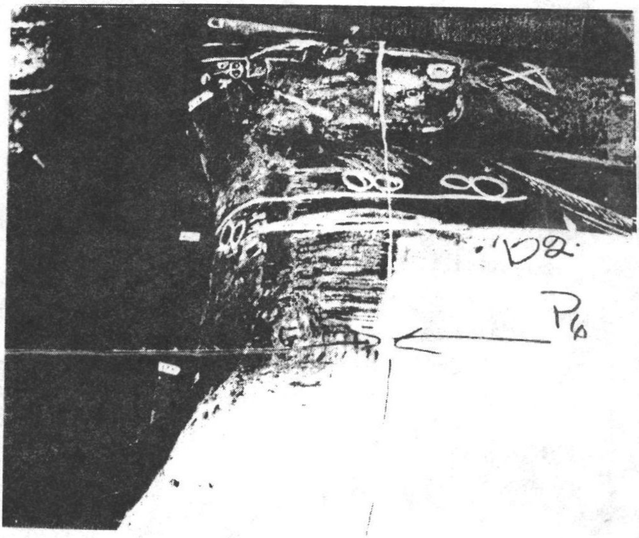


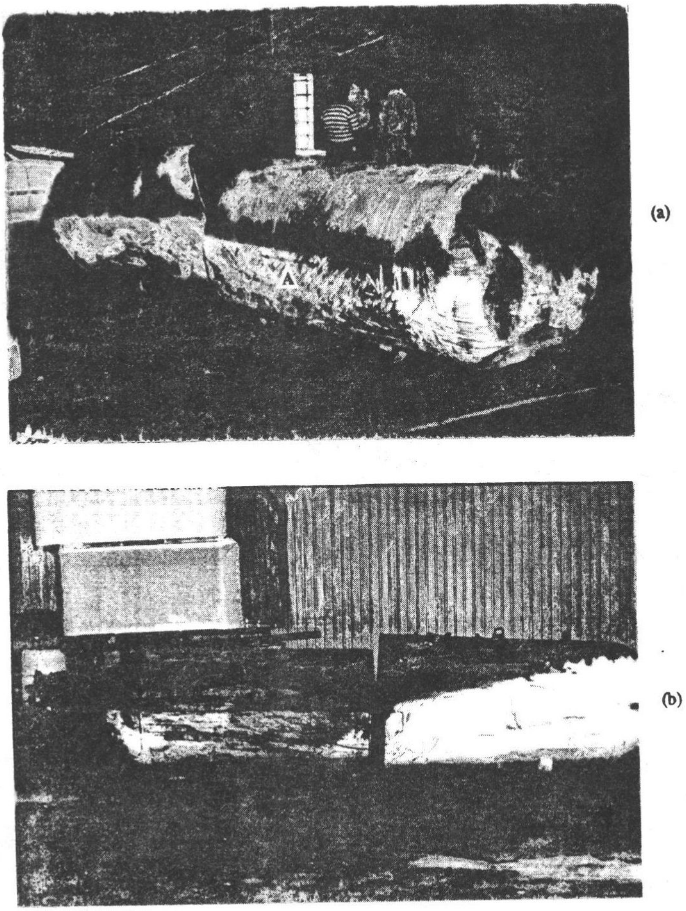
Figure 3. Temperature Distributions; (a) Hot Side, (b) Cold Side and (c) Top, ANSYS Thermal Model, 40% by Volume Fill, Partial Fire Exposure



Photograph 1. A View of a Portion of the Fracture Surface Showing the Point of Initiation, [4].



Photograph 2. Central Top Region of the Tank Showing Molten Zinc Splatter from Regulator and Sooting from Under Dome Fire [4].



Photograph 3. Heated, (a), and Cold, (b), Side Views of the Tank [4].

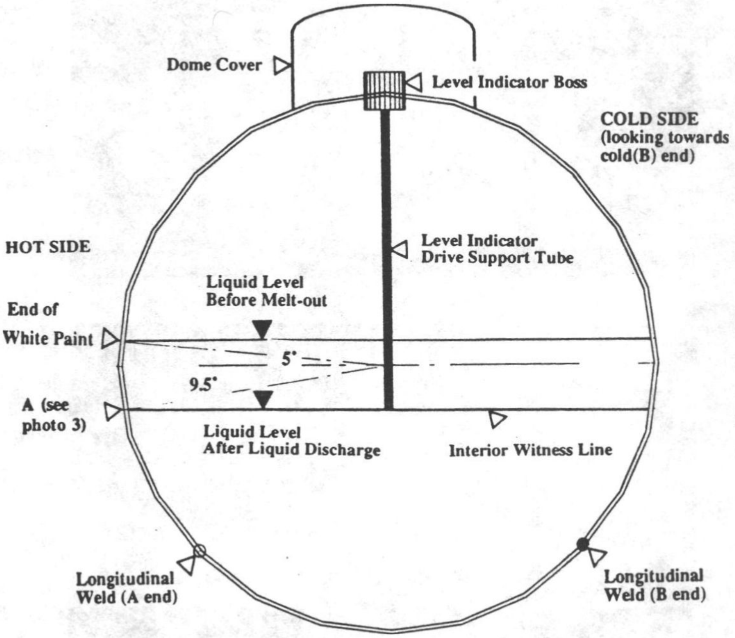


Figure 4 Tank Cross Section at Level Indicator looking towards cold end of the vessel showing Protective Dome cover, inferred liquid levels, and paint residue indications as well as longitudinal weld locations.

ELECTROCHEMICAL DESTRUCTION OF NITROSAMINES

T.Lejen, K.Volchek, C.Ladanowski, D.Velicogna, H.Whittaker
Emergencies Engineering Division
Environmental Technology Centre
Environment Canada
Ottawa, Ontario K1A OH3

Abstract

The electrochemical destruction of N-dimethylnitrosamine (NDMA) on carbon/ platinum electrodes was studied under basic and acidic conditions by means of UV-spectroscopy, GC-MS and colorimetry. Experiments were performed with a solution of 100 ppm NDMA, showing that its electro-reduction is a pH-sensitive process. Reduction experiments at alkaline, neutral, and low acidic pH led to a very slow NDMA destruction. No significant changes in NDMA concentration were detected after six hours at pH 10. Almost 100% reduction of NDMA was observed after the pH decreased to 0.5. A passivation of a platinum electrode was found to occur in sulphuric acid solutions.

Background

N-nitrosamines are of toxicological interest, because some of these compounds are carcinogenic, mutagenic and teratogenic in low concentrations [1, 2]. Furthermore humans are exposed to these toxicants as individual nitrosamines occur in bacon [3], frankfurters [4], cured meat [5,6], tobacco, betel-quid, areca-nut [7], malt [8] and beer [9]. Other potential sources of exposure include the use of cosmetics, certain types of drugs [10], pesticides or their industrial chemicals and chewing and smoking of tobacco. N-nitrosamines are also detected in the environment [11], human biological fluids and tissues [12]. NDMA is found in a number of industrial aqueous streams [13, 14]. N-nitrosamines frequently occur, sometimes in parts per million levels at the work place in rubber, tanning and metal-working industries [15]. NDMA seems to be a ubiquitous contaminant.

High levels of NDMA contamination could result from the decomposition of 1,1-dimethylhydrazine (UDMH). UDMH is a high-energy propellant, used in large volumes in space and missile programs. Utilisation of hydrazine propellants can lead to accidental environmental releases of these fuels during transport, transfer or storage. Due to direct sunlight or contact with metal ions in the soil hydrazines are decomposed to a variety of decomposition products, including N-nitrosamines [16]. In contrast to hydrazines, some nitrosamines are stable in natural ecosystems. No degradation of NDMA was observed in lake water during a 3.5- month period; nearly 30 days passed before it slowly disappeared from soil; it disappeared slowly from sewage but a minimum of 50% remained after 14 days [17]. NDMA undergoes degradation in atmosphere and the rapid photolysis of NDMA leads to a tropospheric half-life of only 5 min [18].

NDMA is in the carcinogenic class B (i.e., a probable human carcinogen). Preliminary risk assessment reveals that 1.7 parts per trillion of NDMA in drinking water can create a cancer risk of one in a million [19]. Therefore, the Ontario Ministry of Environment and Energy set a guideline of 9 ppt in drinking water and 200 ppt in effluents [20]. N-nitrosamines must be treated and carefully disposed of in an environmentally acceptable manner in the event of contamination due to their toxicity.

NDMA is soluble, polar, and highly mobile in groundwater. The extraction efficiency of

NDMA from water is low. Due to the recalcitrant nature of NDMA, many groundwater remediation technologies are ineffective. Presently, innovative and alternative groundwater remediation technologies such as advanced oxidation [21, 22] are being assessed for their effectiveness in destruction of NDMA. These technologies, however, require expensive reagents or equipment, or are only applicable to low concentrations of NDMA (below one ppm), or are associated with secondary contamination caused by the decontamination itself. The electrolytic reduction of NDMA in aqueous medium has been shown to transform NDMA into less toxic products such as amines, ammonia, and nitrogen [23]. Our preliminary results of NDMA electrochemical destruction study have been reported earlier [24].

The present investigation is a part of the Ukrainian Environmental Assessment and Remediation Project (EARP) being led by the Emergencies Engineering Division in conjunction with their Canadian and Ukrainian partners. NDMA is suspected to be one of the most hazardous contaminants on former Soviet ICBM missile sites. Previous work has shown that NDMA decomposes fast during the electrolytic reduction at pH 1 and a potential difference of 3 V [24]. However, under these conditions, approximately 30% of UDMH was formed. Furthermore, operation under acidic conditions and high voltage led to disintegration of carbon graphite electrodes. Using alkaline media for electrochemical reduction of NDMA for the next phase of our investigation seemed reasonable. The most notable advantage of alkaline solutions is that a number of metals can be used as electrode materials. The other major advantage is the absence of electrode poisoning from the reaction media [27]. This is supported by the data that NDMA electrochemical reduction under alkaline conditions produces a small amount of UDMH and substantial amounts of dimethylamine and ammonia [23].

Work objective

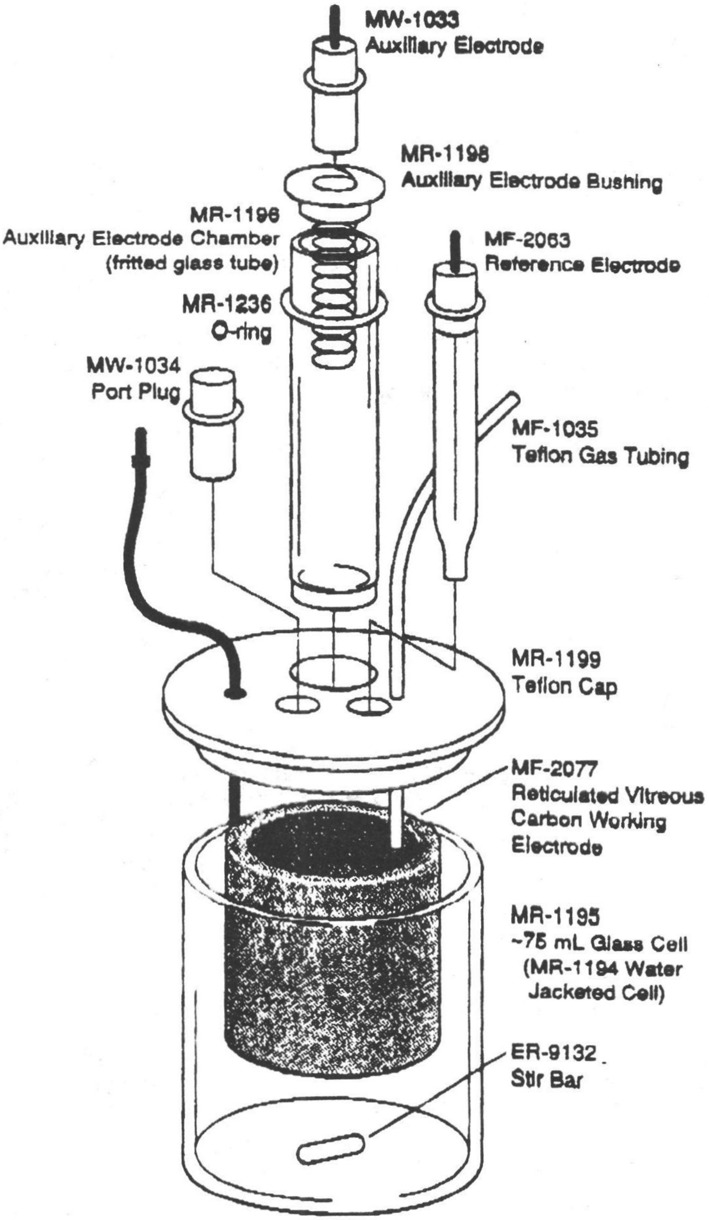
The objective of this work was to optimize treatment conditions of electrolytic destruction of NDMA.

Methodology

All experiments were carried out using a two-electrode cell with replaceable electrodes, as shown in Figure 1. The electrolytic cell (Model MF-1056) was obtained from Bioanalytical Systems, Mc, West Lafayette, Indiana. An essential difference between carbon graphite cathodes used earlier and this one was its resistance to extremely low pH's and 30-time larger a surface area. The carbon cathode and the platinum anode compartments were separated by a porous glass wall to reduce the diffusion of NDMA and minimize possible simultaneous reduction and oxidation processes. A constant voltage in a range of 2.0 to 4.0 volts was applied to the electrodes, using a direct current (DC) power generator. The electrodes were connected in parallel with a voltmeter, and in series with an ammeter and DC generator. A pH metre was placed near the apparatus to monitor fluctuations in pH.

At the beginning of each test, a solution containing 100 ppm of NDMA and specific concentrations of supporting electrolyte (sulphuric acid and/or sodium hydroxide) was placed into the cathode compartment. The anode compartment was filled with a similar solution of the supporting electrolyte which, however, did not contain NDMA. Test solutions were prepared using deionized and degassed water. This was prepared by bubbling helium through water for 20 minutes at a pressure of 30 psi.

Figure 1
MF-1056 Electrolysis Cell



UV spectra of NDMA at different pH were recorded by using Perkin Elmer UV/VIS spectrometer Lambda 2. Calibration curves were generated regularly for both NDMA and UDMH solutions. Scan-mode UV-spectrophotometry was necessary to determine the wavelength at which maximum absorbance of NDMA at different pH occurs. Colorimetric method [26] was used for determination of UDMH concentration. EPA method 607 was applied to analyze the reaction mixture during NDMA electrochemical reduction [26].

A Varian Saturn GC-MS equipped with a Varian 8 100 Auto Sampler was operated in the splitless mode. Injector temperature was 190° C. Injection volume was 1 ul of sample. Chromatography was performed with 30 m x 0.32 mm ID, 0.25 um film thickness capillary column, operated at a head pressure of 7 psi of helium. The column oven temperature was held at 35° C for 2 min and then programmed at 10° C/min to 200° C. Under these conditions, NDMA eluted at approximately 3.5 min. Ions monitored at 74 m/z for NDMA. Reaction mixtures were analyzed after DCM extraction from the water solution according to EPA Method 607 for nitrosamines determination. A calibration curve with a known concentration of NDMA (minimum of five points) was obtained to calculate a final sample concentration. An average percent recovery of NDMA was 32% with a standard deviation of 3.7%.

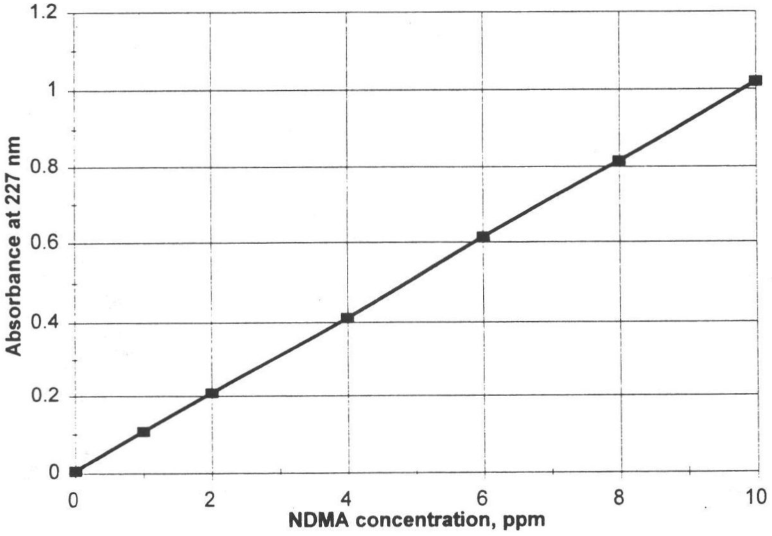
Results and discussion

Figure 2 presents a linear correlation between the NDMA concentration and absorbance in water solutions. UV spectroscopy was found to be a very convenient method for monitoring NDMA concentration during electrochemical reaction. UV-analysis was performed immediately after sampling and the entire procedure required approximately 10 minutes. GC-MS data was used as supporting information and revealed 32% of NDMA recovery. Possible reasons for a low NDMA recovery are as follows: incomplete extraction of NDMA by dichloromethane, evaporation, and decomposition of NDMA during sample preparation.

Table 1
NDMA UV Spectral Characteristics in Water Solutions at Different pH

pH	Wavelength maximum, nm	Absorbance for 10 ppm NDMA solutions
1.0	227	1.0129
3.0	227	1.0144
5.0	227	1.0148
7.0	227	1.0142
9.0	227	1.0 119
11.0	227	1.0140
12.0	227	1.0100

Figure 2
Calibration Curve for UV Analysis
of NDMA Water Solutions



In the first set of tests, the solution pH was maintained in a range 9-12 and the voltage was varied from 0 (control test) to 4.0 volts. It was found that percent of NDMA destruction increased when applied potential increased. Consequently, a constant potential of 3 V was applied to minimize hydrolysis of water which occurs at a higher voltage. The other control experiment was to test whether a voltage was necessary for reduction. The results show that only 0.5% decrease in NDMA concentration occurs without a voltage during 24 hours at acidic conditions and no changes was observed at alkaline conditions. The pH dependence for NDMA electrochemical reaction are represented on Figure 3. As follows from these data, the electrochemical reduction of NDMA is very sensitive to changes in pH.

Results of fifteen experiments, performed at alkaline pH (9 - 12) showed that the average percent NDMA decomposition was 6.3% and the average 2.3% of UDMH was detected in reaction mixture after 6 hours of electrolysis under this conditions. Based on a good reproducibility of the results, the conclusion should be made that no significant reduction of NDMA occurs in alkaline solutions.

Data presented in a Figure 3 indicate that an acceptable reaction rate can be reached only in acidic media. Therefore in subsequent tests, the pH values was maintained in the range of 0.5 to 3.0. Significant improvement in reduction was observed under these experimental conditions The kinetics of NDMA reduction at pH= 0.5 was very fast and almost all detectable amount of NDMA decomposed after 2 hours.

Figure 3
NDMA Reduction at Different pH After 6 Hours

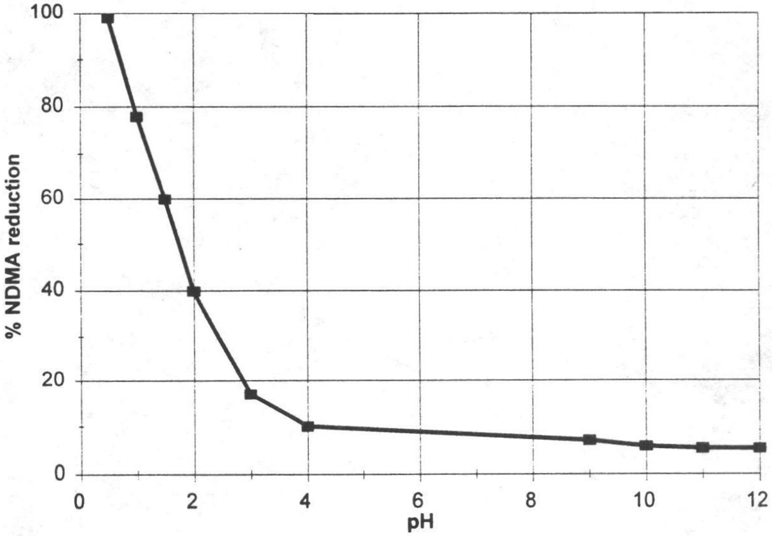
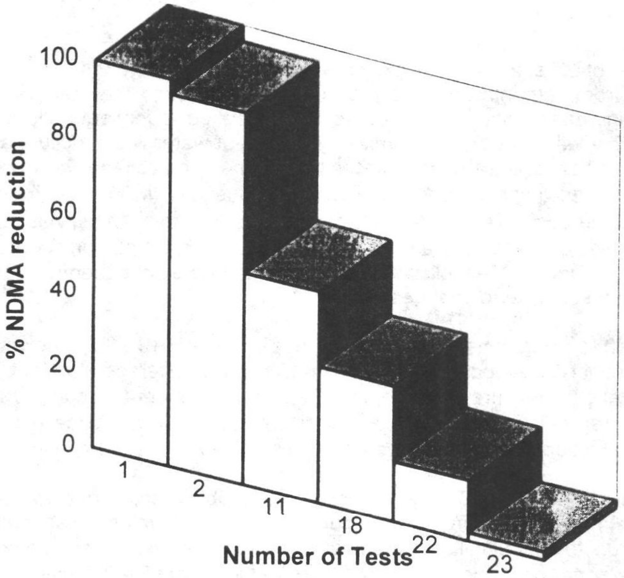


Figure 4
NDMA Reduction Versus Number of Tests



Unfortunately from ten tests performed at pH 0.5 these results were reproduced only in three first replicates. Figure 4 shows that percent reduction went down with each experiment. The major cause of the problem could be the poisoning of platinum electrode possibly as a result of dissociative chemisorption of reaction intermediates or adsorption of sulphate anions themselves [30]. Although fast NDMA decomposition could be reached by means of electrolysis, the search for an appropriate electrode material as well as electrolyte seems to be a serious problem now.

Conclusions

Based on the results of this study, the following conclusions were drawn:

- Electrolytic reduction of N-nitrosodimethylamine (NDMA) was found to be a highly pH sensitive process within range of pH from 0.5 to 4.0.

- Electrolysis was effective for the reduction of NDMA in strong acidic condition. A fast NDMA decomposition occurred at the pH of 0.5 and a potential difference of 3.0 volts.

- No noticeable NDMA reduction was observed in low acidic, neutral and alkaline solutions during 6 hours at applied potential of 3.0 volts.

- Passivation of platinum electrodes was observed in sulphuric acid media. This resulted in a decrease in NDMA reduction efficiency.

References

1. Magee, P.N., Barnes, J.M.: Carcinogenetic Nitroso Compounds. Advan.Cancer Res., 10, 163-246 (1976).

2. Montesano, R. Bartsch: Mutagenic and Carcinogenic N-nitroso Compounds: Possible Environmental Hazard. Mutation Res., 32, 179 (1976).

3. Sen, C.P., Donaldson, B., Iyengar, Jr., et al: Nitrosopyrrolydine and Dimethylnitrosamine in Bacon. Nature (Lond) 245, 473-474, (1973).

4. Wasserman, A.E., Fiddler, W., Doerr,R.C., et al: Dimethylnitrosamine in Frankfurters.Food Cosmet.Toxicol. 10, 681-684 (1972).

5. Scanlan, R.A. N-Nitrosamines in Foods. CRL Crit.Rev.Food .Technol., 5, 357-402.

6. Sen, N.P., Miles, W.F., Donaldson, B. et al: Formation of Nitrosamines in a Meat Curing Mixture. Nature (Lond) 245, 104-105 (1973).

7. IARC Monograph on the Evaluation of the Carcinogenic Risk of Chemicals to Humans. Vol.37. Tobacco Habits Other then Smoking; Betel-Quid and Areca-Nat Chewing and Some Related Nitrosamines. Publ. International Agency for Research on Cancer, Lyon, France, 1986, pp.291, WHO, Geneva, Switzerland.

8. Montag, A: Determination of Nitrosamines in Malt. Evaluation of an Inter-Laboratory Test. Dtsch.Lebensm.-Rundsch, 80 (10) 304-306, Oct.1984

9. Sen ,N.P., Seaman, S., Tessier, L.: Comparison of Two Analytical Methods for Determination of Dimethylnitrosamine in Beer and Ale, and Some Recent Results.J.Food Saf. 4, (4), 243-250, (1982).

10. Lijinsky ,W. Conrad, E., Van De Bogart, R.: Carcinogenic Nitrosamines Formed by Drug/Nitrite Interactions. Nature (Lond) 239, 165-167, (1973).

11. Bogovski, P. and Walker, E.A., eds., N-Nitroso Compounds in the Environment, Lyon, International Agency for Research on Cancer (IARC Scientific Publication No.9), pp.94-100 (1974).

12. Dann, S.R., Pensabene, J.W., Simenoff, M.L.: Analysis Human Blood for Volatile N-Nitrosamines by Gas Chromatography-Chemiluminescence Detection. Chromatog. Biomed. Appl., 25Apr., 50, 35-47 (1986).

13. Fine, D.H. and Rounbehler, D.P. ACS Simposium Series, N0 174: N-Nitroso Compounds,Scanlan and S.R. Tannenbaum, eds., Amer.Chem.Soc. 1981, p.207.

14. Fadlallah, S., Cooper, S.F., Fournier, M., Drolet, D., and Perraut, G., Int.J.Environ.Anal.Chem., 39, 281, (1990).

15. Fajen, J.M., Carson, G.A., Rounbehler, D.P. et al.: N-Nitrosamines in the Rubber and Tyre Industry. Science, N.Y., 205, 1262-1264 (1979).

16. Judeikis, H.S. and Damschen, D.E. Reactions of Hydrazines with Chemicals Found in Environment, Prepared for Space Systems Ltd., Air Force Systems Command, Aerospace Report No.TR-0091(6448)-1, The Aerospace Corporation, El Segundo, California, 1992.

17. Tate III, R.L., Alexander, M: Stability of Nitrosamines in Samples of Lake, Water, Soil and Sewage .J.Natl.Cancer Inst., 54, 237-330 (1975).

18. Tuazon, E.C., Carter,W.P.L., Atkinson, R., Winer, A.M., Pitts, J.N.: Atmospheric Reactions of N-Nitrosodimethylamine. Environ.Sci. Technol.,18, 49-54 (1984).

19. Rizvi, R.: "How Clean is Clean?" - An N-Nitrpsodimethylamine (NDMA) Case Study. The First International Conference on Advanced Oxidation Technologies for Water and Air Remediation, London, Ontario, Canada, June 25-30, 1994.

20. Ontario Ministry of Environtment and Energy, Scientific Criteria Document for Multimedia Standard Development No.01-90: N-Nitrosodimethylamine, March 1991, ISBN 07729-8318-6.

21. Cooper, D. and Keller, L., Advanced Oxidation Technology Demonstration at Oshweken Six Nations Indian Reserve, Proceedings of the Tenth Seminar on Chemical Spills, St.John, New Brunswick, 1993, p.p.51-62.

22. Solarchem Environmental Systems, NDMA - Ultraviolet Photolysis: Summary of Rayox® Installations Treating Nitrosanimes, Technical Information Sheet,

Markham, Ontario, 1993.

23. Whitnack, G.C., Weaver, R.D., Kruse, H.W. Polarographic Behaviour and Large-Scale Electrolysis of Some Alkylnitrosamines, Report No.AD413029, U.S. Naval Ordnance Test Station, China Lake, California, 1963.

24. Volchek, K., Ladanowski, C., Somers, A., Whittaker H.: Electrolytic Decomposition of N-Nitrosodimethylamine in Water. Proceedings of the Twelfth Technical Seminar on Chemical Spills, Edmonton, Alberta, 1995, p.39-47.

25. Pinkerton, M.K., Lauer, J.K., Diamond, P., and Tamas, A.A.,: A Colourimetric Determination for 1,1-dimethylhydrazine (UDMH) in Air, Blood, and Water, Industrial Hygiene Journal, May-June 1963: 239-244.

26. EPA Test Methods. Methods for Organic Chemical Analysis of Municipal and Industrial Wastewater, EPA-600/4-82-057, July 1982.

27. Parsons, R. And Vandernoon, T.: The Oxidation of Small Organic Molecules. A Survey of Recent Fuel Cell Related Research. J.Electroanal.Chem, 257, 9-45, 1988.

28. Haszeldine,R.N., & Jander, J. Studies in Spectroscopy, part VI, Ultraviolet and Infra-Red Spectra of Nitrosamines, Nitrites and Related Compounds. J.Chem.Soc., 691-695, (1954).

29. Druckrey, H., Preussman, R., Ivankovic,S. & Schmahl,D.: Organotrope Carcinogen Wirkungen Bei 65 verschiedenen N-Nitroso Verbindungen an BD-Ratten. Z. Krebsforsch., 69, 103-201, (1967).

30. Parsons, R. And VanderNoot, T.: The Oxidation of Small Organic Molecules. A Survey of Recent Fuel Cell Related Research. J.Electroanal.Chem., 257, 9-45, 1988.

MEMBRANE-ASSISTED PROCESSES
TO REMOVE HEAVY METALS FROM SOIL AND WATER

K.Volchek, B.Veysov, L.Ananieva, V.Atamaniouk
S.Mortazavi, C.Ladanowski, H.Whittaker
Emergencies Engineering Division
Environmental Technology Centre
Environment Canada
3439 River Road
Ottawa, Ontario K1A 0H3

ABSTRACT

A series of bench-scale tests was carried out to evaluate two membrane-based processes. The first process was designed to remove heavy metals from soil. It incorporated slurry leaching coupled with membrane filtration. The soil slurry was continuously filtered through a semipermeable membrane. This resulted in a removal of leaching product from the system during its operation and helped maximize the driving force of leaching.

The second process was intended to remove heavy metals from aqueous streams. It involved the binding of metals with lignosulfonates followed by ultrafiltration. Ultrafiltration membranes used in the study rejected metals ions bound to lignosulfonate molecules thus removing the metals from water.

Both processes appeared to be feasible for the removal of heavy metals from respective contaminated media. Test results are discussed in this paper and recommendations for future work is provided.

BACKGROUND

Heavy metals have been extensively used in various industrial processes, as well as in agriculture. This activity caused wide spread environmental pollution of both soil and ground water.

Hazardous metals present in the soil often migrate into groundwater and may contaminate sources of drinking water. To prevent this contamination, a number of technologies has been used [1, 2, 3, 4, 5]. Ex-situ soil leaching involves an acid and/or chelant-enhanced extraction of metals form the soil slurry. As the extraction progresses, the concentration of lead in the liquid phase (leachate) increases. This increase in the concentration reduces the "driving force" of the leaching process. To minimize this negative factor, the Emergencies Engineering Division of Environment Canada proposed a membrane-assisted soil leaching (MASL) process to treat contaminated soil.

Similarly to a conventional batch leaching, MASL involves metal extraction from the slurry. A portion of the slurry is being filtered through a semipermeable membrane. The membrane rejects soil particles while allowing for the permeation of heavy metal ions and other products of leaching. Since the leached metals are constantly removed from the system, their concentration in the liquid phase is maintained at a relatively low level. Subsequently, this increases the rate of leaching.

Contaminated groundwater, as well as the soil washing leachate, also require metals removal [6]. A number of metals removal processes have been applied both commercially and on a lab scale level. One of the most commonly used technologies is chemical precipitation when heavy metal ions form insoluble compounds (normally, hydroxides at a high pH). These compounds are then separated from water by gravity settling, filtration, or centrifugation. Other metals removal technologies include ion exchange, liquid extraction, reverse osmosis, electrodialysis, etc. [7].

These technologies are effective in the treatment of various waste streams; however, they have drawbacks such as high capital and operating cost, secondary pollution, as well as the necessity to treat concentrates. These limitations stimulate a search for more effective technologies, especially those utilizing inexpensive natural minerals (coal, peat), agricultural products (wool, starch), and wastes (wooden chips, bark, nut shell), as well as industrial wastes (ash, soot, rubber crumbs) [8, 9, 10, 11].

Many of the above products contain polyphenyl compounds, such as tannin and lignin, which are responsible for binding the heavy metals. Lignin and its derivatives, lignosulfonates (LS), are among major by-products of pulp and paper industry [12]. Each year, this industry generates millions of tons of LS in North America alone.

The ability of lignin to act as a sequestering agent for heavy metal ions is well known. The binding of heavy metals with lignin has been extensively studied [13, 14, 15, 16, 17]. It was demonstrated that the binding is practically irreversible and increases as the solution pH increases. Patent [18] suggests using the lignin mixed with sodium bisulphite to effectively absorb mercury vapours. It was reported [15, 16] that copper and cadmium may be removed from waste waters by binding with lignin at certain pH's. The removal of chromium (III) from water was reported to be as high as 100% at pH of 5.5 [13].

LS are capable of binding metal ions and have been used for water softening and providing a controlled release of microelements for the plants [12]. In both cases, however, metals remain in the media (water, soil), instead of being removed from it. The removal of heavy metals from water using LS has not been studied. Once having formed soluble compounds with LS, metals cannot easily be removed from water. Consequently, a method that would allow for a separation of LS-metal compounds from the remainder of the aqueous stream, should be developed and applied.

Among a variety of separation processes, ultrafiltration is a commonly used technique for concentrating dissolved high molecular weight components of solutions [19]. Ultrafiltration membranes allow for a free passage of water, inorganic ions and low molecular organic substances, while rejecting compounds with larger (polymeric) molecules. Ultrafiltration is a highly efficient and cost effective separation process [20]. It appears logical to use it for separating metal-LS complexes from unbound components of the aqueous stream. Even though ultrafiltration membranes do not reject unbound metal ions, ultrafiltration can be very effective in separating metal-polymeric complexes [21].

OBJECTIVES

- To compare the effectiveness of the conventional batch leaching and MASL, in terms of the rate of metal extraction and the quality of treated soil.
- To evaluate the process of metals removal consisting of binding with lignosulfonates followed by ultrafiltration.

MATERIALS AND METHODS

Soil Segregation

Finest soil fractions are known to be the most contaminated and can accumulate more than 80% of total content of heavy metals, depending on the soil type and metal speciation. Therefore it is a common procedure to carry out the mechanical segregation of soil fraction by separating the more contaminated fines from the cleaner coarse fractions. In this study, contaminated soil sample was separated through a series of sieves. A size fraction of less than 150 micron was used in subsequent leaching tests.

Leaching

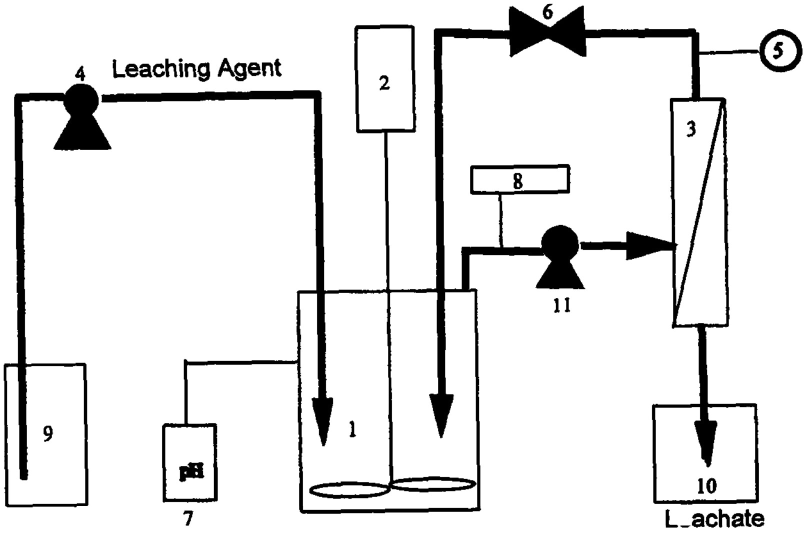
Due to non-homogeneity of soil, all experiments were carried out in triplicates or duplicates. Furthermore, each sample was taken in duplicate.

Batch Leaching. One litre of a 10% by weight suspension was prepared from soil fines and deionized water. The slurry was placed into a two litre beaker and a concentrated solution of hydrochloric acid was added to it to bring the pH to 1. The slurry was agitated using a propeller stirrer. The pH was controlled throughout the tests and maintained at 1 by adding a solution of hydrochloric acid..

Membrane-Assisted Leaching. A simplified diagram of the bench scale system is shown in Figure 1. One litre of a 10% by weight suspension was prepared from soil fines and deionized water. The slurry was placed into a leaching reactor 1 (two litre multi neck flask) and a concentrated solution of hydrochloric acid was added to it to bring the pH to 1. The slurry was agitated using a propeller stirrer 2. The pH was controlled throughout the tests and maintained at 1 by adding a solution of hydrochloric acid. A portion of slurry was pumped through a membrane unit 3, using a heavy-duty peristaltic pump 4. Operating pressure was controlled by pressure gauge 5 and valve 6.

Tubular membranes manufactured by ENKA and US Filters were used in this study. An ENKA module had polypropylene membranes with a filtration surface area of 360 sq.cm. and an average pore diameter of 0.2 micron. A US Filter module had zirconia oxide membranes with a filtration surface area of 44 sq.cm. and an average pore diameter of 0.05 micron. The membrane rejected soil particles, which have been returned back to the reactor 1, while allowing the leachate to permeate through the membrane. The flow rate of fresh HCl added to the system was adjusted to be equal to the rate of the permeate. The volume of the slurry circulating withing the system was therefore maintained constant.

Figure 1
Membrane-Assisted Soil Leaching System



1 - leaching reactor (extractor); 2 - stirrer; 3 - membrane module; 4,11 - pumps; 5 - pressure gauge; 6 - pressure control valve; 7 - pH meter; 8 - thermocouple; 9 - container for leaching agent (hydrochloric acid); 10 - container for leachate.

Sampling and Sample Preparation. Samples ob both the soil and the aqueous phase (leachate) were taken at the following time intervals from the beginning of the test, expressed in hours: 0; 0.25; 0.5; 1; 2; 4; 6; and 24. Aqueous samples were preserved with concentrated nitric acid and stored in the refrigerator.

Soil samples were collected and centrifuged. Solids were filtered and rinsed with deionized water, to remove traces of acid. Solids then were pulverized, incinerated, and digested, according to [EPA, Method 3050; IWSOLID MOE Sampling Guidelines 900925].

Binding with Lignosulfonates/Ultrafiltration

Samples of industrial lignosulfonates were obtained from Earth Sciences Corp. Their average moisture content was 10%. More than 98% of LS had a molecular weight of 2,500 Dalton and higher.

Spiked solutions of lead and mercury were prepared from their nitrates and deionized water. Sodium chromate and deionized water were used to make spiked solutions of chromium. The concentration of each metal was 100 ppm.

All experiments were carried out using a 450 ml stirred cell distributed by Cole-Parmer. Proprietary thin film membranes used in the tests were supplied by Desalination Systems, Inc. The membranes with product names G-5 and G-10 had a molecular weight cut-off of 1,000 and 2,500, respectively. . An ambient temperature of 20-22^{0}C was maintained, while operating pressure varied from 20 to 50 psi.

Spiked solutions or actual waste water samples were mixed with LS in a desired ratio. The pH was adjusted using solutions of hydrochloric acid or sodium hydroxide. After each test solution was placed in the cell, its pH was measured and a 5 ml solution sample taken. During ultrafiltration, first 20 ml of the permeate were discharged; then two 5 ml samples of the concentrate and two 5 ml samples of the permeate were collected. Upon completion of the test, the concentrate pH was measured. Samples were preserved with concentrated nitric acid. Test solutions and samples were stored in the refrigerator at 4^{0}C.

Analyses

Concentration of LS in solution was determined using a Perkin Elmer Lambda 2 UV/VIS spectrophotometer. Lead and chromium were analysed in-house using a Perkin-Elmer 3100 atomic absorption spectrophotometer. Mercury containing samples were sent to a commercial laboratory and analysed using atomic absorption spectroscopy. In each test, the rejection (R) of a metal by the membrane was determined as

$$R = (1 - C_p/C_c) * 100\% \qquad (1)$$

where C_p and C_c are metal concentrations in the permeate and the concentrate, respectively.

RESULTS AND DISCUSSIONS

Soil Leaching

Test results reveal that in case of batch leaching, the concentration of leached metals grows steadily until it reaches an equilibrium between metal concentrations in the liquid and solid phases (Figure.2). In same experiments, a decrease in the metal concentration in the liquid phase was observed after several hours of leaching. This phenomenon should be attributed to the resorption of metal ions onto soil particles. In diafiltration tests, metal concentration first increased then decreased due to the removal of metals with the permeate. This greatly reduced chances for resorption.

In light of the above, the incorporation of a membrane into the leaching process appears to be logical. When slurry is pumped through the module, heavy metal ions are continuously removed from the system; therefore, their accumulation is largely eliminated. Since the metal concentration in the aqueous phase remains at a relatively low level, the "driving force" of the membrane-assisted leaching is higher then one of the batch leaching.

Figures 3 and 4 illustrate the concentration of metals remaining in the soil, as a function of time, for the batch and diafiltration modes. For both the lead and chromium, the initial rate of metal removal was substantially higher in case of diafiltration. After six hours of extraction, soil treated with MASL had only 29% of initial chromium and 30% of initial lead, compared to 39% and 48% achieved in the batch process.

Figure 2

Lead Concentration in the Leachate as a Function of Time

Initial average Pb concentration in soil = 28 g/g soil.

Membrane: tubular ENKA 0.2 micron. Pressure = 8 psi.

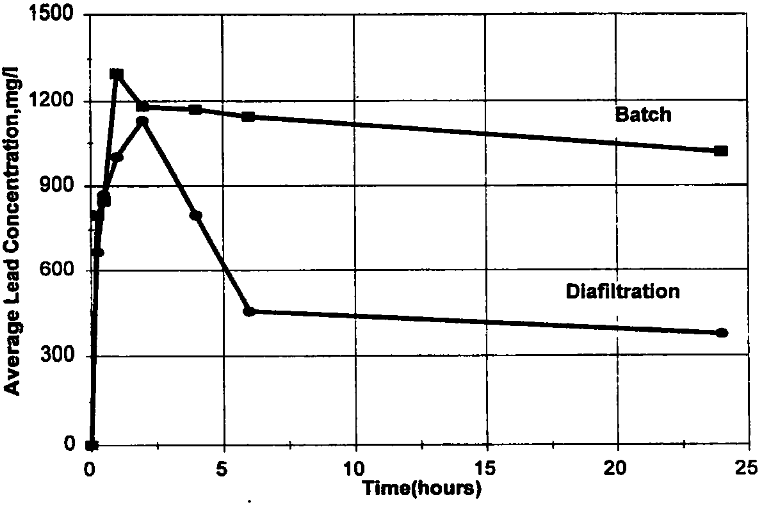


Figure 3

Percent of Lead Remaining in the Soil vs. Time

for Batch and Diafiltration Modes

Initial average Pb concentration in soil = 28 g/g soil.

Membrane: tubular ENKA 0.2 micron. Pressure = 8 psi.

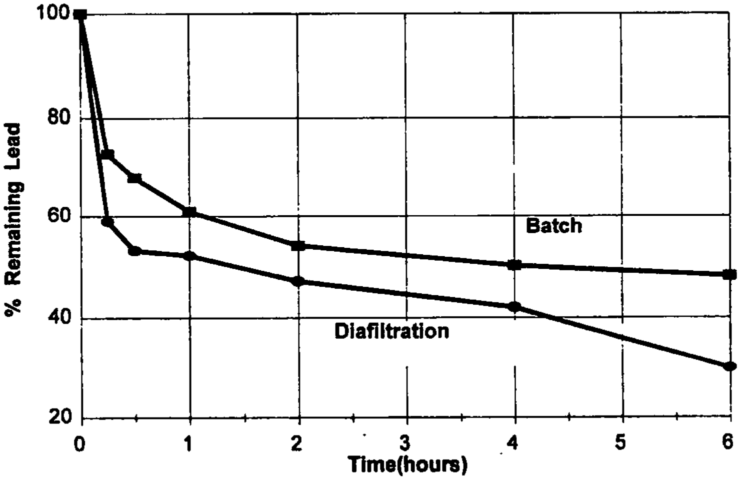
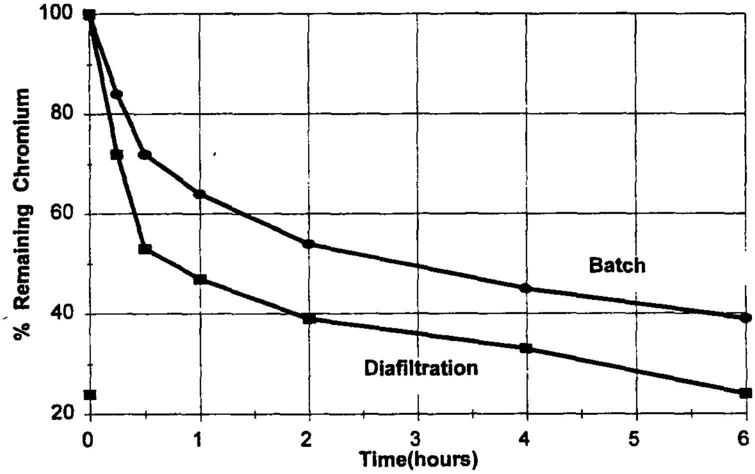


Figure 4
Percent of Chromium Remaining in the Soil vs. Time for Batch and Diafiltration Modes
Initial average Cr concentration in soil = 30 g/g soil.
Membrane: tubular ENKA 0.2 micron. Pressure = 5 psi.



Lignosulfonate Sequestering

Lead

Figure 5 illustrates the rejection of lead by the membrane, calculated using Eq.1, as a function of the solution pH. The lower curve corresponds to the tests where no lignosulfonates were added while the upper curve relates to the tests with 1,000 ppm of LS present in the solution. The fact that the rejection of lead is much higher in the presence of LS confirms that lead is being bound by LS. In the range of pH between 7 and 11, the rejection is higher than 95%, being the highest and equal to 99.76% at pH 8.3.

This phenomenon can be explained by the fact that the groups in LS molecules responsible for lead binding are more active in neutral and basic conditions rather than in acidic. A slight decrease in rejection at pH higher than 9 is likely a result of increasing lead hydrolysis. The formation of lead hydroxide and the binding of lead with LS are competitive reactions. Higher pH values enhance both reactions. Binding with LS seems to prevail in neutral and slightly basic conditions whereas hydrolysis is prevalent in more basic conditions.

Figure 6 presents the rejection of lead as a function of the weight ratio of LS to lead. This series of tests was carried out at pH 7.6±0.1. As expected, more LS present in the solution binds more lead; this subsequently results in a higher rejection of lead by the membrane.

Figure 5
Rejection of Lead by the Membrane G-10
as a Function of pH
Initial Pb concentration = 100 ppm. Pressure = 40 psi.

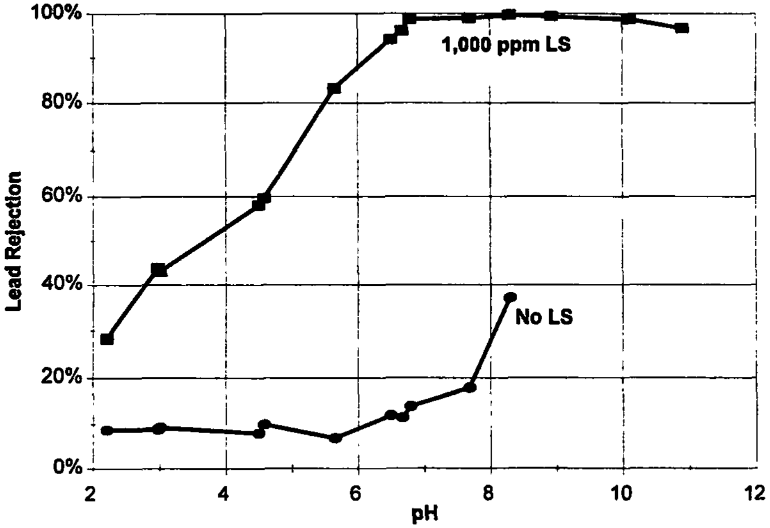
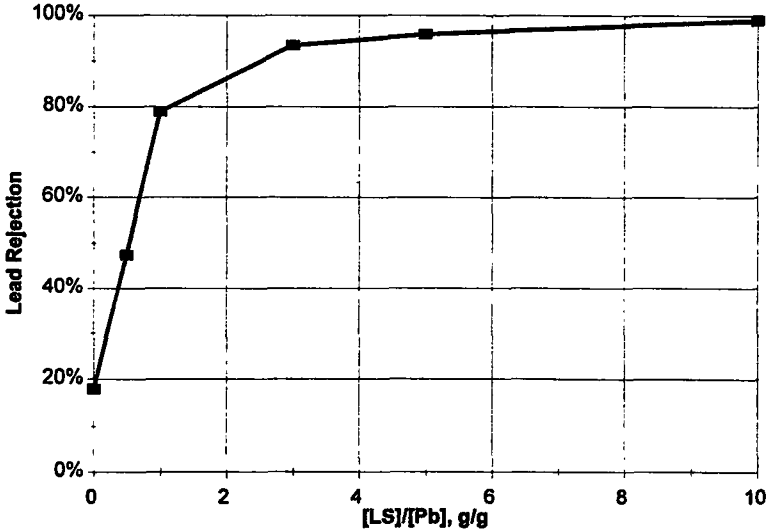


Figure 6
Rejection of Lead by the Membrane G-10
as a Function of Lignosulfonate/Lead Weight Ratio
Initial Pb concentration = 100 ppm. Solution pH = 7.6±0.1.
Pressure = 40 psi.



Chromium

Results of chromium binding are presented in Table 1. Lignosulfonates do not seem to affect the rejection of chromates. The rejection increases with pH at almost the same rate for Cr(VI) alone and its mixture with LS. The lack of interaction between LS and Cr(VI) was not unexpected. It is known that LS are binding metal cations; however, there was no data available on its interaction with anions.

A high rejection (greater than 90%) of chromate is more surprising. Chromates are normally well rejected by reverse osmosis and nanofiltration membranes; however, the observed data suggest that even ultrafilters used in this study can effectively reject chromates in basic conditions. This phenomenon may be attributed to a possible repulsion between chromate ions and the negatively charged membrane surface.

Table 1
Rejection of Chromium (VI) by the Membrane
at Different pH

pH	Chromium Rejection* (%)	
	0 ppm Lignosulfonate	1,000 ppm Lignosulfonate
1.9	24	
2.6		43
7.0		76
7.7	91	
11.6		89
12.3	94	

* Initial chromium concentration: 100 ppm

Mercury

Results of the tests carried out on mercury solutions revealed that in a pH range of 4 to 6, the rejection of mercury is 10% to 40% higher than in its absence.

CONCLUSIONS AND RECOMMENDATIONS

- The membrane-assisted leaching process (MASL) was found to be more effective than the conventional batch process. Removal rates for both the lead and chromium were substantially higher for MASL. MASL generated cleaner soil than the batch leaching.
- The method of binding onto lignosulfonates followed by ultrafiltration was found to be effective for the removal of lead from aqueous systems. Results of tests carried out on spiked solutions revealed that at a pH higher than 7 and a weight ratio of LS to lead of 10, more than 98% of lead could be removed from the

solution.

- Lignosulfonates were less effective in binding mercury and practically ineffective in binding hexavalent chromium. The rejection of chromium observed in basic conditions should be attributed to the repulsion between chromate ions and the membrane surface whose negative charge is greater at a higher pH.

In terms of lead removal from aqueous streams, the following factors of the process should be studied to evaluate its efficiency:

- affinity of LS to lead in the presence of other cations. It is important that LS primarily bind lead instead of interacting equally with all cations present in the solution.

- a maximum concentration factor that can be achieved in ultrafiltration. The smaller the volume of the residual concentrate, the easier the task to treat the concentrate.

- concentrate treatment options. There is no need to regenerate LS for reuse as they are cheap. Concentrates resulting from ultrafiltration require, however, a subsequent treatment such as solidification or incineration.

- membranes. Ultrafiltration membranes used in this work had a low molecular weight cut-off (MWCO) of 1,000 and 2,500 Dalton and, accordingly, a low water permeability. These membranes were selected to assure a complete rejection of LS which had a broad molecular weight distribution. If, however, a higher molecular weight fraction of LS is used, membranes with a higher MWCO and a higher permeability could be utilized. An increase in the water flux will reduce the process cost.

It appears to be worthwhile to study further the effect of chromate rejection at higher pH. Even though LS were not found to be affecting the removal, the fact that chromium can be effectively rejected by an ultrafiltration membrane may be of a practical interest.

ACKNOWLEDGEMENTS

The authors express their appreciations to Dr. Martin Weber of McGill University and Drs. Wayne Parker and Paul VanGeel of Carleton University for their contributions and that of their students to this work.

LITERATURE

1. "Remedial Action, Treatment, and Disposal of Hazardous Waste", *Proc. of the 17th Annual Hazardous Waste Research Symp.*, Cincinnati, Ohio, April 9-11, 1991, 695 p.p.

2. Krishnan, E. R; Kemner, W.F., "Innovative Eletromembrane Process for Recovery of Lead From Contaminated Soils"; *Proc. of the 80th APCA Annul. Meeting*, 1987, v. 1.1, 87-20.5, 22 pp.

3. Trnovsky, M.; Oxer, J.P.; Rudy R.; et al., "Site Remediation of Heavy Metals Contaminated Soils and Groundwater at Former Battery Reclamation Site in Florida"; *Hazardous Waste: Detection, Control,Treatment*: Amsterdam, 1988, pp. 1581- 1590.

4. Tuin, B.J.W.; Tels M., "Distribution of Six Heavy Metals in Contaminated Clay Soils Before and After Extractive Cleaning", *Environmental Technology*, v.11, pp. 935-948.

5. Linn J.H., Elliot A., "Mobilization of Cu and Zn in Contaminated Soil by Nitrilotriacetic Acid"; *Water, Air, Soil Pollut.*, 1988, **37** (3-4), 449-58.

6. Buckley, L.P.; Killey, R.W.D.; Vijayan, S.; et al., "Treatment of Groundwater and Soil Wash Leachate Solutions Containing Mixed Waste Contaminants", *Proc. of Spectrum 1992: Hazardous Waste Management International Meeting*, Boise, Idaho, August 23-27, 1992.

7. *Encyclopaedia of Wastewater Treatment Technology*, Edited by Cheremisinoff, P.N.; Gulf Publishing Co., 1989.

8. Coupal, B. And Labanceite, J.M., "The Treatment of Wastewaters with Peatmoss", *Waste Research*, 1976, **10**, 1071.

9. Masri, M.S.; Reuter, F.F.; and Frieman, M. , "Binding of Metal Cations by Natural Substances", *J. Appl. Polym. Sci.*, 1976, **18**, 675.

10. Wing, R.E. and Rayford, W.E., "Starch Based Products Effective in Heavy Metal Removal", *Proc. Purdue Ind. Waste Conf.*, 1976, **30**, 1068.

11. Friedman, M.; Harrison, G.S.; Ward, W.H.; et al. , "Sorption Behaviour of Mercury and Mercuric Salts on Wool", *J. Appl. Polym. Sci.*, 1973, **17**, 377.

12. "Lignin", *Kirk-Othmer's Encyclopaedia of Chemical Technology*, Edited by Howe-Grant, M.; v.15, John Wiley & Sons, 1995.

13. Kosenko, V.A.; Rudenko, V.I.; Romaschenko; et al. V.E. , "Study of Heavy-Metal Ion sorption by Hydrolyzed Lignin", *Voprosy Khimii I Khimicheskoi Tekhnologii*, 1991, **94**, 23-5.

14. Laatikainen, M., "Adsorption of Cationic Compounds on Groundwater and on Cellulose and Lignin Surfaces", *J.Colloid and Interface Sci.*, 1989, **132**, No. 2, 451-61.

15. Varma, K.V.R.; Swaminathan, T.; and Subrahmanyam, P.V.R., "Studies on Copper Removal by Lignin Solution/Suspension", *J. Envir. Sci. Health*, 1989, **A24(8)**, 847-61.

16. Varma, K.V.R.; Swaminathan, T.; and Subrahmanyam, V.P.R., 'Heavy Metal Removal with Lignin", *J. Envir. Sci. Health*, 1990, **A25(3)**, 243-65.

17. Kulik, F.; Wieber, J.; Pethica, B.; et al., "Binding of Copper (II) and Zinc (II) Ions on Various Lignins", *J. Electroanal. Chem.*, 1986, **214**, 331-42.

18. Anarbayev, A.A.; Batkayev, J.J.; Ospanov, S.S, et al., "Method of Cleaning Gases from Mercury", *SU Pat. No. 1,816,488.*

19. "Advances in Reverse Osmosis and Ultrafiltration", *Proc. of Symp. on Advances in Reverse Osmosis and Ultrafiltration*, Toronto, Ont., June 7-10, 1989.

20. Scott, K. Membrane Separation Technology. Industrial Applications and Market, *Scientific and Technical Information*, Oxford, U.K., 1990.

21. Michaels, A.S., "Membranes, Membrane Processes, and their Applications: Needs, Unsolved Problems, and Challenges in the 1990's", *Desalination*, 1990, **77**, 5-34.

"The Use of Optical Remote Sensing with Pre-Set PPM-M Trigger Levels to Rapidly Assess the Potential Off-Site Impact of Accidental Releases"

Thomas H. Pritchett
Pritchett Air & Environmental Services, Inc.
Easton, PA 18042

Orman Simpson
ETG Electro-optics Division
Norcross, GA 30071

Over the past few years, Optical Remote Sensing (ORS) technologies have been proposed and used for leak detection and fence line monitoring for industrial installations throughout the world. However, because ORS technologies measure the total concentration in the beam (units - ppm-m), it has required an atmospheric dispersion modeler to convert the ppm-m reading from a detected release to the ppm maximum plume concentration that was actually crossing the beam. Since such staff are rarely available 24 hours a day 7 days a week, this modeling requirement has severely hampered the use of ORS for performing the rapid impact assessment needed during accidental releases. The authors have developed an approach in which upfront modeling is used to pre-define three levels of ppm-m trigger values that enable the plant staff to quickly evaluate the potential impact based upon the trigger level crossed by the observed reading. In addition. the authors have developed a set of recommended actions corresponding based upon the magnitude of the release as determined by the tripped trigger level.

RECENT CHEMICAL SPILL DATA

Merv Fingas
Emergencies Science Division
Environmental Technology Centre
Environment Canada
Ottawa, Ontario

Carol Lau
Environmental Emergencies Branch
Hull, Quebec

Introduction

In 1979, the Environmental Emergencies Branch (as it was then known) 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.[1]

Spill Priority Lists

The first spill priority list was developed in 1980.[2,3] 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.

Candidate chemicals and hazardous substances other than oil, were taken from all known spill priority lists such as those published by the United States Environmental Protection Agency, The American Association of Rail Roads and The United States Coast Guard. Lists of materials from the Transport of Dangerous Goods Act were also included. The United States Environmental Protection Agency has published a "List of Lists" which includes substances noted in RCRA, SARA and CERCLA legislation. References 4 to 13 provide details on these.

The next priority list (1990) was completed using a five-way categorization of spill priorities including spill numbers, spill volume, mammalian toxicity, aquatic toxicity and supply volume. The resulting lists will be referred to later in this paper. The details of this priority exercise are given in references 14 and 15.

New Spill Data

Almost ten years have passed since the last chemical data set was thoroughly analysed. Recently another ten year record was derived from the NATES data base. This data has not been verified in detail. However, It is felt to be important to release this data so that use can be made of it in priority planning exercises and countermeasures preparations. Tables 1, 2 and 3 present this data in orders of spill numbers, chemical name and spill mass.

Table 4 lists the chemicals in the existing spill priority list and Table 5 gives the complete listing. Table 6 provides the data on the complete list by name and Table 7 by priority rank.

References

1. Beach, R.A., "Information Systems Used in Environmental Emergencies", *Spill Technology Newsletter*, Vol.3, No. 5, pp. 283-287, 1978.

2. 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.

3. Fingas, M.F., *Papers, Tables and Other Data Relating to the Development of a Chemical Spill Priority List for the Environmental Protection Service*, Environmental Emergencies Technology Division, Environment Canada, Ottawa, 1984.

4. U.S. Coast Guard, *Chemical Hazards Response Information System*, Manual 2, 1978.

5. U.S. Environmental Protection Agency, *Federal Register*, 44, No. 128, 38746-38776, 1979.

6. Hobbs, John R., *Monitoring Devices for Railroad Response Teams*, U.S. Department of Transport, Cambridge, Ma., 1985.

7. U.S. Environmental Protection Agency, *Federal Register*, 51, No. 188, 34534-34549, 1986.

8. U.S. Environmental Protection Agency, *Hazardous Material Intelligence Report*, December 1985.

9. "Regulations respecting the handling, offering for transport, and transporting of dangerous goods", *Canada Gazette*, 1985.

10. U.S. Environmental Protection Agency, *Toxic Substances Control Act Chemical Substances Inventory*, Cumulative Supplement II, 1982.

11. U.S. Environmental Protection Agency, *Perspectives on the Top 50 Production Volume Chemicals*, 1980.

12. Association of American Railroads, *The AAR Hazardous Materials Data Base*, Part I and II, 1981.

13. U.S. Environmental Protection Agency, *List of lists*, July 1987.

14. Fingas, M.F., "The Development of a new Spill Priority List", *Spill Technology Newsletter*, *Vol. 16*, *No.3*, pp. 1-8, 1991.

15. 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 1 **Annual Spill Rate - By Numbers (based on data from 1985-1994)**

Annual spill Amount Substance	**#**	**Mass (tons)**	**Volume (L)**	**Annual spill Amount Substance**	**#**	**Mass (tons)**	**Volume (L)**
chemical nos	23.4	29586.9	23427224	calcium hydroxide	1.4	6.7	957.1
sulfuric acid	22	7583.8	5531984.6	ethanol	1.4	21	26572.4
crude/salt water emulsion	18.7	142.4	149195	*isophthalic acid*	1.4	2656.3	2653668
hydrochloric acid	18.4	104.4	83924.6	molybdate	1.4	7.7	7777
sodium hydroxide	16.3	1869.2	331659.9	viscose nos	1.4	14	
sulfur	8.2	2425.1	355880.7	bacillus thuringiensis	1.3	1.3	180.6
fertilizer nos	7.9	7907.7	165078.3	ammonium phosphate	1.2	137	64278.1
ethylene glycol	7.8	16.1	10196.7	calcium hypochlorite	1.2	3.9	507
ammonia anhydrous	6.7	72.4	11413.3	lead conc or ore nos	1.2	212.9	26711.1
paint and materials	6.3	35.2	9605.9	freon	1.1	6.3	6150.8
ammonium nitrate	5.7	247.1	76093.8	nitrogen	1.1	17.6	12850.2
ammonium hydroxide	5.6	2027.6	3341783.5	potassium hydroxide	1.1	2	788.3
methanol	4.7	276.4	16041	propylene glycol	1.1	2.5	1178.1
phosphoric acid	3.8	17.7	10786.1	aluminum sulfate	0.9	18.7	4674.4
quicklime	3.7	117.5	28847.1	carbon disulfide	0.9	9304.2	7371163
sodium chlorate	3.4	70.6	50583	*dye or dye intermediate*	0.9	21.4	21167.2
nitric acid	3.1	2.8	865.1	ethylbenzene	0.9	34.5	18895.3
calcium chloride	3	70.4	42705.2	ferric nitrate	0.9	52.4	52426.5
iron and ores	2.8	7680.3	7650734.9	green liquor	0.9	26.3	0
sodium chloride	2.7	834.4	26742.3	hydrogen peroxide	0.9	0.4	203.5
zinc and concentrates	2.7	133.1	63882.9	hydrogen peroxide	0.9	9.9	9391.1
drilling mud	2.6	101.1	35739.5	phenolsulfonic acid	0.9	4.9	2967.4
dielectric fluid nos	2.5	11.4	8838.3	polyvinyl acetate	0.9	17	1058.1
cleanser	2.4	18	104.7	*sodium bisulfate*	0.9	46.9	28922.2
copper ores	2.3	1118.3	1087611.6	sodium hydrosulfide	0.9	0.8	676
sodium hypochlorite	2.3	12.9	12050.5	sulfur dioxide	0.9	30.1	9247.3
caustic alkali liquid nos	2.2	11.5	4477.9	aluminum sulfate	0.8	15.6	4794.8
inorganic chromate nos	2.2	10	7788.4	fluosilicic acid	0.8	13.9	11510.9
nickel ores and concentrate	2.2	1095.6	1075509.1	isopropanol	0.8	0.5	163.7
phenol	2.2	142.4	142281	pesticide nos	0.8	3.3	0
potassium chloride	2.2	1162.8	14293.3	polyvinyl chloride	0.8	4	1612.9
sodium sulfate	2.2	22.4	8954.5	vinyl acetate	0.8	0.4	267.8
urea	2.2	28.5	9625.8	acetonitrile	0.7	9.1	7146.5
chromic acid	2.1	6.4	5214.5	acrylonitrile	0.7	120.9	137907
formaldehyde	2	5.9	2630.7	adhesives nos	0.7	0.5	48.8
vinyl chloride	2	12.8	13186.8	butyl alcohol	0.7	2135.3	2669884
latex	1.9	6.9	1437.5	*difenzoquat methyl sulfate*	0.7	0.3	128.6
liquid fertilizer nos	1.8	17	465.1	ferric chloride	0.7	4.8	
phenolic resin	1.7	13.2	10988.4	herbicide nos	0.7	1.4	174.4
sodium dichromate	1.7	3.2	1831	hydrofluoric acid	0.7	16.7	2093
2.4-d	1.5	1.9	1676.5	hydrogen chloride anhydro	0.7	21.3	20767.5
calcium carbonate	1.5	638.4	635703.7	jeffamine	0.7	0.1	
chlorine	1.5	588.5	243652.7	lacquer base	0.7	0.7	
sodium cyanide	1.5	11.4	11314.3	pentachlorophenol	0.7	4.9	3084.4
styrene monomer	1.5	10.8	11720.1	*acetic anhydride*	0.6	19.5	16624.3
surfactant	1.5	73935.5	741.7	calcium lignosulfonate	0.6	4	2185.7
acid nos	1.4	19.2	12535.5	corrosion inhibitor	0.6	1.6	
cyclohexylamine	0.6	0.2	122.2	asbestos white	0.3	7.1	
dimethoate	0.6	0.6	631.8	ash	0.3	32.6	428.6
dowtherm	0.6	4.3	0	cement	0.3	1	114.3
flammable liquid nos	0.6	0.2	45.6	chlorine dioxide	0.3	9.5	9428.9
flocculant nos	0.6	59.2	132.3	cresol	0.3	0.1	
mdi	0.6	0.5	0	diethanolamine	0.3	1.1	1062.2
polyethylene	0.6	1.9	823.3	dipel	0.3	0.1	0
sodium pentachlorophenate	0.6	0.4	429	dithane	0.3	0.3	
sodium sulfite	0.6	41.2	6451.6	firefighting foam	0.3	0.3	281.3
toluene diisocyanate	0.6	0.3	107.5	glyphosate	0.3	0.3	247.7
trichloroethylene	0.6	1.4	80.8	hydrofluorosilicic acid	0.3	0.7	13
aluminum chloride	0.5	4.2	3720.9	hydrogen	0.3	1.6	486.1
atrazine	0.5	0.3	316.3	iron sulfite	0.3	0.2	

Table 1 **Annual Spill Rate - By Numbers (based on data from 1985-1994)**

Annual spill Amount Substance	**#**	**Mass (tons)**	**Volume (L)**	**Annual spill Amount Substance**	**#**	**Mass (tons)**	**Volume (L)**
calcium carbide	0.5	0.3	32.6	isocyanate nos	0.3	0.1	0
coagulant nos	0.5	0.1		ketones liquid nos	0.3	0.1	
diphenyloxide	0.5	0.2		liquid pesticide nos	0.3	0.1	57.1
fenitrothion	0.5	1.1	533.4	monomethylamine	0.3	1.9	266.7
ferrous chloride	0.5	0.7		picloram	0.3	0.2	
hydrazine	0.5	5.7	5488.4	recycled ash water	0.3	1428.6	
lignosol	0.5	14.3		sodium carbonate	0.3	2.8	2473.1
methyl chloride	0.5	8.2	7674.4	sodium dithionite	0.3	1.3	1268.8
methyl methacrylate	0.5	3		urea formaldehyde	0.3	1.6	856.3
mine feed slurry nos	0.5	9.3	8571.4	xylenes	0.3	0.2	133.5
nitrite nos	0.5	4.7	4669.3	2-ethylhexanol	0.2	0.3	344.6
nitrogen dioxide	0.5	3.3	3347.9	adipic acid	0.2	0.6	
paraquat	0.5	0.6	634.9	aluminum oxide	0.2	2.7	2709.7
pyrrhotite	0.5	21.6	4651.2	ammonium chloride	0.2	0.5	534.9
sodium chlorite	0.5	66.4	192.9	ansilex	0.2	0.2	
sodium nitrate	0.5	5	26.9	antimony trioxide	0.2	0	
sodium nitrite	0.5	0.1	125.6	arborgreen	0.2	0.5	
sodium thiocyanate	0.5	10.6	10465.1	azinphos-methyl	0.2	0.1	107.4
tetraethyl lead	0.5	0.7		basic waste	0.2	2.1	
aminocarb	0.4	0.5	416.8	benzene sulfonic acid	0.2	1	
barium sulfate	0.4	10.6	5000	benzoyl chloride	0.2	0	
calcium	0.4	0.8	568.8	betasan	0.2	0.1	
carboxin	0.4	0.1		betz 2040	0.2	0.1	121.6
emulsifier nos	0.4	1	837.2	biocide	0.2	0.3	316.3
ethanolamine	0.4	0.8	0	butyl acetate	0.2	0.1	79.1
fatty acid nos	0.4	1.1	0	butylate	0.2	0.2	209.3
liquor nos	0.4	0.8	838.5	butylene	0.2	1.9	1860.5
mercury	0.4	18.2	1.3	carbon dioxide	0.2	69.8	
zinc sulfate	0.4	219.4	4520.1	cast iron	0.2	20.9	
acephate	0.3	0.1	56.4	cement seal	0.2	0.1	
alkaline solution	0.3	1007.3	1007311.8	chromium salt	0.2	2.1	
ammonium sulfate	0.3	2.8	1366.7	corn liquor	0.2	5.3	
aqueous film forming foam	0.3	0.6	601.9	corrosive liquid poisons	0.2	1.2	
arsenic	0.3	22.9	22885.7	dalapon	0.2	0.1	
diacetone	0.2	0.5		sodium dodecylbenzenesulphon	0.2	0	46.5
diazinon	0.2	3.2	22.2	stannic chloride	0.2	0	
dichlorfop	0.2	0		sulfur trioxide	0.2	0.6	581.4
diisobutylene	0.2	0.2		tin fluoborate	0.2	0.2	126.7
dimethylacetamide	0.2	0.3		trichlorfon	0.2	20.9	20930.2
dimethylcyclohexylamine	0.2	0	46.5	triethanolamine	0.2	0.1	81.4
dinitrotoluene	0.2	125.6	125581.4	urea nitrate	0.2	0.3	
dioctylphthalate	0.2	1.3	1348.8	urethane	0.2	0.3	
diphenyl	0.2	0.1		wetting agent nos	0.2	0	
dormet	0.2	0	34.9	wood preservative	0.2	9.3	9302.3
eptc	0.2	0.1		zinc phosphate	0.2	0.2	158.6
ethyl acrylate	0.2	0.1		zylvol	0.2	0	
ethylene	0.2	1.6		acrylamide	0.1	0	28.6
ethylene dibromide	0.2	0.8	823.3	aluminexpo	0.1	0.4	428.6
ferric phosphate	0.2	0.5		aluminum alkyl compound	0.1	0.2	215.1
ferrous persulfate	0.2	0.1	121.6	aluminum fluoride	0.1	0.3	
fluoboric acid	0.2	0.2	84.4	amine nos	0.1	0.1	
fluorescein	0.2	29.3	29302.3	ammonium bisulfite	0.1	0	
fly ash	0.2	3.5		ammonium thiosulfate	0.1	1	
formic acid	0.2	0	60.5	arsenic trioxide	0.1	0.1	142.9
germicide nos	0.2	0.7	639.5	barium chlorate	0.1	0.8	
isopropane	0.2	3.5		barium sulfate	0.1	5	5028.6
isothiazol	0.2	0.2		benzoic acid	0.1	0.1	78.9
krenite	0.2	0.1	116.3	bithanem45	0.1	0	
lead acetate	0.2	0.1		bromine	0.1	0	39.1
lead sulphate	0.2	5.4	5399.2	bromotrifluoromethane	0.1	0.8	782

Table 1 **Annual Spill Rate - By Numbers (based on data from 1985-1994)**

Annual spill Amount Substance	**#**	**Mass (tons)**	**Volume (L)**	**Annual spill Amount Substance**	**#**	**Mass (tons)**	**Volume (L)**
liquid nos	0.2	0.6		bromoxynil	0.1	0	
lithium metal	0.2	2.3	2325.6	calcium lignosulfate	0.1	1	1000
magnesite	0.2	0.5		carbamate	0.1	0	22.8
magnesium chloride	0.2	0.1	104.7	carbaryl	0.1	0.2	164.3
maleic anhydride	0.2	1	1046.5	carbofuran	0.1	0.1	64.3
mcpa	0.2	0.5		chloride nos	0.1	1.6	1571.4
metachlor	0.2	0.9	860.5	chloro-alkali brine	0.1	0.5	500
methylphosphoric acid	0.2	0		chlorpyrifos	0.1	0.1	
naphthalene	0.2	0.2	158.1	counter 5g	0.1	0	
naphthalenesulfonic acid	0.2	0		cupric sulfate	0.1	0.3	122.2
nitrate nos	0.2	11.3	11302.3	cyanide solution nos	0.1	0.2	222.2
nitrilotriacetic acid	0.2	0.1		diethylamine	0.1	2.2	2250
phenoxy nos	0.2	0.3		diethylene glycol	0.1	0.2	178.7
potassium nitrate	0.2	0		diethylenetriamine	0.1	1.4	
propylene oxide	0.2	0.8		diisocyanate	0.1	0.2	215.1
pyrite slurry	0.2	9.3		dimethyl disulfide	0.1	340.6	
silicic acid	0.2	1		epoxy resin	0.1	0	
soap	0.2	0.2		ferric sulfate	0.1	0.4	285.7
sodium ethyl sulfate	0.2	0.1		formic acid	0.1	2.4	2000
sodium sulfide	0.2	0.1	116.3	hydrogen fluoride anhydro	0.1	1.1	1075.3
sodium thiosulfate	0.2	0.1		hydrogen sulfate	0.1	1.3	1285.7
hypochlorite solution	0.1	0.1	111.1				
lead/zinc concentrate	0.1	5.3					
magnesium hydroxide	0.1	0.2	77.8				
manganese	0.1	0	17.9				
metal hydroxide nos	0.1	4.2					
methyl isopropenyl ketone	0.1	0					
mmt	0.1	0.1					
molten aluminum	0.1	1.6	1623.6				
ore nos	0.1	0					
ortho dichlorobenzene	0.1	0					
parathion-methyl	0.1	0.1					
phosphorus pentoxide	0.1	3.2					
phosphorus white	0.1	1.1	580.6				
polyol	0.1	0.2	215.1				
polystyrene	0.1	0.3					
polyurethane	0.1	0.1					
residual herbicide	0.1	0.1					
silver concentrate	0.1	1.9					
sodium	0.1	1.3	1428.6				
sodium aluminate	0.1	0.2	161.3				
sodium isopropylxanthate	0.1	0	15.6				
solibor	0.1	0					
sulfamic acid	0.1	2	2000				
tetrafluoroethylene	0.1	0	34.1				
titanium dioxide	0.1	0.3					
tricresyl phosphate	0.1	0	50				
trifluralin	0.1	0					
vitaflo 280	0.1	0	21.5				
weed and feed	0.1	2.7					
electroplated tin	0	0.5	267.4				
Total	209	110881	18722194				

Table 2 **Annual Spill Rate - By Name (based on data from 1985-1994)**

Annual spill Amount Substance	**#**	**Mass (tons)**	**Volume (L)**	**Annual spill Amount Substance**	**#**	**Mass (tons)**	**Volume (L)**
2,4-d	1.5	1.9	1676.5	betz 2040	0.2	0.1	121.6
2-ethylhexanol	0.2	0.3	344.6	biocide	0.2	0.3	316.3
acephate	0.3	0.1	56.4	bithanem45	0.1	0	
acetic anhydride	0.6	19.5	16624.3	bromine	0.1	0	39.1
acetonitrile	0.7	9.1	7146.5	bromotrifluoromethane	0.1	0.8	782
acid nos	1.4	19.2	12535.5	bromoxynil	0.1	0	
acrylamide	0.1	0	28.6	butyl acetate	0.2	0.1	79.1
acrylonitrile	0.7	120.9	137907	butyl alcohol	0.7	2135.3	2669884
adhesives nos	0.7	0.5	48.8	butylate	0.2	0.2	209.3
adipic acid	0.2	0.6		butylene	0.2	1.9	1860.5
alkaline solution	0.3	1007.3	1007312	calcium	0.4	0.8	568.8
aluminexpo	0.1	0.4	428.6	calcium carbide	0.5	0.3	32.6
aluminum alkyl compound	0.1	0.2	215.1	calcium carbonate	1.5	638.4	635703.7
aluminum chloride	0.5	4.2	3720.9	calcium chloride	3	70.4	42705.2
aluminum fluoride	0.1	0.3		calcium hydroxide	1.4	6.7	957.1
aluminum oxide	0.2	2.7	2709.7	calcium hypochlorite	1.2	3.9	507
aluminum sulfate	0.9	18.7	4674.4	calcium lignosulfate	0.1	1	1000
aluminum sulfate	0.8	15.6	4794.8	calcium lignosulfonate	0.6	4	2185.7
amine nos	0.1	0.1		carbamate	0.1	0	22.8
aminocarb	0.4	0.5	416.8	carbaryl	0.1	0.2	164.3
ammonia anhydrous	6.7	72.4	11413.3	carbofuran	0.1	0.1	64.3
ammonium bisulfite	0.1	0		carbon dioxide	0.2	69.8	
ammonium chloride	0.2	0.5	534.9	carbon disulfide	0.9	9304.2	7371163
ammonium hydroxide	5.6	2027.6	3341784	carboxin	0.4	0.1	
ammonium nitrate	5.7	247.1	76093.8	cast iron	0.2	20.9	
ammonium phosphate	1.2	137	64278.1	caustic alkali liquid nos	2.2	11.5	4477.9
ammonium sulfate	0.3	2.8	1366.7	cement	0.3	1	114.3
ammonium thiosulfate	0.1	1		cement seal	0.2	0.1	
ansilex	0.2	0.2		coagulant nos	0.5	0.1	
antimony trioxide	0.2	0		chemical nos	23.4	29586.9	23427224
aqueous film forming foam	0.3	0.6	601.9	chloride nos	0.1	1.6	1571.4
arborgreen	0.2	0.5		chlorine	1.5	588.5	243652.7
arsenic	0.3	22.9	22885.7	chlorine dioxide	0.3	9.5	9428.9
arsenic trioxide	0.1	0.1	142.9	chloro-alkali brine	0.1	0.5	500
asbestos white	0.3	7.1		chlorpyrifos	0.1	0.1	
ash	0.3	32.6	428.6	chromic acid	2.1	6.4	5214.5
atrazine	0.5	0.3	316.3	chromium salt	0.2	2.1	
azinphos-methyl	0.2	0.1	107.4	cleanser	2.4	18	104.7
bacillus thuringiensis	1.3	1.3	180.6	copper ores	2.3	1118.3	1087612
barium chlorate	0.1	0.8		corn liquor	0.2	5.3	
barium sulfate	0.1	5	5028.6	*corrosion inhibitor*	0.6	1.6	
barium sulfate	0.4	10.6	5000	corrosive liquid poisons	0.2	1.2	
basic waste	0.2	2.1		counter 5g	0.1	0	
benzene sulfonic acid	0.2	1		cresol	0.3	0.1	
benzoic acid	0.1	0.1	78.9	crude/salt water emulsion	18.7	142.4	149195
benzoyl chloride	0.2	0		cupric sulfate	0.1	0.3	122.2
betasan	0.2	0.1		cyanide solution nos	0.1	0.2	222.2

Table 2 **Annual Spill Rate - By Name (based on data from 1985-1994)**

Annual spill Amount ***Substance***	**#**	**Mass** ***(tons)***	**Volume** **(L)**	**Annual spill Amount** ***Substance***	**#**	**Mass** ***(tons)***	**Volume** **(L)**
cyclohexylamine	0.6	0.2	122.2	firefighting foam	0.3	0.3	281.3
dalapon	0.2	0.1		flammable liquid nos	0.6	0.2	45.6
diacetone	0.2	0.5		flocculant nos	0.6	59.2	132.3
diazinon	0.2	3.2	22.2	fluoboric acid	0.2	0.2	84.4
dichlorfop	0.2	0		*fluorescein*	0.2	29.3	29302.3
dielectric fluid nos	2.5	11.4	8838.3	fluosilicic acid	0.8	13.9	11510.9
diethanolamine	0.3	1.1	1062.2	fly ash	0.2	3.5	
diethylamine	0.1	2.2	2250	formaldehyde	2	5.9	2630.7
diethylene glycol	0.1	0.2	178.7	formic acid	0.2	0	60.5
diethylenetriamine	0.1	1.4		formic acid	0.1	2.4	2000
difenzoquat methyl sulfat	0.7	0.3	128.6	freon	1.1	6.3	6150.8
diisobutylene	0.2	0.2		germicide nos	0.2	0.7	639.5
diisocyanate	0.1	0.2	215.1	glyphosate	0.3	0.3	247.7
dimethoate	0.6	0.6	631.8	green liquor	0.9	26.3	0
dimethyl disulfide	0.1	340.6		herbicide nos	0.7	1.4	174.4
dimethylacetamide	0.2	0.3		hydrazine	0.5	5.7	5488.4
dimethylcyclohexylamine	0.2	0	46.5	hydrochloric acid	18.4	104.4	83924.6
dinitrotoluene	0.2	125.6	125581	hydrofluoric acid	0.7	16.7	2093
dioctylphthalate	0.2	1.3	1348.8	hydrofluorosilicic acid	0.3	0.7	13
dipel	0.3	0.1	0	hydrogen	0.3	1.6	486.1
diphenyl	0.2	0.1		hydrogen chloride anh	0.7	21.3	20767.5
diphenyloxide	0.5	0.2		hydrogen fluoride anh	0.1	1.1	1075.3
dithane	0.3	0.3		hydrogen peroxide	0.9	0.4	203.5
dormet	0.2	0	34.9	hydrogen peroxide	0.9	9.9	9391.1
dowtherm	0.6	4.3	0	hydrogen sulfate	0.1	1.3	1285.7
drilling mud	2.6	101.1	35739.5	hypochlorite solution	0.1	0.1	111.1
dye or dye intermediate	0.9	21.4	21167.2	inorganic chromate nos	2.2	10	7788.4
electroplated tin	0	0.5	267.4	iron and ores	2.8	7680.3	7650735
emulsifier nos	0.4	1	837.2	iron sulfite	0.3	0.2	
epoxy resin	0.1	0		isocyanate nos	0.3	0.1	0
eptc	0.2	0.1		isophthalic acid	1.4	2656.3	2653668
ethanol	1.4	21	26572.4	isopropane	0.2	3.5	
ethanolamine	0.4	0.8	0	isopropanol	0.8	0.5	163.7
ethyl acrylate	0.2	0.1		isothiazol	0.2	0.2	
ethylbenzene	0.9	34.5	18895.3	jeffamine	0.7	0.1	
ethylene	0.2	1.6		ketones liquid nos	0.3	0.1	
ethylene dibromide	0.2	0.8	823.3	krenite	0.2	0.1	116.3
ethylene glycol	7.8	16.1	10196.7	lacquer base	0.7	0.7	
fatty acid nos	0.4	1.1	0	latex	1.9	6.9	1437.5
fenitrothion	0.5	1.1	533.4	lead acetate	0.2	0.1	
ferric chloride	0.7	4.8		lead conc or ore nos	1.2	212.9	26711.1
ferric nitrate	0.9	52.4	52426.5	lead sulphate	0.2	5.4	5399.2
ferric phosphate	0.2	0.5		lead/zinc concentrate	0.1	5.3	
ferric sulfate	0.1	0.4	285.7	*lignosol*	0.5	14.3	
ferrous chloride	0.5	0.7		liquid fertilizer nos	1.8	17	465.1
ferrous persulfate	0.2	0.1	121.6	liquid nos	0.2	0.6	
fertilizer nos	7.9	7907.7	165078.3	liquid pesticide nos	0.3	0.1	57.1

Table 2 **Annual Spill Rate - By Name (based on data from 1985-1994)**

Annual spill Amount		**Mass**	**Volume**	**Annual spill Amount**		**Mass**	**Volume**
Substance	**#**	**(tons)**	**(L)**	**Substance**	**#**	**(tons)**	**(L)**
liquor nos	0.4	0.8	838.5	polyol	0.1	0.2	215.1
lithium metal	0.2	2.3	2325.6	polystyrene	0.1	0.3	
magnesite	0.2	0.5		*polyurethane*	0.1	0.1	
magnesium chloride	0.2	0.1	104.7	polyvinyl acetate	0.9	17	1058.1
magnesium hydroxide	0.1	0.2	77.8	polyvinyl chloride	0.8	4	1612.9
maleic anhydride	0.2	1	1046.5	potassium chloride	2.2	1162.8	14293.3
manganese	0.1	0	17.9	potassium hydroxide	1.1	2	788.3
mcpa	0.2	0.5		potassium nitrate	0.2	0	
mdi	0.6	0.5	0	*propylene glycol*	1.1	2.5	1178.1
mercury	0.4	18.2	1.3	propylene oxide	0.2	0.8	
metachlor	0.2	0.9	860.5	pyrite slurry	0.2	9.3	
metal hydroxide nos	0.1	4.2		pyrrhotite	0.5	21.6	4651.2
methanol	4.7	276.4	16041	quicklime	3.7	117.5	28847.1
methyl chloride	0.5	8.2	7674.4	recycled ash water	0.3	1428.6	
methyl isopropenyl ketone	0.1	0		residual herbicide	0.1	0.1	
methyl methacrylate	0.5	3		silicic acid	0.2	1	
methylphosphoric acid	0.2	0		silver concentrate	0.1	1.9	
mine feed slurry nos	0.5	9.3	8571.4	soap	0.2	0.2	
mmt	0.1	0.1		sodium	0.1	1.3	1428.6
molten aluminum	0.1	1.6	1623.6	sodium aluminate	0.1	0.2	161.3
molybdate	1.4	7.7	7777	sodium bisulfate	0.9	46.9	28922.2
monomethylamine	0.3	1.9	266.7	sodium carbonate	0.3	2.8	2473.1
naphthalene	0.2	0.2	158.1	sodium chlorate	3.4	70.6	50583
naphthalenesulfonic acid	0.2	0		sodium chloride	2.7	834.4	26742.3
nickel ores and concentrat	2.2	1095.6	1075509	sodium chlorite	0.5	66.4	192.9
nitrate nos	0.2	11.3	11302.3	sodium cyanide	1.5	11.4	11314.3
nitric acid	3.1	2.8	865.1	sodium dichromate	1.7	3.2	1831
nitrilotriacetic acid	0.2	0.1		sodium dithionite	0.3	1.3	1268.8
nitrite nos	0.5	4.7	4669.3	sodium ethyl sulfate	0.2	0.1	
nitrogen	1.1	17.6	12850.2	sodium hydrosulfide	0.9	0.8	676
nitrogen dioxide	0.5	3.3	3347.9	*sodium hydroxide*	16.3	1869.2	331659.9
ore nos	0.1	0		sodium hypochlorite	2.3	12.9	12050.5
orthodichlorobenzene	0.1	0		sodium isopropylxanthate	0.1	0	15.6
paint and materials	6.3	35.2	9605.9	sodium nitrate	0.5	5	26.9
paraquat	0.5	0.6	634.9	sodium nitrite	0.5	0.1	125.6
parathion-methyl	0.1	0.1		sodium pentachlorophenat	0.6	0.4	429
pentachlorophenol	0.7	4.9	3084.4	sodium sulfate	2.2	22.4	8954.5
pesticide nos	0.8	3.3	0	sodium sulfide	0.2	0.1	116.3
phenol	2.2	142.4	142281	sodium sulfite	0.6	41.2	6451.6
phenolic resin	1.7	13.2	10988.4	sodium thiocyanate	0.5	10.6	10465.1
phenolsulfonic acid	0.9	4.9	2967.4	sodium thiosulfate	0.2	0.1	
phenoxy nos	0.2	0.3		sodiumdodecylbenzenesul	0.2	0	46.5
phosphoric acid	3.8	17.7	10786.1	solibor	0.1	0	
phosphorus pentoxide	0.1	3.2		stannic chloride	0.2	0	
phosphorus white	0.1	1.1	580.6	styrene monomer	1.5	10.8	11720.1
picloram	0.3	0.2		sulfamic acid	0.1	2	2000
polyethylene	0.6	1.9	823.3	sulfur	8.2	2425.1	355880.7

Table 2 **Annual Spill Rate - By Name (based on data from 1985-1994)**

Annual spill Amount		**Mass**	**Volume**	**Annual spill Amount**		**Mass**	**Volume**
Substance	**#**	**(tons)**	**(L)**	**Substance**	**#**	**(tons)**	**(L)**
sulfur dioxide	0.9	30.1	9247.3				
sulfur trioxide	0.2	0.6	581.4				
sulfuric acid	22	7583.8	5531985				
surfactant	1.5	73935.5	741.7				
tetraethyl lead	0.5	0.7					
tetrafluoroethylene	0.1	0	34.1				
tin fluoborate	0.2	0.2	126.7				
titanium dioxide	0.1	0.3					
toluene diisocyanate	0.6	0.3	107.5				
trichlorfon	0.2	20.9	20930.2				
trichloroethylene	0.6	1.4	80.8				
tricresyl phosphate	0.1	0	50				
triethanolamine	0.2	0.1	81.4				
trifluralin	0.1	0					
urea	2.2	28.5	9625.8				
urea formaldehyde	0.3	1.6	856.3				
urea nitrate	0.2	0.3					
urethane	0.2	0.3					
vinyl acetate	0.8	0.4	267.8				
vinyl chloride	2	12.8	13186.8				
viscose nos	1.4	14					
vitaflo 280	0.1	0	21.5				
weed and feed	0.1	2.7					
wetting agent nos	0.2	0					
wood preservative	0.2	9.3	9302.3				
xylenes	0.3	0.2	133.5				
zinc and concentrates	2.7	133.1	63882.9				
zinc phosphate	0.2	0.2	158.6				
zinc sulfate	0.4	219.4	4520.1				
zylvol	0.2	0					
Total	**209**	**110881**	**1.9E+07**				

Table 3 **Annual Spill Rate - By Mass (based on data from 1985-1994)**

Annual spill Amount		**Mass**	**Volume**	**Annual spill Amount**		**Mass**	**Volume**
Substance	**#**	**(tons)**	**(L)**	**Substance**	**#**	**(tons)**	**(L)**
surfactant	1.5	73935.5	741.7	urea	2.2	28.5	9625.8
chemical nos	23.4	29586.9	23427224	green liquor	0.9	26.3	0
carbon disulfide	0.9	9304.2	7371163	arsenic	0.3	22.9	22885.7
fertilizer nos	7.9	7907.7	165078.3	sodium sulfate	2.2	22.4	8954.5
iron and ores	2.8	7680.3	7650734.9	pyrrhotite	0.5	21.6	4651.2
sulfuric acid	22	7583.8	5531984.6	dye or dye intermediate	0.9	21.4	21167.2
isophthalic acid	1.4	2656.3	2653667.9	hydrogen chloride anhydro	0.7	21.3	20767.5
sulfur	8.2	2425.1	355880.7	ethanol	1.4	21	26572.4
butyl alcohol	0.7	2135.3	2669884	cast iron	0.2	20.9	
ammonium hydroxide	5.6	2027.6	3341783.5	trichlorfon	0.2	20.9	20930.2
sodium hydroxide	16.3	1869.2	331659.9	acetic anhydride	0.6	19.5	16624.3
recycled ash water	0.3	1428.6		acid nos	1.4	19.2	12535.5
potassium chloride	2.2	1162.8	14293.3	aluminum sulfate	0.9	18.7	4674.4
copper ores	2.3	1118.3	1087611.6	mercury	0.4	18.2	1.3
nickel ores and concentrat	2.2	1095.6	1075509.1	cleanser	2.4	18	104.7
alkaline solution	0.3	1007.3	1007311.8	phosphoric acid	3.8	17.7	10786.1
sodium chloride	2.7	834.4	26742.3	*nitrogen*	1.1	17.6	12850.2
calcium carbonate	1.5	638.4	635703.7	liquid fertilizer nos	1.8	17	465.1
chlorine	1.5	588.5	243652.7	polyvinyl acetate	0.9	17	1058.1
dimethyl disulfide	0.1	340.6		hydrofluoric acid	0.7	16.7	2093
methanol	4.7	276.4	16041	ethylene glycol	7.8	16.1	10196.7
ammonium nitrate	5.7	247.1	76093.8	aluminum sulfate	0.8	15.6	4794.8
zinc sulfate	0.4	219.4	4520.1	lignosol	0.5	14.3	
lead conc. or ore nos	1.2	212.9	26711.1	viscose nos	1.4	14	
crude/salt water emulsion	18.7	142.4	149195	fluosilicic acid	0.8	13.9	11510.9
phenol	2.2	142.4	142281	phenolic resin	1.7	13.2	10988.4
ammonium phosphate	1.2	137	64278.1	sodium hypochlorite	2.3	12.9	12050.5
zinc and concentrates	2.7	133.1	63882.9	vinyl chloride	2	12.8	13186.8
dinitrotoluene	0.2	125.6	125581.4	caustic alkali liquid nos	2.2	11.5	4477.9
acrylonitrile	0.7	120.9	137907	dielectric fluid nos	2.5	11.4	8838.3
quicklime	3.7	117.5	28847.1	sodium cyanide	1.5	11.4	11314.3
hydrochloric acid	18.4	104.4	83924.6	nitrate nos	0.2	11.3	11302.3
drilling mud	2.6	101.1	35739.5	styrene monomer	1.5	10.8	11720.1
ammonia anhydrous	6.7	72.4	11413.3	sodium thiocyanate	0.5	10.6	10465.1
sodium chlorate	3.4	70.6	50583	barium sulfate	0.4	10.6	5000
calcium chloride	3	70.4	42705.2	inorganic chromate nos	2.2	10	7788.4
carbon dioxide	0.2	69.8		hydrogen peroxide	0.9	9.9	9391.1
sodium chlorite	0.5	66.4	192.9	chlorine dioxide	0.3	9.5	9428.9
flocculant nos	0.6	59.2	132.3	mine feed slurry nos	0.5	9.3	8571.4
ferric nitrate	0.9	52.4	52426.5	pyrite slurry	0.2	9.3	
sodium bisulfate	0.9	46.9	28922.2	wood preservative	0.2	9.3	9302.3
sodium sulfite	0.6	41.2	6451.6	acetonitrile	0.7	9.1	7146.5
paint and materials	6.3	35.2	9605.9	methyl chloride	0.5	8.2	7674.4
ethylbenzene	0.9	34.5	18895.3	molybdate	1.4	7.7	7777
ash	0.3	32.6	428.6	asbestos white	0.3	7.1	
sulfur dioxide	0.9	30.1	9247.3	latex	1.9	6.9	1437.5
fluorescein	0.2	29.3	29302.3	calcium hydroxide	1.4	6.7	957.1

Table 3 **Annual Spill Rate - By Mass (based on data from 1985-1994)**

Annual spill Amount Substance	#	Mass (tons)	Volume (L)	Annual spill Amount Substance	#	Mass (tons)	Volume (L)
chromic acid	2.1	6.4	5214.5	urea formaldehyde	0.3	1.6	856.3
freon	1.1	6.3	6150.8	ethylene	0.2	1.6	
formaldehyde	2	5.9	2630.7	chloride nos	0.1	1.6	1571.4
hydrazine	0.5	5.7	5488.4	molten aluminum	0.1	1.6	1623.6
lead sulphate	0.2	5.4	5399.2	herbicide nos	0.7	1.4	174.4
corn liquor	0.2	5.3		trichloroethylene	0.6	1.4	80.8
lead/zinc concentrate	0.1	5.3		diethylenetriamine	0.1	1.4	
sodium nitrate	0.5	5	26.9	bacillus thuringiensis	1.3	1.3	180.6
barium sulfate	0.1	5	5028.6	sodium dithionite	0.3	1.3	1268.8
phenolsulfonic acid	0.9	4.9	2967.4	dioctylphthalate	0.2	1.3	1348.8
pentachlorophenol	0.7	4.9	3084.4	hydrogen sulfate	0.1	1.3	1285.7
ferric chloride	0.7	4.8		sodium	0.1	1.3	1428.6
nitrite nos	0.5	4.7	4669.3	corrosive liquid poisons	0.2	1.2	
dowtherm	0.6	4.3	0	fenitrothion	0.5	1.1	533.4
aluminum chloride	0.5	4.2	3720.9	fatty acid nos	0.4	1.1	0
metal hydroxide nos	0.1	4.2		diethanolamine	0.3	1.1	1062.2
polyvinyl chloride	0.8	4	1612.9	hydrogen fluoride anh	0.1	1.1	1075.3
calcium lignosulfonate	0.6	4	2185.7	phosphorus white	0.1	1.1	580.6
calcium hypochlorite	1.2	3.9	507	emulsifier nos	0.4	1	837.2
fly ash	0.2	3.5		cement	0.3	1	114.3
isopropane	0.2	3.5		benzene sulfonic acid	0.2	1	
pesticide nos	0.8	3.3	0	maleic anhydride	0.2	1	1046.5
nitrogen dioxide	0.5	3.3	3347.9	silicic acid	0.2	1	
sodium dichromate	1.7	3.2	1831	ammonium thiosulfate	0.1	1	
diazinon	0.2	3.2	22.2	calcium lignosulfate	0.1	1	1000
phosphorus pentoxide	0.1	3.2		metachlor	0.2	0.9	860.5
methyl methacrylate	0.5	3		sodium hydrosulfide	0.9	0.8	676
nitric acid	3.1	2.8	865.1	calcium	0.4	0.8	568.8
ammonium sulfate	0.3	2.8	1366.7	ethanolamine	0.4	0.8	0
sodium carbonate	0.3	2.8	2473.1	liquor nos	0.4	0.8	838.5
aluminum oxide	0.2	2.7	2709.7	ethylene dibromide	0.2	0.8	823.3
weed and feed	0.1	2.7		propylene oxide	0.2	0.8	
propylene glycol	1.1	2.5	1178.1	barium chlorate	0.1	0.8	
formic acid	0.1	2.4	2000	bromotrifluoromethane	0.1	0.8	782
lithium metal	0.2	2.3	2325.6	lacquer base	0.7	0.7	
diethylamine	0.1	2.2	2250	ferrous chloride	0.5	0.7	
basic waste	0.2	2.1		tetraethyl lead	0.5	0.7	
chromium salt	0.2	2.1		hydrofluorosilicic acid	0.3	0.7	13
potassium hydroxide	1.1	2	788.3	germicide nos	0.2	0.7	639.5
sulfamic acid	0.1	2	2000	dimethoate	0.6	0.6	631.8
2,4-d	1.5	1.9	1676.5	paraquat	0.5	0.6	634.9
polyethylene	0.6	1.9	823.3	aqueous film forming foam	0.3	0.6	601.9
monomethylamine	0.3	1.9	266.7	adipic acid	0.2	0.6	
butylene	0.2	1.9	1860.5	liquid nos	0.2	0.6	
silver concentrate	0.1	1.9		sulfur trioxide	0.2	0.6	581.4
corrosion inhibitor	0.6	1.6		isopropanol	0.8	0.5	163.7
hydrogen	0.3	1.6	486.1	adhesives nos	0.7	0.5	48.8

Table 3 **Annual Spill Rate - By Mass (based on data from 1985-1994)**

Annual spill Amount		**Mass**	**Volume**	**Annual spill Amount**		**Mass**	**Volume**
Substance	**#**	**(tons)**	**(L)**	**Substance**	**#**	**(tons)**	**(L)**
mdi	0.6	0.5	0	aluminum alkyl compound	0.1	0.2	215.1
aminocarb	0.4	0.5	416.8	carbaryl	0.1	0.2	164.3
ammonium chloride	0.2	0.5	534.9	cyanide solution nos	0.1	0.2	222.2
arborgreen	0.2	0.5		diethylene glycol	0.1	0.2	178.7
diacetone	*0.2*	*0.5*		*diisocyanate*	*0.1*	*0.2*	*215.1*
ferric phosphate	0.2	0.5		magnesium hydroxide	0.1	0.2	77.8
magnesite	0.2	0.5		polyol	0.1	0.2	215.1
mcpa	0.2	0.5		sodium aluminate	0.1	0.2	161.3
chloro-alkali brine	0.1	0.5	500	jeffamine	0.7	0.1	
electroplated tin	0	0.5	267.4	coagulant nos	0.5	0.1	
hydrogen peroxide	0.9	0.4	203.5	sodium nitrite	0.5	0.1	125.6
vinyl acetate	0.8	0.4	267.8	carboxin	0.4	0.1	
sodium pentachlorophenat	0.6	0.4	429	acephate	0.3	0.1	56.4
aluminexpo	0.1	0.4	428.6	cresol	0.3	0.1	
ferric sulfate	0.1	0.4	285.7	dipel	0.3	0.1	0
difenzoquat methyl sulfat	0.7	0.3	128.6	isocyanate nos	0.3	0.1	0
toluene diisocyanate	0.6	0.3	107.5	ketones liquid nos	0.3	0.1	
atrazine	0.5	0.3	316.3	liquid pesticide nos	0.3	0.1	57.1
calcium carbide	0.5	0.3	32.6	azinphos-methyl	0.2	0.1	107.4
dithane	0.3	0.3		betasan	0.2	0.1	
firefighting foam	0.3	0.3	281.3	betz 2040	0.2	0.1	121.6
glyphosate	0.3	0.3	247.7	butyl acetate	0.2	0.1	79.1
2-ethylhexanol	0.2	0.3	344.6	cement seal	0.2	0.1	
biocide	0.2	0.3	316.3	dalapon	0.2	0.1	
dimethylacetamide	0.2	0.3		diphenyl	0.2	0.1	
phenoxy nos	0.2	0.3		eptc	0.2	0.1	
urea nitrate	0.2	0.3		ethyl acrylate	0.2	0.1	
urethane	0.2	0.3		ferrous persulfate	0.2	0.1	121.6
aluminum fluoride	0.1	0.3		krenite	0.2	0.1	116.3
cupric sulfate	0.1	0.3	122.2	lead acetate	0.2	0.1	
polystyrene	0.1	0.3		magnesium chloride	0.2	0.1	104.7
titanium dioxide	0.1	0.3		nitrilotriacetic acid	0.2	0.1	
cyclohexylamine	0.6	0.2	122.2	sodium ethyl sulfate	0.2	0.1	
flammable liquid nos	*0.6*	*0.2*	*45.6*	*sodium sulfide*	0.2	0.1	116.3
diphenyloxide	0.5	0.2		sodium thiosulfate	0.2	0.1	
iron sulfite	0.3	0.2		triethanolamine	0.2	0.1	81.4
picloram	0.3	0.2		amine nos	0.1	0.1	
xylenes	0.3	0.2	133.5	arsenic trioxide	0.1	0.1	142.9
ansilex	0.2	0.2		benzoic acid	0.1	0.1	78.9
butylate	0.2	0.2	209.3	carbofuran	0.1	0.1	64.3
diisobutylene	0.2	0.2		chlorpyrifos	0.1	0.1	
fluoboric acid	0.2	0.2	84.4	hypochlorite solution	0.1	0.1	111.1
isothiazol	0.2	0.2		mmt	0.1	0.1	
naphthalene	0.2	0.2	158.1	parathion-methyl	0.1	0.1	
soap	0.2	0.2		polyurethane	0.1	0.1	
tin fluoborate	0.2	0.2	126.7	residual herbicide	0.1	0.1	
zinc phosphate	0.2	0.2	158.6	antimony trioxide	0.2	0	

Table 3 **Annual Spill Rate - By Mass (based on data from 1985-1994)**

Annual spill Amount Substance	**#**	**Mass (tons)**	**Volume (L)**	**Annual spill Amount Substance**	**#**	**Mass (tons)**	**Volume (L)**
benzoyl chloride	0.2	0					
dichlorfop	0.2	0					
dimethylcyclohexylamine	0.2	0	46.5				
dormet	0.2	0	34.9				
formic acid	0.2	0	60.5				
methylphosphoric acid	0.2	0					
naphthalenesulfonic acid	0.2	0					
potassium nitrate	0.2	0					
sodiumdodecylbenzenesul	0.2	0	46.5				
stannic chloride	0.2	0					
wetting agent nos	0.2	0					
zylvol	0.2	0					
acrylamide	0.1	0	28.6				
ammonium bisulfite	0.1	0					
bithanem45	0.1	0					
bromine	0.1	0	39.1				
bromoxynil	0.1	0					
carbamate	0.1	0	22.8				
counter 5g	0.1	0					
epoxy resin	0.1	0					
manganese	0.1	0	17.9				
methyl isopropenyl ketone	0.1	0					
ore nos	0.1	0					
orthodichlorobenzene	0.1	0					
sodium isopropylxanthate	0.1	0	15.6				
solibor	0.1	0					
tetrafluoroethylene	0.1	0	34.1				
tricresyl phosphate	0.1	0	50				
trifluralin	0.1	0					
vitaflo 280	0.1	0	21.5				
Total	**209**	**110881**	**18722194**				

Table 4

SUMMARY OF THE PRIORITY CHEMICAL LISTS

THE TOP TEN MATERIALS	
Ammonia	Potassium chloride
Chlorine	Sodium cyanide
Hydrochloric acid	Styrene
PCBs	Sulfuric acid
Pentachlorophenol	Tetraethyl lead

THE TOP TWENTY FIVE MATERIALS	
Ammonia	Phosphorus
Ammonium hydroxide	Potassium chloride
Ammonium sulfate	Sodium chlorate
Benzene	Sodium chloride
Calcium chloride	Sodium cyanide
Calcium hypochlorite	Sodium hydroxide
Chlorine	Styrene
Copper sulfate	Sulfuric acid
Formaldehyde	Tetraethyl lead
Hydrochloric acid	Toluene
PCBs	Xylene
Pentachlorophenol	Zinc sulfate
Phenol	

THE TOP 50 MATERIALS	
Acetic acid	Nonylphenol
Aldrin	PCBs
Aminocarb	Pentachlorophenol
Ammonia	Perchloroethylene
Ammonium hydroxide	Phenol
Ammonium nitrate	Phosphamidon
Ammonium phosphates	Phosphoric acid
Ammonium sulfate	Phosphorus
Benzene	Potassium chloride
Calcium chloride	Propylene oxide
Calcium hydroxide	Sodium carbonate
Calcium hypochlorite	Sodium chlorate
Carbon tetrachloride	Sodium chloride
Chlorine	Sodium cyanide
Copper sulfate	Sodium hydroxide
Ethylbenzene	Styrene
Ethylene dichloride	Sulfur
Ethylene glycol	Sulfur dioxide
Ethylhexanol	Sulfuric acid
Fenitrothion	Tetraethyl lead
Ferric chloride	*Toluene*
Formaldehyde	Vinyl acetate
Hydrochloric acid	Xylene
Methyl alcohol	Zinc sulfate
Nitric acid	2,4-dichlorophenoxyacetic acid (2,4-D)

Table 5 The Top Five Hundred Priority Chemicals

THE TOP FIVE HUNDRED PRIORITY MATERIALS

Acetaldehyde
Acetic acid
Acetic anhydride
Acetone
Acetone cyanohydrin
Acetophenone
Acetyl chloride
Acetylene
Acrolein
Acrylamide
Acrylonitrile
Adipic acid
Adiponitrile
Alachlor
Aldicarb
Aldrin
Allyl alcohol
Allyl chloride
Aluminum chloride
Aluminum phosphate
Aluminum sulfate
Aminocarb
Amiton
Ammonia
Ammonium chloride
Ammonium hydroxide
Ammonium nitrate
Ammonium phosphates
Ammonium picrate
Ammonium stearate
Ammonium sulfamate
Ammonium sulfate
Aniline
Anthracene
Antimony trioxide
Arsenic
Arsenic acid
Arsenic pentoxide
Arsenic trioxide
Arsine
Asbestos
Atlox
Atrazine
Azinphos ethyl
Azinphosmethyl
Barban
Barium sulfate
Benzaldehyde
Benzene
Benzene hexachloride (Lindane)
Benzidine
Benzoic acid
Benzonitrile
Benzophenone
Benzotrifluoride
Benzoyl chloride
Benzyl alcohol
Benzyl chloride
Benzyl n-butyl phthalate
Beryllium
Bisphenol A
Borax
Boric acid
Bromine
Bromoform
Brucine
Butadiene
Butyl alcohol
Butyl formate
Butyl mercaptan
Butylamine
Butylene
Butyraldehyde
Butyric acid
Cadmium
Cadmium chloride
Cadmium nitrate
Cadmium sulfate
Calcium arsenate
Calcium carbide
Calcium carbonate
Calcium chloride
Calcium cyanide
Calcium fluoride
Calcium hydroxide
Calcium hypochlorite
Calcium nitrate
Calcium oxide
Calcium phosphate
Camphor oil
Cantharidin
Caprolactam
Carbaryl
Carbofuran
Carbon dioxide
Carbon disulfide

Table 5 The Top Five Hundred Priority Chemicals

Carbon tetrachloride
Carbonyl sulfide
Carboxymethylcellulose
Cesium 137
Chlordane
Chlorine
Chlorine dioxide
Chloroaniline
Chlorobenzene
Chlorodifluoromethane
Chloroethylvinyl ether
Chloroform
Chlorohydrin
Chlorophacinone
Chlorophenol
Chloroxuron
Chlorpropham
Chlorpyrifos
Choline chloride
Chromic acid
Chromic sulfate
Chromium
Chromous chloride
Cobaltous bromide
Cobaltous chloride
Cobaltous hydroxide
Cobaltous nitrate
Copper acetate
Copper chloride
Copper cyanide
Copper nitrate
Copper sulfate
Coumaphos
Cresol
Crimidine
Crotonaldehyde
Cumene
Cyanogen bromide
Cyclohexane
Cyclohexanone
Cycloheximide
Cyclohexylamine
Dalapon
DDT
Decyl alcohol
Decyl octyl phthalate
Demeton
Diallate
Diazinon
Dibromomethane
Dibutyl amine
Dibutyl ether
Dicamba
Dichlobenil
Dichlone
Dichlorodifluoromethane
Dichloroethyl amino uracil
Dichloroethyl ether
Dichloroethylene
Dichlorvos
Dicrotophos
Dieldrin
Diethanolamine
Diethyl chlorophosphate
Diethyl phthalate
Diethyl-m-toluamide
Diethyl-p-nitrophenyl phosphate
Diethylamine
Diisopropylamine
Dimefox
Dimethoate
Dimethyl ethyl amine
Dimethyl phthalate
Dimethyl sulfate
Dimethylamine
Dimethylaniline
Dinitramine
Dinitroaniline
Dinitrobenzene
Dinitrocresols
Dinoseb
Dioxathion
Diphacinone
Diphenyl
Diphenyl ether
Diphenylamine
Diphenylmethane-4,4'-diisocyanate
Diquat
Disulfoton
Dithiobiuret
Diuron
Dodecylbenzenesulfonic acid
Endosulfan
Endothall
Endrin
Epichlorohydrin

Table 5 The Top Five Hundred Priority Chemicals

EPN
Eptam
Ethanolamine
Ethion
Ethyl acetate
Ethyl acrylate
Ethyl alcohol
Ethyl chloride
Ethyl mercaptan
Ethylamine
Ethylbenzene
Ethylene
Ethylene dibromide
Ethylene dichloride
Ethylene glycol
Ethylene glycol monobutyl ether
Ethylene oxide
Ethylene thiourea
Ethyleneimine
Ethylhexanol
Fenitrothion
Fensulfothion
Ferric chloride
Ferric hydroxide
Ferric oxide
Ferrous sulfate
Flamprop-methyl
Fluenetil
Fluometuron
Fluoranthene
Fluorine
Fluoroacetamide
Fluoroacetic acid
Fonofos
Formaldehyde
Formic acid
Fumaric acid
Furazolidone
Furfural
Furfuryl alcohol
Glycerine
Glycidyl methacrylate
Glyphosate
Heavy water
Heptanol
Hexachlorobenzene
Hexachlorobutadiene
Hexachlorocyclopentadiene
Hexachloroethane
Hexachlorophene
Hexaethyl tetraphosphate
Hexaldehyde
Hexane
Hexanol
Hydrazine
Hydrochloric acid
Hydrocyanic acid
Hydrofluoric acid
Hydrogen
Hydrogen peroxide
Hydrogen sulfide
Hydroquinone
Iodomethane
Isobenzan
Isobutyl acrylate
Isobutyl alcohol
Isodrin
Isooctyl alcohol
Isophorone
Isopropyl alcohol
Isopropylmethylpyrazolyl dimet.car.
Isovaleraldehyde
Kepone
Lactonitrile
Lead arsenate
Lead chloride
Lead fluoroborate
Lead oxide
Lignin sulfonate
Lithium bromide
Magnesium hydroxide
Magnesium oxide
Malathion
Maleic acid
Maleic anhydride
Malononitrile
Maneb
MCPA
Melamine
Mephosfolan
Mercuric acetate
Mercuric chloride
Mercuric sulfide
Mercuric thiocyanate
Mercurous nitrate
Mercury

Table 5 The Top Five Hundred Priority Chemicals

Methanesulfonyl fluoride
Methiocarb
Methoxychlor
Methoxyethylmercuric acetate
Methyl alcohol
Methyl amyl alcohol
Methyl bromide
Methyl chloride
Methyl ethyl ketone
Methyl ethyl ketone peroxide
Methyl hexyl ketone
Methyl isobutyl ketone
Methyl methacrylate
Methyl parathion
Methyl phenkapton
Methylamine
Methylene chloride
Methylstyrene
Metobromuron
Mevinphos
Mexacarbate
Monocrotophos
Morpholine
N,N-Dimethylaniline
N-Nitrosodiphenylamine
Naled
Naphtha
Naphthalene
Naphthol
Neopentyl glycol
Nickel carbonyl
Nickel chloride
Nicotine sulfate
Nitralin
Nitric acid
Nitrilotriacetic acid
Nitroaniline
Nitrobenzene
Nitrogen (liquefied)
Nitrogen dioxide
Nitroglycerin
Nitromethane
Nitrophenol
Nitropropane
Nitrosodimethylamine
Nitrotoluene
Nitrous oxide
Nonane
Nonanol
Nonylphenol
Octanol
Oleic acid
Oleum
Oxalic acid
Oxygen (liquefied)
Paraquat
Parathion
PCBs
Pentachlorobenzene
Pentachlorophenol
Perchloroethylene
Phenanthrene
Phenol
Phenolsulfonic acid
Phenyl mercuric acetate
Phenylenediamine
Phenylthiourea
Phorate
Phosgene
Phosmet
Phosphamidon
Phosphine
Phosphoric acid
Phosphorus
Phosphorus pentoxide
Phthalic anhydride
Picloram
Potassium aluminate
Potassium carbonate
Potassium chlorate
Potassium chloride
Potassium cyanide
Potassium dichromate
Potassium hydroxide
Potassium permanganate
Potassium sulfate
Propargyl alcohol
Propionaldehyde
Propionic acid
Propionic anhydride
Propylamine
Propylene
Propylene chlorohydrin
Propylene glycol
Propylene oxide
Pyridine

Table 5 The Top Five Hundred Priority Chemicals

Pyrocatechol
Quinoline
Quinone
Resorcinol
Rotenone
Salicylic acid
Silver nitrate
Sodium
Sodium aluminate
Sodium anthraquinone sulfate
Sodium arsenate
Sodium arsenite
Sodium azide
Sodium bisulfite
Sodium borohydride
Sodium carbonate
Sodium chlorate
Sodium chloride
Sodium chromate
Sodium cyanide
Sodium dichromate
Sodium fluoride
Sodium fluoroacetate
Sodium fluorosilicate
Sodium hydrosulfide
Sodium hydrosulfite
Sodium hydroxide
Sodium hypochlorite
Sodium nitrate
Sodium nitrilotriacetic acid
Sodium phosphate
Sodium phosphate, tribasic
Sodium selenite
Sodium silicate
Sodium sulfate
Sodium sulfite
Sodium thioglycolate
Stannic chloride
Stannous chloride
Strychnine
Strychnine sulfate
Styrene
Sulfamic acid
Sulfotepp
Sulfur
Sulfur chloride
Sulfur dioxide
Sulfuric acid
Sulfuryl chloride
Temephos
Terephthalic acid
Terphenyl
Tetrachloroethylene
Tetraethyl lead
Tetraethyl pyrophosphate
Tetrahydronaphthalene
Tetramethyl lead
Thallium
Thallium acetate
Thallium sulfate
Thioglycolic acid
Thionyl chloride
Thiosemicarbazide
Thiourea
Thiram
Titanium dioxide
Toluene
Toluene-2,4-diamine
Toluene-2,4-diisocyanate
Toluidine
Toxaphene
Tributyl phosphate
Trichlorobenzene
Trichloroethane
Trichloroethylene
Trichlorofon
Trichlorophenol
Trichlorophenoxy propionic acid
Tridecyl alcohol
Triethanolamine
Triethylamine
Trifluralin
Trimethylamine
Trimethylene bromide
Trinitrotoluene
Turpentine
Uranyl nitrate
Urea
Valeraldehyde
Vanadium pentoxide
Vinyl acetate
Vinyl chloride
Warfarin
Xylene
Xylenol
Yellow cake

Table 5 The Top Five Hundred Priority Chemicals

Zinc acetate
Zinc bromide
Zinc chloride
Zinc cyanide
Zinc oxide
Zinc phosphate
Zinc sulfate
1,1-Dichloropropane
1,2,4,5-Tetrachlorobenzene
2,2'-Thiobis(4,6-dichlorophenol)
2,3,4,6-Tetrachlorophenol
2,3-Dibromo-1-propanol phosphate
2,4,5-Trichlorophenoxyacetic . (2,4,5-T)
2,4-Dichlorophenol
2,4-dichlorophenoxyacetic acid (2,4-D)
2,4-Dinitrophenol
2,4-Dinitrotoluene
2-Phenylphenol
4-Aminopyridine
5-[Bis(2-chloroethyl)amino] uracil

Table 6 Spill Priority List		SPILL	SPILL	SUPPLY
CHEMICAL	RANK	NUMBERS	VOLUME	VOLUME
Acetaldehyde	214			8.5
Acetic acid	26	9	73	71
Acetic anhydride	107	8	1.5	
Acetone	77	4	9.9	23
Acetone cyanohydrin	199			
Acetophenone	369			
Acetyl chloride	490			
Acetylene	143	1	0.013	5.3
Acrolein	200			
Acrylamide	249			
Acrylonitrile	63	1	4.6	16
Adipic acid	307			72
Adiponitrile	359			
Alachlor	330			
Aldicarb	163			
Aldrin	47	2	1.3	
Allyl alcohol	226			
Allyl chloride	354			
Aluminum chloride	176			14
Aluminum phosphate	265	3	8.5	
Aluminum sulfate	90	9	120	220
Aminocarb	41	12	55	
Amiton	443			
Ammonia	1	107	470	3700
Ammonium chloride	94	1	0.7	2.7
Ammonium hydroxide	21	15	130	
Ammonium nitrate	30	63	4200	910
Ammonium phosphates	33	5	140	1400
Ammonium picrate	433			
Ammonium stearate	400	1	0.1	
Ammonium sulfamate	458			
Ammonium sulfate	20	8	260	330
Aniline	88	1	0.1	0.62
Anthracene	388			
Antimony trioxide	209			1500
Arsenic	344			
Arsenic acid	201			
Arsenic pentoxide	261			
Arsenic trioxide	290			
Arsine	237	1	0	
Asbestos	154	15	310	
Atlox	396	1	0.2	
Atrazine	116	2	0.85	
Azinphos ethyl	167			
Azinphosmethyl	91	1	0	
Barban	291	1	0.009	
Barium sulfate	215	1	820	
Benzaldehyde	355			
Benzene	22	12	14	740

Table 6 Spill Priority List		SPILL	SPILL	SUPPLY
CHEMICAL	RANK	NUMBERS	VOLUME	VOLUME
Benzene hexachloride (Lindane)	104	1	0.0009	
Benzidine	397			
Benzoic acid	85	2	34	28
Benzonitrile	370			
Benzophenone	350			
Benzotrifluoride	123	1	50	
Benzoyl chloride	287			
Benzyl alcohol	404			
Benzyl chloride	324			
Benzyl-n-butyl phthalate	416			
Beryllium	444			
Bisphenol A	497			1.9
Borax	202			52
Boric acid	275			2
Bromine	445			
Bromoform	134	1	0.014	
Brucine	208			
Butadiene	339			
Butyl alcohol	100	1	2	
Butyl formate	222	1	0.04	
Butyl mercaptan	345			
Butylamine	389			
Butylene	334			230
Butyraldehyde	465			0.2
Butyric acid	452			
Cadmium	197			
Cadmium chloride	271			
Cadmium nitrate	268			
Cadmium sulfate	205			
Calcium arsenate	169	1	0.045	
Calcium carbide	164	1	1.8	82
Calcium carbonate	331			250
Calcium chloride	17	20	3700	340
Calcium cyanide	83	1	0.09	
Calcium fluoride	262	1	1	
Calcium hydroxide	36	17	360	2600
Calcium hypochlorite	24	4	17	7.9
Calcium nitrate	173	1	1.8	
Calcium oxide	56	12	530	2600
Calcium phosphate	98	3	100	160
Camphor oil	480			
Cantharidin	491			
Caprolactam	403			12
Carbaryl	54	2	70	
Carbofuran	124	4	0.06	
Carbon dioxide	158	1	0	2500
Carbon disulfide	180			21
Carbon tetrachloride	42	1	1.8	26
Carbonyl sulfide	419			

Table 6 Spill Priority List		SPILL NUMBERS	SPILL VOLUME	SUPPLY VOLUME
CHEMICAL	RANK			
Carboxymethylcellulose	459			2.5
Cesium 137	156	3	0.000003	
Chlordane	68	2	0.003	
Chlorine	2	36	120	1700
Chlorine dioxide	159	2	0.3	
Chloroaniline	195	1	0.5	
Chlorobenzene	352			
Chlorodifluoromethane	380	1	0.22	
Chloroethylvinyl ether	384			
Chloroform	190			3.7
Chlorohydrin	175	1	0.8	
Chlorophacinone	423			
Chlorophenol	121	1	0.04	
Chloroxuron	428			
Chlorpropham	341			
Chlorpyrifos	192			
Choline chloride	471			5.8
Chromic acid	86	8	8.8	2.8
Chromic sulfate	466			
Chromium	486			
Chromous chloride	371			
Cobaltous bromide	372			
Cobaltous chloride	270			
Cobaltous hydroxide	364	1	5.1	
Cobaltous nitrate	111	1	0.9	
Copper acetate	277			
Copper chloride	223			
Copper cyanide	150	1	2.2	
Copper nitrate	293			
Copper sulfate	15	5	23	24
Coumaphos	228			
Cresol	95	2	13	
Crimidine	401			
Crotonaldehyde	282			
Cumene	157			45
Cyanogen bromide	179	1	0.00005	
Cyclohexane	96	1	0.11	60
Cyclohexanone	460			
Cycloheximide	183			
Cyclohexylamine	196	1	0.07	
Dalapon	420			
DDT	184			
Decyl alcohol	360			
Decyl octyl phthalate	319	1	0.1	
Demeton	170			
Diallate	152	3	0.08	
Diazinon	76	4	0.3	
Dibromomethane	297			
Dibutyl amine	320			

Table 6 Spill Priority List

CHEMICAL	RANK	SPILL NUMBERS	SPILL VOLUME	SUPPLY VOLUME
Dibutyl ether	461			
Dicamba	115	2	0.17	
Dichlobenil	407			
Dichlone	218			
Dichlorodifluoromethane	347			
Dichloroethyl amino uracil	481			
Dichloroethyl ether	351			
Dichloroethylene	429			
Dichlorvos	97	1	0.1	
Dicrotophos	242			
Dieldrin	75	1	0.004	
Diethanolamine	131	1	0.2	
Diethyl chlorophosphate	494			
Diethyl phthalate	498			
Diethyl-m-toluamide	430			
Diethyl-p-nitrophenyl phosphate	417			
Diethylamine	113	2	1.8	
Diisopropylamine	373			
Dimefox	390			
Dimethoate	315			
Dimethyl ethyl amine	266	1	0	
Dimethyl phthalate	467			
Dimethyl sulfate	298			
Dimethylamine	73	4	33	
Dimethylaniline	432	1	0.005	
Dinitramine	129	2	0.007	
Dinitroaniline	326			
Dinitrobenzene	300			
Dinitrocresols	240			
Dinoseb	82	1	0.91	
Dioxathion	232			
Diphacinone	408			
Diphenyl	244	1	1.3	
Diphenyl ether	128	1	1.5	
Diphenylamine	409	1	0.03	
Diphenylmethane-4,4'-diisocyanate	434			
Diquat	120	2	0	
Disulfoton	191			
Dithiobiuret	462			
Diuron	356			
Dodecylbenzenesulfonic acid	312			
Endosulfan	162			
Endothall	239			
Endrin	146			
Epichlorohydrin	313			
EPN	253			
Eptam	386			
Ethanolamine	252			15
Ethion	203			

Table 6 Spill Priority List **CHEMICAL**	**RANK**	**SPILL NUMBERS**	**SPILL VOLUME**	**SUPPLY VOLUME**
Ethyl acetate	308			6.2
Ethyl acrylate	153	3	1.1	
Ethyl alcohol	53	3	51	
Ethyl chloride	126	2	0.2	15
Ethyl mercaptan	168	6	0.01	
Ethylamine	207	1	1.3	
Ethylbenzene	38	4	0.79	730
Ethylene	80	2	180	2200
Ethylene dibromide	309			
Ethylene dichloride	29	1	780	820
Ethylene glycol	39	31	590	410
Ethylene glycol monobutyl ether	464			
Ethylene oxide	142			370
Ethylene thiourea	487			
Ethyleneimine	263			
Ethylhexanol	50	1	100	
Fenitrothion	40	49	100	
Fensulfothion	424			
Ferric chloride	49	8	1000	
Ferric hydroxide	279	2	5	
Ferric oxide	211	5	23	
Ferrous sulfate	234	1	21	
Flamprop-methyl	188	3	0.16	
Fluenetil	469			
Fluometuron	500			
Fluoranthene	453			
Fluorine	259			
Fluoroacetamide	260			
Fluoroacetic acid	455			
Fonofos	160			2500
Formaldehyde	25	10	41	130
Formic acid	145	1	0.2	
Fumaric acid	410			1.2
Furazolidone	418			
Furfural	301			
Furfuryl alcohol	361			
Glycerine	450			7.7
Glycidyl methacrylate	335			
Glyphosate	245	1	0.003	
Heavy water	246	2	22	
Heptanol	446			
Hexachlorobenzene	299			
Hexachlorobutadiene	235			
Hexachlorocyclopentadiene	280			
Hexachloroethane	343			
Hexachlorophene	219			
Hexaethyl tetraphosphate	477			
Hexaldehyde	440			
Hexane	65	5	8	

Table 6 Spill Priority List		**SPILL**	**SPILL**	**SUPPLY**
CHEMICAL	**RANK**	**NUMBERS**	**VOLUME**	**VOLUME**
Hexanol	374			
Hydrazine	60	3	4.5	
Hydrochloric acid	8	123	3300	170
Hydrocyanic acid	186			
Hydrofluoric acid	51	5	0.68	77
Hydrogen	441			1200
Hydrogen peroxide	92	7	0.71	34
Hydrogen sulfide	236			
Hydroquinone	248			
Iodomethane	391			
Isobenzan	463			
Isobutyl acrylate	382			
Isobutyl alcohol	492			1.5
Isodrin	151			
Isooctyl alcohol	437			
Isophorone	472			
Isopropyl alcohol	67	4	9	
Isopropylmethylpyrazolyl dimethylcarbamate	495			
Isovaleraldehyde	402			
Kepone	198			
Lactonitrile	256			
Lead arsenate	269			
Lead chloride	488			
Lead fluoroborate	283			
Lead oxide	144	2	2.1	34
Lignin sulfonate	136	5	180	
Lithium bromide	399	1	0.13	
Magnesium hydroxide	185	1	11	15
Magnesium oxide	365	1	5	
Malathion	61	7	0.29	
Maleic acid	327			
Maleic anhydride	81	1	2.8	15
Malononitrile	257			
Maneb	130	1	1.3	
MCPA	57	5	0.91	
Melamine	468			6.8
Mephosfolan	484			
Mercuric acetate	204			
Mercuric chloride	155			
Mercuric sulfide	306	1	30	
Mercuric thiocyanate	210			
Mercurous nitrate	212			
Mercury	87	11	20	
Methanesulfonyl fluoride	425			
Methiocarb	213			
Methoxychlor	117	1	0.05	
Methoxyethylmercuric acetate	181			
Methyl alcohol	27	18	740	
Methyl amyl alcohol	482			

Table 6 Spill Priority List CHEMICAL	RANK	SPILL NUMBERS	SPILL VOLUME	SUPPLY VOLUME
Methyl bromide	314			
Methyl chloride	84	2	2.5	4.1
Methyl ethyl ketone	108	4	7.7	12
Methyl ethyl ketone peroxide	302	1	0	
Methyl hexyl ketone	381	1	0.94	
Methyl isobutyl ketone	438			8.7
Methyl methacrylate	74	3	3.4	18
Methyl parathion	216			
Methyl phenkapton	431			
Methylamine	125	1	5.3	6.3
Methylene chloride	58	4	6.2	10
Methylstyrene	405			
Metobromuron	426			
Mevinphos	205			
Mexacarbate	258			
Monocrotophos	483			
Morpholine	284			0.88
N,N-Dimethylaniline	421			
N-Nitrosodiphenylamine	348			
Naled	247			
Naphtha	473			
Naphthalene	79	3	6.4	
Naphthol	454			
Neopentyl glycol	415	1	0.01	
Nickel carbonyl	171	1	0.3	
Nickel chloride	310			
Nicotine sulfate	274			
Nitralin	412			
Nitric acid	45	48	140	890
Nitrilotriacetic acid	427			
Nitroaniline	139	1	0.001	
Nitrobenzene	375			
Nitrogen (liquefied)	118	3	1.8	340
Nitrogen dioxide	161	3	0.001	
Nitroglycerin	311			
Nitromethane	470			
Nitrophenol	278			
Nitropropane	447			
Nitrosodimethylamine	362			
Nitrotoluene	376			
Nitrous oxide	229	1	0.6	
Nonane	294	1	0.006	
Nonanol	363			
Nonylphenol	37	2	8.8	7
Octanol	448			
Oleic acid	377			2.6
Oleum	337			
Oxalic acid	411			1.1
Oxygen (liquefied)	89	5	24	2700

Table 6 Spill Priority List		**SPILL**	**SPILL**	**SUPPLY**
CHEMICAL	**RANK**	**NUMBERS**	**VOLUME**	**VOLUME**
Paraquat	59	2	44	
Parathion	55	1	0.01	
PCBs	5	334	89	
Pentachlorobenzene	336			
Pentachlorophenol	10	19	110	1.5
Perchloroethylene	35	10	15	27
Phenanthrene	439			
Phenol	11	10	14	68
Phenolsulfonic acid	243	2	23	
Phenyl mercuric acetate	177	1	0.005	
Phenylenediamine	357	1	0	
Phenylthiourea	442			
Phorate	392			
Phosgene	254	1	0	
Phosmet	272			
Phosphamidon	46	8	16	
Phosphine	255	1	0.004	
Phosphoric acid	48	12	37	520
Phosphorus	13	16	46	68
Phosphorus pentoxide	217	1	0.6	
Phthalic anhydride	103	3	7.2	34
Picloram	112	3	0.53	
Potassium aluminate	383	1	0.7	
Potassium carbonate	165	1	100	
Potassium chlorate	496			
Potassium chloride	9	31	12000	
Potassium cyanide	69	1	0.005	
Potassium dichromate	349			
Potassium hydroxide	102	2	1.2	12
Potassium permanganate	70	4	9.8	
Potassium sulfate	338			72
Propargyl alcohol	233			
Propionaldehyde	435			
Propionic acid	147	1	2	
Propionic anhydride	456			
Propylamine	493			
Propylene	137	1	9.1	660
Propylene chlorohydrin	346	1	8.9	
Propylene glycol	119	1	8.3	19
Propylene oxide	34	2	22	61
Pyridine	109	2	0.005	
Pyrocatechol	316			
Quinoline	342			
Quinone	328			
Resorcinol	366			
Rotenone	194			
Salicylic acid	499			
Silver nitrate	451			
Sodium	387	1	0.5	

Table 6 Spill Priority List

CHEMICAL	RANK	SPILL NUMBERS	SPILL VOLUME	SUPPLY VOLUME
Sodium aluminate	187	1	14	9
Sodium anthraquinone sulfate	449			
Sodium arsenate	276			
Sodium arsenite	230	1	0	
Sodium azide	224			
Sodium bisulfite	406			
Sodium borohydride	193	1	4.5	17
Sodium carbonate	32	3	25	570
Sodium chlorate	19	23	7700	440
Sodium chloride	16	12	1400	12000
Sodium chromate	220	1	0.02	
Sodium cyanide	7	3	83	12
Sodium dichromate	182			
Sodium fluoride	122	1	0.2	
Sodium fluoroacetate	393			
Sodium fluorosilicate	322			
Sodium hydrosulfide	264	2	2.3	
Sodium hydrosulfite	140	2	29	8.4
Sodium hydroxide	18	92	8200	1800
Sodium hypochlorite	93	11	58	170
Sodium nitrate	172	1	2.5	
Sodium nitrilotriacetic acid	332			
Sodium phosphate	225			65
Sodium phosphate, tribasic	368			
Sodium selenite	478			
Sodium silicate	62	1	3.8	120
Sodium sulfate	329			410
Sodium sulfite	127	4	29	16
Sodium thioglycolate	398	1	0.2	
Stannic chloride	303	1	0	
Stannous chloride	285			
Strychnine	178			
Strychnine sulfate	436			
Styrene	4	24	5000	630
Sulfamic acid	457			
Sulfotepp	394			
Sulfur	31	68	70000	7400
Sulfur chloride	273	3	3.5	
Sulfur dioxide	44	16	90	140
Sulfuric acid	6	155	13000	3700
Sulfuryl chloride	281	2	4.4	
Temephos	325			
Terephthalic acid	135	1	0.18	45
Terphenyl	286	2	1.1	
Tetraethyl lead	3	4	72	26
Tetraethyl pyrophosphate	166			
Tetrahydronaphthalene	267	1	0.09	
Tetramethyl lead	333			
Thallium	485			

Table 6 Spill Priority List		SPILL	SPILL	SUPPLY
CHEMICAL	RANK	NUMBERS	VOLUME	VOLUME
Thallium acetate	321			
Thallium sulfate	99	1	0.03	
Thioglycolic acid	149	1	0	
Thionyl chloride	288	1	53	
Thiosemicarbazide	489			
Thiourea	323			
Thiram	221	1	0.3	
Titanium dioxide	133	2	0.5	110
Toluene	14	13	110	430
Toluene-2,4-diamine	141	2	11	
Toluene-2,4-diisocyanate	52	7	2	
Toluidine	413			
Toxaphene	174			
Tributyl phosphate	132	1	0.3	
Trichlorobenzene	318			
Trichloroethane	64	4	0.81	
Trichloroethylene	110	1	0.13	3
Trichlorofon	78	3	2.6	
Trichlorophenol	295			
Trichlorophenoxy propionic acid	289			
Tridecyl alcohol	378			
Triethanolamine	189	1	0.19	
Triethylamine	385			
Trifluralin	114	9	4.6	
Trimethylamine	379	1	1.5	
Trimethylene bromide	241	1	0.4	
Trinitrotoluene	101	1	17	
Turpentine	474			11
Uranyl nitrate	138	3	0.21	
Urea	227			2600
Valeraldehyde	422			
Vanadium pentoxide	250			
Vinyl acetate	43	8	7.4	44
Vinyl chloride	71	31	180	440
Warfarin	414			
Xylene	23	14	47	290
Xylenol	305			
Yellow cake	296	1	0.21	
Zinc acetate	292			
Zinc bromide	395	1	0.38	
Zinc chloride	106	1	13	
Zinc cyanide	105	1	0.2	
Zinc oxide	66	3	55	47
Zinc phosphate	148	1	0.9	
Zinc sulfate	12	3	68	1500
1,1-Dichloropropane	475			
1,2,4,5-Tetrachlorobenzene	358			
2,2'-Thiobis(4,6-dichlorophenol)	476			
2,3,4,6-Tetrachlorophenol	238			

Table 6 Spill Priority List CHEMICAL	RANK	SPILL NUMBERS	SPILL VOLUME	SUPPLY VOLUME
2,3-Dibromo-1-propanol phosphate	304			
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	72	2	0.24	
2,4-Dichlorophenol	317			
2,4-dichlorophenoxyacetic acid (2,4-D)	28	37	130	3
2,4-Dinitrophenol	213			
2,4-Dinitrotoluene	340			
2-Phenylphenol	353			
4-Aminopyridine	251			
5-[Bis(2-chloroethyl)amino] uracil	479			

Table 7 Spill Priority List		**SPILL**	**SPILL**	**SUPPLY**
CHEMICAL	**RANK**	**NUMBERS**	**VOLUME**	**VOLUME**
Ammonia	1	107	470	3700
Chlorine	2	36	120	1700
Tetraethyl lead	3	4	72	26
Styrene	4	24	5000	630
PCBs	5	334	89	
Sulfuric 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 sulfate	12	3	68	1500
Phosphorus	13	16	46	68
Toluene	14	13	110	430
Copper sulfate	15	5	23	24
Sodium chloride	16	12	1400	12000
Calcium chloride	17	20	3700	340
Sodium hydroxide	18	92	8200	1800
Sodium chlorate	19	23	7700	440
Ammonium sulfate	20	8	260	330
Ammonium hydroxide	21	15	130	
Benzene	22	12	14	740
Xylene	23	14	47	290
Calcium hypochlorite	24	4	17	7.9
Formaldehyde	25	10	41	130
Acetic acid	26	9	73	71
Methyl alcohol	27	18	740	
2,4-dichlorophenoxyacetic acid (2,4-D)	28	37	130	3
Ethylene dichloride	29	1	780	820
Ammonium nitrate	30	63	4200	910
Sulfur	31	68	70000	7400
Sodium carbonate	32	3	25	570
Ammonium phosphates	33	5	140	1400
Propylene oxide	34	2	22	61
Perchloroethylene	35	10	15	27
Calcium hydroxide	36	17	360	2600
Nonylphenol	37	2	8.8	7
Ethylbenzene	38	4	0.79	730
Ethylene glycol	39	31	590	410
Fenitrothion	40	49	100	
Aminocarb	41	12	55	
Carbon tetrachloride	42	1	1.8	26
Vinyl acetate	43	8	7.4	44
Sulfur dioxide	44	16	90	140
Nitric acid	45	48	140	890
Phosphamidon	46	8	16	
Aldrin	47	2	1.3	
Phosphoric acid	48	12	37	520
Ferric chloride	49	8	1000	

Table 7 Spill Priority List CHEMICAL	RANK	SPILL NUMBERS	SPILL VOLUME	SUPPLY VOLUME
Ethylhexanol	50	1	100	
Hydrofluoric acid	51	5	0.68	77
Toluene-2,4-diisocyanate	52	7	2	
Ethyl alcohol	53	3	51	
Carbaryl	54	2	70	
Parathion	55	1	0.01	
Calcium oxide	56	12	530	2600
MCPA	57	5	0.91	
Methylene chloride	58	4	6.2	10
Paraquat	59	2	44	
Hydrazine	60	3	4.5	
Malathion	61	7	0.29	
Sodium silicate	62	1	3.8	120
Acrylonitrile	63	1	4.6	16
Trichloroethane	64	4	0.81	
Hexane	65	5	8	
Zinc oxide	66	3	55	47
Isopropyl alcohol	67	4	9	
Chlordane	68	2	0.003	
Potassium cyanide	69	1	0.005	
Potassium permanganate	70	4	9.8	
Vinyl chloride	71	31	180	440
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	72	2	0.24	
Dimethylamine	73	4	33	
Methyl methacrylate	74	3	3.4	18
Dieldrin	75	1	0.004	
Diazinon	76	4	0.3	
Acetone	77	4	9.9	23
Trichlorofon	78	3	2.6	
Naphthalene	79	3	6.4	
Ethylene	80	2	180	2200
Maleic anhydride	81	1	2.8	15
Dinoseb	82	1	0.91	
Calcium cyanide	83	1	0.09	
Methyl chloride	84	2	2.5	4.1
Benzoic acid	85	2	34	28
Chromic acid	86	8	8.8	2.8
Mercury	87	11	20	
Aniline	88	1	0.1	0.62
Oxygen (liquefied)	89	5	24	2700
Aluminum sulfate	90	9	120	220
Azinphosmethyl	91	1	0	
Hydrogen peroxide	92	7	0.71	34
Sodium hypochlorite	93	11	58	170
Ammonium chloride	94	1	0.7	2.7
Cresol	95	2	13	
Cyclohexane	96	1	0.11	60
Dichlorvos	97	1	0.1	
Calcium phosphate	98	3	100	160

Table 7 Spill Priority List		SPILL	SPILL	SUPPLY
CHEMICAL	RANK	NUMBERS	VOLUME	VOLUME
Thallium sulfate	99	1	0.03	
Butyl alcohol	100	1	2	
Trinitrotoluene	101	1	17	
Potassium hydroxide	102	2	1.2	12
Phthalic anhydride	103	3	7.2	34
Benzene hexachloride (Lindane)	104	1	0.0009	
Zinc cyanide	105	1	0.2	
Zinc chloride	106	1	13	
Acetic anhydride	107	8	1.5	
Methyl ethyl ketone	108	4	7.7	12
Pyridine	109	2	0.005	
Trichloroethylene	110	1	0.13	3
Cobaltous nitrate	111	1	0.9	
Picloram	112	3	0.53	
Diethylamine	113	2	1.8	
Trifluralin	114	9	4.6	
Dicamba	115	2	0.17	
Atrazine	116	2	0.85	
Methoxychlor	117	1	0.05	
Nitrogen (liquefied)	118	3	1.8	340
Propylene glycol	119	1	8.3	19
Diquat	120	2	0	
Chlorophenol	121	1	0.04	
Sodium fluoride	122	1	0.2	
Benzotrifluoride	123	1	50	
Carbofuran	124	4	0.06	
Methylamine	125	1	5.3	6.3
Ethyl chloride	126	2	0.2	15
Sodium sulfite	127	4	29	16
Diphenyl ether	128	1	1.5	
Dinitramine	129	2	0.007	
Maneb	130	1	1.3	
Diethanolamine	131	1	0.2	
Tributyl phosphate	132	1	0.3	
Titanium dioxide	133	2	0.5	110
Bromoform	134	1	0.014	
Terephthalic acid	135	1	0.18	45
Lignin sulfonate	136	5	180	
Propylene	137	1	9.1	660
Uranyl nitrate	138	3	0.21	
Nitroaniline	139	1	0.001	
Sodium hydrosulfite	140	2	29	8.4
Toluene-2,4-diamine	141	2	11	
Ethylene oxide	142			370
Acetylene	143	1	0.013	5.3
Lead oxide	144	2	2.1	34
Formic acid	145	1	0.2	
Endrin	146			
Propionic acid	147	1	2	

Table 7 Spill Priority List CHEMICAL	RANK	SPILL NUMBERS	SPILL VOLUME	SUPPLY VOLUME
Zinc phosphate	148	1	0.9	
Thioglycolic acid	149	1	0	
Copper cyanide	150	1	2.2	
Isodrin	151			
Diallate	152	3	0.08	
Ethyl acrylate	153	3	1.1	
Asbestos	154	15	310	
Mercuric chloride	155			
Cesium 137	156	3	0.000003	
Cumene	157			45
Carbon dioxide	158	1	0	2500
Chlorine dioxide	159	2	0.3	
Fonofos	160			2500
Nitrogen dioxide	161	3	0.001	
Endosulfan	162			
Aldicarb	163			
Calcium carbide	164	1	1.8	82
Potassium carbonate	165	1	100	
Tetraethyl pyrophosphate	166			
Azinphos ethyl	167			
Ethyl mercaptan	168	6	0.01	
Calcium arsenate	169	1	0.045	
Demeton	170			
Nickel carbonyl	171	1	0.3	
Sodium nitrate	172	1	2.5	
Calcium nitrate	173	1	1.8	
Toxaphene	174			
Chlorohydrin	175	1	0.8	
Aluminum chloride	176			14
Phenyl mercuric acetate	177	1	0.005	
Strychnine	178			
Cyanogen bromide	179	1	0.00005	
Carbon disulfide	180			21
Methoxyethylmercuric acetate	181			
Sodium dichromate	182			
Cycloheximide	183			
DDT	184			
Magnesium hydroxide	185	1	11	15
Hydrocyanic acid	186			
Sodium aluminate	187	1	14	9
Flamprop-methyl	188	3	0.16	
Triethanolamine	189	1	0.19	
Chloroform	190			3.7
Disulfoton	191			
Chlorpyrifos	192			
Sodium borohydride	193	1	4.5	17
Rotenone	194			
Chloroaniline	195	1	0.5	
Cyclohexylamine	196	1	0.07	

Table 7 Spill Priority List CHEMICAL	RANK	SPILL NUMBERS	SPILL VOLUME	SUPPLY VOLUME
Cadmium	197			
Kepone	198			
Acetone cyanohydrin	199			
Acrolein	200			
Arsenic acid	201			
Borax	202			52
Ethion	203			
Mercuric acetate	204			
Mevinphos	205			
Cadmium sulfate	205			
Ethylamine	207	1	1.3	
Brucine	208			
Antimony trioxide	209			1500
Mercuric thiocyanate	210			
Ferric oxide	211	5	23	
Mercurous nitrate	212			
Methiocarb	213			
Acetaldehyde	214			8.5
Barium sulfate	215	1	820	
Methyl parathion	216			
Phosphorus pentoxide	217	1	0.6	
Dichlone	218			
Hexachlorophene	219			
Sodium chromate	220	1	0.02	
Thiram	221	1	0.3	
Butyl formate	222	1	0.04	
Copper chloride	223			
Sodium azide	224			
Sodium phosphate	225			65
Allyl alcohol	226			
Urea	227			2600
Coumaphos	228			
Nitrous oxide	229	1	0.6	
Sodium arsenite	230	1	0	
2,4-Dinitrophenol	213			
Dioxathion	232			
Propargyl alcohol	233			
Ferrous sulfate	234	1	21	
Hexachlorobutadiene	235			
Hydrogen sulfide	236			
Arsine	237	1	0	
2,3,4,6-Tetrachlorophenol	238			
Endothall	239			
Dinitrocresols	240			
Trimethylene bromide	241	1	0.4	
Dicrotophos	242			
Phenolsulfonic acid	243	2	23	
Diphenyl	244	1	1.3	
Glyphosate	245	1	0.003	

Table 7 Spill Priority List CHEMICAL	RANK	SPILL NUMBERS	SPILL VOLUME	SUPPLY VOLUME
Heavy water	246	2	22	
Naled	247			
Hydroquinone	248			
Acrylamide	249			
Vanadium pentoxide	250			
4-Aminopyridine	251			
Ethanolamine	252			15
EPN	253			
Phosgene	254	1	0	
Phosphine	255	1	0.004	
Lactonitrile	256			
Malononitrile	257			
Mexacarbate	258			
Fluorine	259			
Fluoroacetamide	260			
Arsenic pentoxide	261			
Calcium fluoride	262	1	1	
Ethyleneimine	263			
Sodium hydrosulfide	264	2	2.3	
Aluminum phosphate	265	3	8.5	
Dimethyl ethyl amine	266	1	0	
Tetrahydronaphthalene	267	1	0.09	
Cadmium nitrate	268			
Lead arsenate	269			
Cobaltous chloride	270			
Cadmium chloride	271			
Phosmet	272			
Sulfur chloride	273	3	3.5	
Nicotine sulfate	274			
Boric acid	275			2
Sodium arsenate	276			
Copper acetate	277			
Nitrophenol	278			
Ferric hydroxide	279	2	5	
Hexachlorocyclopentadiene	280			
Sulfuryl chloride	281	2	4.4	
Crotonaldehyde	282			
Lead fluoroborate	283			
Morpholine	284			0.88
Stannous chloride	285			
Terphenyl	286	2	1.1	
Benzoyl chloride	287			
Thionyl chloride	288	1	53	
Trichlorophenoxy propionic acid	289			
Arsenic trioxide	290			
Barban	291	1	0.009	
Zinc acetate	292			
Copper nitrate	293			
Nonane	294	1	0.006	

Table 7 Spill Priority List		SPILL	SPILL	SUPPLY
CHEMICAL	RANK	NUMBERS	VOLUME	VOLUME
Trichlorophenol	295			
Yellow cake	296	1	0.21	
Dibromomethane	297			
Dimethyl sulfate	298			
Hexachlorobenzene	299			
Dinitrobenzene	300			
Furfural	301			
Methyl ethyl ketone peroxide	302	1	0	
Stannic chloride	303	1	0	
2,3-Dibromo-1-propanol phosphate	304			
Xylenol	305			
Mercuric sulfide	306	1	30	
Adipic acid	307			72
Ethyl acetate	308			6.2
Ethylene dibromide	309			
Nickel chloride	310			
Nitroglycerin	311			
Dodecylbenzenesulfonic acid	312			
Epichlorohydrin	313			
Methyl bromide	314			
Dimethoate	315			
Pyrocatechol	316			
2,4-Dichlorophenol	317			
Trichlorobenzene	318			
Decyl octyl phthalate	319	1	0.1	
Dibutyl amine	320			
Thallium acetate	321			
Sodium fluorosilicate	322			
Thiourea	323			
Benzyl chloride	324			
Temephos	325			
Dinitroaniline	326			
Maleic acid	327			
Quinone	328			
Sodium sulfate	329			410
Alachlor	330			
Calcium carbonate	331			250
Sodium nitrilotriacetic acid	332			
Tetramethyl lead	333			
Butylene	334			230
Glycidyl methacrylate	335			
Pentachlorobenzene	336			
Oleum	337			
Potassium sulfate	338			72
Butadiene	339			
2,4-Dinitrotoluene	340			
Chlorpropham	341			
Quinoline	342			
Hexachloroethane	343			

Table 7 Spill Priority List		SPILL	SPILL	SUPPLY
CHEMICAL	RANK	NUMBERS	VOLUME	VOLUME
Arsenic	344			
Butyl mercaptan	345			
Propylene chlorohydrin	346	1	8.9	
Dichlorodifluoromethane	347			
N-Nitrosodiphenylamine	348			
Potassium dichromate	349			
Benzophenone	350			
Dichloroethyl ether	351			
Chlorobenzene	352			
2-Phenylphenol	353			
Allyl chloride	354			
Benzaldehyde	355			
Diuron	356			
Phenylenediamine	357	1	0	
1,2,4,5-Tetrachlorobenzene	358			
Adiponitrile	359			
Decyl alcohol	360			
Furfuryl alcohol	361			
Nitrosodimethylamine	362			
Nonanol	363			
Cobaltous hydroxide	364	1	5.1	
Magnesium oxide	365	1	5	
Resorcinol	366			
Tetrachloroethylene	367			
Sodium phosphate, tribasic	368			
Acetophenone	369			
Benzonitrile	370			
Chromous chloride	371			
Cobaltous bromide	372			
Diisopropylamine	373			
Hexanol	374			
Nitrobenzene	375			
Nitrotoluene	376			
Oleic acid	377			2.6
Tridecyl alcohol	378			
Trimethylamine	379	1	1.5	
Chlorodifluoromethane	380	1	0.22	
Methyl hexyl ketone	381	1	0.94	
Isobutyl acrylate	382			
Potassium aluminate	383	1	0.7	
Chloroethylvinyl ether	384			
Triethylamine	385			
Eptam	386			
Sodium	387	1	0.5	
Anthracene	388			
Butylamine	389			
Dimefox	390			
Iodomethane	391			
Phorate	392			

Table 7 Spill Priority List

CHEMICAL	RANK	SPILL NUMBERS	SPILL VOLUME	SUPPLY VOLUME
Sodium fluoroacetate	393			
Sulfotepp	394			
Zinc bromide	395	1	0.38	
Atlox	396	1	0.2	
Benzidine	397			
Sodium thioglycolate	398	1	0.2	
Lithium bromide	399	1	0.13	
Ammonium stearate	400	1	0.1	
Crimidine	401			
Isovaleraldehyde	402			
Caprolactam	403			12
Benzyl alcohol	404			
Methylstyrene	405			
Sodium bisulfite	406			
Dichlobenil	407			
Diphacinone	408			
Diphenylamine	409	1	0.03	
Fumaric acid	410			1.2
Oxalic acid	411			1.1
Nitralin	412			
Toluidine	413			
Warfarin	414			
Neopentyl glycol	415	1	0.01	
Benzyl-n-butyl phthalate	416			
Diethyl-p-nitrophenyl phosphate	417			
Furazolidone	418			
Carbonyl sulfide	419			
Dalapon	420			
N,N-Dimethylaniline	421			
Valeraldehyde	422			
Chlorophacinone	423			
Fensulfothion	424			
Methanesulfonyl fluoride	425			
Metobromuron	426			
Nitrilotriacetic acid	427			
Chloroxuron	428			
Dichloroethylene	429			
Diethyl-m-toluamide	430			
Methyl phenkapton	431			
Dimethylaniline	432	1	0.005	
Ammonium picrate	433			
Diphenylmethane-4,4'-diisocyanate	434			
Propionaldehyde	435			
Strychnine sulfate	436			
Isooctyl alcohol	437			
Methyl isobutyl ketone	438			8.7
Phenanthrene	439			
Hexaldehyde	440			
Hydrogen	441			1200

Table 7 Spill Priority List		SPILL	SPILL	SUPPLY
CHEMICAL	RANK	NUMBERS	VOLUME	VOLUME
Phenylthiourea	442			
Amiton	443			
Beryllium	444			
Bromine	445			
Heptanol	446			
Nitropropane	447			
Octanol	448			
Sodium anthraquinone sulfate	449			
Glycerine	450			7.7
Silver nitrate	451			
Butyric acid	452			
Fluoranthene	453			
Naphthol	454			
Fluoroacetic acid	455			
Propionic anhydride	456			
Sulfamic acid	457			
Ammonium sulfamate	458			
Carboxymethylcellulose	459			2.5
Cyclohexanone	460			
Dibutyl ether	461			
Dithiobiuret	462			
Isobenzan	463			
Ethylene glycol monobutyl ether	464			
Butyraldehyde	465			0.2
Chromic sulfate	466			
Dimethyl phthalate	467			
Melamine	468			6.8
Fluenetil	469			
Nitromethane	470			
Choline chloride	471			5.8
Isophorone	472			
Naphtha	473			
Turpentine	474			11
1,1-Dichloropropane	475			
2,2'-Thiobis(4,6-dichlorophenol)	476			
Hexaethyl tetraphosphate	477			
Sodium selenite	478			
5-[Bis(2-chloroethyl)amino] uracil	479			
Camphor oil	480			
Dichloroethyl amino uracil	481			
Methyl amyl alcohol	482			
Monocrotophos	483			
Mephosfolan	484			
Thallium	485			
Chromium	486			
Ethylene thiourea	487			
Lead chloride	488			
Thiosemicarbazide	489			
Acetyl chloride	490			

Table 7 Spill Priority List		SPILL	SPILL	SUPPLY
CHEMICAL	RANK	NUMBERS	VOLUME	VOLUME
Cantharidin	491			
Isobutyl alcohol	492			1.5
Propylamine	493			
Diethyl chlorophosphate	494			
Isopropylmethylpyrazolyl dimethylcarbamate	495			
Potassium chlorate	496			
Bisphenol A	497			1.9
Diethyl phthalate	498			
Salicylic acid	499			
Fluometuron	500			
Iodine	501			
Potassium arsenite	502			
Acetonitrile	503			
Dioctyl phthalate	504			18
Ethylene glycol diacetate	505			
Acridine	506			
Amyl alcohol	507			
Formaldehyde cyanohydrin	508			
Tetraethyltin	509			
Coumatetralyl	510			
Cyclohexanol	511			
Ethylenediaminetetraacetic acid	512			
Mercuric oxide	513			
Propyleneimine	514			
TOTALS		1947	138139.71	67145.9

PRELIMINARY ENVIRONMENTAL ASSESSMENT AT AN ICBM SITE IN UKRAINE

Caroline Ladanowski[1], John Payne[2], Laurence Davidson[3]

[1]Emergencies Engineering Division, Environmental Technology Centre
Environment Canada
3439 River Road, Ottawa, Ontario K1A OH3

[2]Fenco MacLaren Inc
Atria North - Phase II, 2235 Sheppard Avenue East, Willowdale, Ontario M2J 5A6

[3]Gartner Lee International Inc.
140 Renfrew Drive, Suite 102, Markham, Ontario L3R 6B3

INTRODUCTION

Following independence, Ukraine has pursued a nuclear disarmament policy, including a commitment to rehabilitate the 176 former Russian Intercontinental Ballistic Missile (ICBM) launch sites, located in the regions of Pervomaisk and Khmelnitsky, to their former land use (predominantly agricultural). Rehabilitation will include environmental assessment to delineate and characterize contamination remaining from the military operation of the launch sites, and subsequent remedial activities as necessary.

The Ukrainian Environmental Assessment and Remediation Project (EARP) is designed to provide Ukraine with a small cadre of engineers and scientists trained in Canadian techniques and equipment for environmental site assessment and remediation. The EARP is structured as a Canadian public and private joint project to be carried out by the Emergencies Engineering Division and its private sector partners Fenco MacLaren Inc. and Gartner Lee International Inc. Nine Ukrainians arrived in Canada in June 1995 for a one year training period focusing on environmental site assessment. Eight of the trainees along with their Canadian colleagues participated in a demonstration of environmental site assessment activities at a former Intercontinental Ballistic Missile (ICBM) site, near the city of Khmelnitsky, in Ukraine during September 1995. The results of this investigation are summarized in this paper with additional details found in referenced report [1].

SITE DESCRIPTION

The command centre/missile silo complex is designated as missile position K38. Along with K35 and K37, they are located southeast of the town of Khmelnitsky. K38, on the southwestern slope of a forested upland is surrounded by the Podolskaya upland. To the east is the Dnieperside upland and to the northeast is the Colynskaya upland. The facilities at the base included : a silo, an underground command position, a power generating station with two underground diesel fuel tanks, a gas station with five underground fuel tanks; an oil tank; groundwater well; refrigeration building; vehicle maintenance area; and barracks.

The site topography is flat but on a hill top. The soils are fine-grained. The local land use is primarily agricultural with many trees.

PURPOSE

The purpose of the demonstration was three-fold: (1) to acquaint the team with the history, layout and environmental conditions of a typical Ukrainian launch site and command post; (2) to provide an opportunity for the Ukrainians to obtain hands-on assessment training and experience at a launch site; and (3) to familiarize the team with the current infrastructure in Ukraine for undertaking environmental assessment and remediation activities.

LITERATURE REVIEW

Initially, representatives from the Ministry of Defence, Ministry of Environmental Protection and the Ukrainian Scientific-Technical Centre (called SENSOR in Russian) were interviewed to determine past activities on the base and the availability of any reports. A preliminary report by SENSOR in 1995 indicated that the first missile complex was placed on the Khmelnitsky base in 1970 with subsequent modifications in later years and its eventual dismantlement in 1993 with the missile and its fuel being removed; their surface sampling and analysis program indicated very little contamination.

This information as well as a visual reconnaissance assisted in planning the activities for the preliminary environmental site investigation. The base personnel were briefed on planned activities, questioned whether they were aware of any environmental problems on the base, and asked for assistance with logistical needs.

CONTAMINANTS OF CONCERN

Based on review of documentation and discussions with base personnel, the potential contaminants of concern and related chemical compounds associated with the rocket fuel, silo command post and facilities are shown in Table 1. The potential contaminants of concern and related chemical compounds associated with the vehicle maintenance facility, fuel depot and power distribution building are shown in Table 2.

TABLE 1. Potential Contaminants of Concern Associated with the Rocket Fuel, Silo Command Post and Facilities

Contaminant of Concern	**Associated Chemical Compounds**
Hydrazines	Unsymmetrical dimethylhydrazine (UDMH), Monomethylhydrazine (MMH)
Breakdown Products of Hydrazine	Nitrosodimethylamine (NDMA), Formaldehyde, Diethyl Amine, Ammonia
Freezer Units for Command Post	Refrigerants, Ammonia, Methyl Chloride, Ethylene glycol, Metals

TABLE 2. Potential Contaminants of Concern Associated with the Vehicle Maintenance Facility, Fuel Depot and Power Distribution Building

Contaminant of Concern	**Associated Chemical Compound/Parameter**
Gasoline	Total petroleum hydrocarbon (TPH), Benzene, Toluene, Ethylbenzene, Xylenes (BTEX), Phenol, Aliphatic hydrocarbons, Metals
Diesel, fuel	TPH
Oil, kerosene	Polyaromatic hydrocarbons (PAHs)
Used Oil	TPH, PAHs, Metals, PCBs
Antifreeze Coolant	Ethylene glycol, Metals, pH
Windshield Wiper Fluid	Methyl alcohol
Electrical Equipment	TPH, Polychlorinated biphenyls (PCBs)

PROPERTIES OF PRIORITY CONTAMINANTS

The priority contaminants of concern are nitrosodimethylamine (NDMA) and unsymmetrical dimethylhydrazine (UDMH) due to their carcinogenity.

NDMA is a yellow, oily liquid with a faint characteristic odor having an odor threshold of 0.0079-0.013 ppm. The half life varies from 21 days to 6 months in soil; 0.5 to 1 hour in air; 0.5 to 1 hour in surface water; and 42 days to 12 months in ground water. [2]

UDMH is a colorless liquid with an ammonia or fish-like odor having an odor threshold of 6.1-14 ppm. The American Conference of Government Industrial Hygienists' (AGGIH) TWA is 0.5 ppm while the IDLH is 50 ppm. The half life varies from 8 to 22 days in soil; 0.8 to 7.7 hours in air; 8-22 days in surface water; and 16-44 days in ground water. [2]

INVESTIGATION PROCEDURES

The investigation procedures are summarized in this section with additional details found in referenced report [1]. Radiation and air quality monitoring were routinely conducted to ensure the health and safety of those working in the area. A survey grid was laid out across the area of interest. All buildings and site features were located relative to this grid. A series of 57 shallow soil and water samples were collected and logged. A geophysical survey was conducted to determine the presence of anomalies (e.g., underground storage tanks, buried drums, buried pipes). A soil gas vapour survey was conducted to determine the presence of any significant volatile organics. Based on the geophysical and soil gas vapour surveys, fourteen boreholes were drilled and ten monitoring wells were installed in select locations to obtain 108 subsurface soil and groundwater samples. An elevation survey was conducted to tie in the groundwater levels. Sixty-nine (69) samples were analysed in the field laboratories while 74 samples were analyzed in the EED laboratory. As part of the work, a Ukrainian drill rig was used for the soil investigation near the silo and field analytical equipment was set up in two Ukrainian military mobile analytical laboratories.

TRAINING PROCESS

The trainees had received some training at the facilities of the Canadian private sector partners located in Toronto and at EED in Ottawa prior to their participation in the preliminary environmental assessment of missile position K38. The formal training took place in the classroom while the informal training consisted of demonstrations and visits.

The training in Canada was designed to prepare them for their participation in the preliminary environmental assessment and covered : English, Computers, Workplace Hazardous Materials Information; Laboratory Safety; Steps for Conducting Environmental Site Assessment; Field and Laboratory Analytical Methods; Personal Protective Equipment and Clothing; Environmental Philosophy; Environmental Regulations and Criteria; Identification, Classification and Assessment of Contaminated Sites; Geophysical Investigation Techniques; Drilling; Installing Monitoring Wells; Sample Collection, Logging and Analysis; Quality Assurance/Quality Control; Risk Assessment; Steps for Choosing and Implementing Remedial Technologies; Health and Safety; Public Involvement and Community Relations; Site Closure; and Long-term Monitoring.

A number of activities at missile position K38, including those identified in the investigative procedures, occurred simultaneously and small groups of trainees rotated through the activities on a daily basis according to a pre-determined schedule. The activities included, but were not limited to: unloading and unpacking equipment; setting up field laboratories for water and soil analysis; determining surface and subsurface sampling locations; drilling boreholes; installing monitoring wells; sampling and logging surface and subsurface water and soil samples; decontaminating equipment and materials; conducting soil vapour survey; conducting geophysical survey; conducting level survey; conducting field analysis of soil and water samples; and preparing for technical meetings.

CHEMICAL ANALYSIS

Table 3 shows the parameters analyzed in the Ukrainian field mobile laboratories and in the EED laboratory. The field techniques comprised of the use of air tubes, immunoassay kits and wet chemistry kits for the analysis of air, water and soil samples. The laboratory techniques included the use of gas chromatography with purge & trap, gas chromatography with mass spectrophotometer, ultraviolet/visible spectrophotometry, flame atomic absorption spectrophotometry and inductively coupled plasma spectrophotometry for the analysis of water and soil samples.

TABLE 3.Analytical Measurements

PARAMETER	AIR	WATER	SOIL
UDMH	field	lab	lab
nitrosamine		lab	lab
formaldehyde	field	field	
nitrous fumes	field		
TPHs	field	field, lab	field, lab
BTEXs		field. lab	field, lab
ethylene glycol		field	field
heavy metals		field, lab	field, lab
PCBs		lab	field, lab
PAHs		lab	lab

RESULTS

The results of the investigation indicated the nature, extent and migration of contaminants. The results generally confirmed the preliminary work by SENSOR that the former ICBM site was relatively clean; although there were some minor gasoline, diesel and fuel oil impacts around the support buildings. However, there are concerns about the future potential dispersion of contaminants in the silo area when the silo is demolished with explosives.

CONCLUSION

The team concluded their demonstration with a one-day technical meeting with representatives from the Ukrainian Ministries of Defence, Environmental Protection, and SENSOR to discuss findings, methods and future work.

The objectives of the work were achieved as no further work at missile position K38 was deemed necessary as a result of the preliminary environmental assessments by the Canadian-Ukrainian team and by SENSOR. It is anticipated that future work will uncover more seriously contaminated missile sites.

REFERENCES

1. Emergencies Engineering Division/Fenco MacLaren Inc./Gartner Lee Limited, Preliminary Environmental Assessment of Missile Position K38 Near the City of Khmelnitsky, prepared for Ukrainian Ministry of Defence, May 1996.
2. Howard, P.H., Handbook of Environmental Degradation Rates, Lewis Publishers, inc., Chelsea, Michigan, USA, 1991.
3. SENSOR, Measures for Assurance of Ecological Safety at Elimination of Missile-Nuclear Weapons in Ukraine, Town - Khmelnitskij, Stage 1 - Book 2.1, Code ID-EL-43, Ministry of Central Design Institute, Defence of Ukraine, 1995.
4. SENSOR, Measures for Assurance of Ecological Safety at Elimination of Missile-Nuclear Weapons in Ukraine, Town - Pervomajsk, Stage 1 - Book 2, Code ID-EL-43, Ministry of Central Design Institute, Defence of Ukraine, 1995.
5. SENSOR, Measures for Assurance of Ecological Safety at Elimination of Missile-Nuclear Weapons in Ukraine, Town - Cherkasse, Stage 1 - Book 3, Ukrainian Scientific-Technical Center = Sensor, 1995.
6. SENSOR, Organizational-Technical Directions on Assurance of Environmental Safety of the Liquidation Work, Stage 1 - Book 1, Code OTU-EL-43, Ministry of Central Design Institute, Defence of Ukraine, Kyiv, 1995.

ENVIRONMENTAL SITE ASSESSMENT IN LATVIA

Harry Whittaker[1], Caroline Ladanowski[1], Mark Sungaila[2], Shawn Bonneville[2], Ruta Whittaker[3], Juris Malers[4], Janis Millers[4]

[1] Emergencies Engineering Division, Environmental Technology Centre
Environment Canada
3439 River Road, Ottawa, Ontario K1A OH3

[2]Gartner Lee International Inc.
140 Renfrew Drive, Suite 102, Markham, Ontario L3R 6B3

[3]Environmental Health Directorate
Health Canada
Tunney's Pasture, Ottawa, Ontario K1A OL2

[4]Riga Technical University
Riga, Latvia

INTRODUCTION TO ECEP

Following the collapse of the Soviet Union, Latvia was left with over 400 former Soviet military installations, including missile bases, many in a deplorable state. The environment was, in many cases, contaminated to varying degrees by spills of toxic chemicals to the soil and groundwater which pose environmental risks. Consequently, large scale cleanups are required to return this land to profitable use.

Until 1995, Latvia had not conducted any systematic environmental assessment or remediation of its Soviet military installations. However, it is known from past experience with former military bases that severe environmental problems can be anticipated which involve missile fuels, petroleum products, kerosene, polychlorinated biphenyls, pesticides, and acids. "SAMIN" missile fuel which contains xylidine and "MELANGE" red fuming nitric acid (oxidant) were used in many missiles and were spilled.

Latvia cannot effectively manage such contamination since it does not have the skills or equipment necessary to do so and have sought Canadian cooperation and technical assistance. This has led to the formation of the Latvian Environmental Centre of Excellence Project (ECEP). The goal of ECEP is to give Latvia the independent capability to undertake environmental assessment and remediation of contaminated sites including former military installations. The goal will be achieved by providing them with Canadian techniques and equipment for continuing environmental assessment and remediation by training and equipping a cadre of Latvian engineers and scientists. With this they will be able to establish their own training programs using the Canadian-trained experts and train other Latvians in Canadian procedures and technology, thereby establishing an Environmental Centre of Excellence at the Chemical Technology Faculty of Riga Technical University (RTU) in Latvia.

The ECEP is structured as a Canadian public and private joint project to be carried out by the Emergencies Engineering Division (EED) of Environment Canada, private sector partner Gartner Lee Limited (GLL) and Riga Technical University (RTU). The philosophy for this structure is to promote Canadian techniques and equipment in Latvia and other eastern european countries with the support of the Canadian government. The ECEP is primarily funded by the Central and Eastern Europe Branch of the Canadian International Development Agency with additional funding by EED, GLL, RTU, and the Canadian Latvian community.

Under the ECEP, eight Latvian engineers and scientists will be trained in Canada each for a period of six to twelve months. The first group of four trainees arrived in June 1994 while the second group of four trainees arrived in July 1995. The trainees for the ECEP are all from the Chemical Technology Faculty of Riga Technical University.

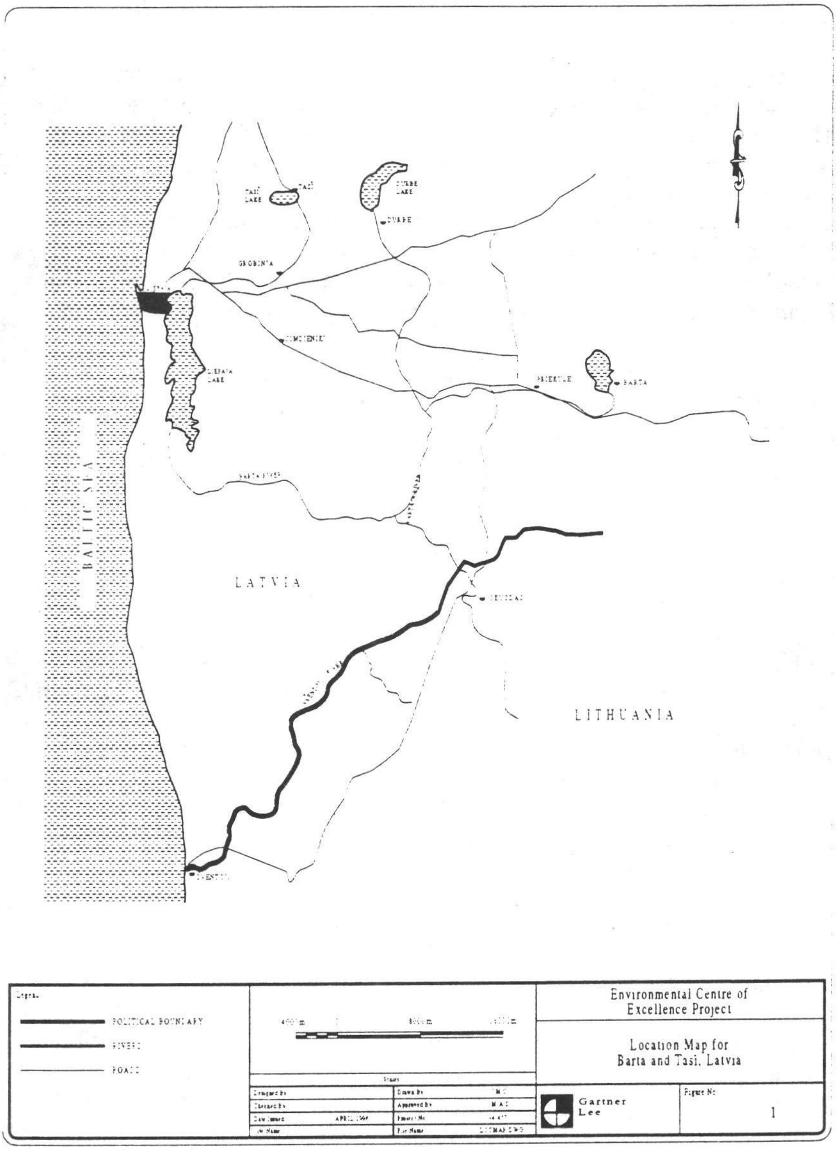
BACKGROUND FOR ESA

The focal point of the ECEP was environmental assessment and remediation training demonstration carried out at actual contaminated sites in Latvia. The World Bank suggested that work be carried out in the Liepaja region where they were active. Thus, military bases at Barta and Tasi, as shown in Figure 1, were selected as demonstration sites for that training. A short environmental assessment demonstration took place at Barta and Tasi in August 1995 while the environmental remediation demonstration at Barta is planned for August 1996. It was known that these sites were contaminated by xylidine and/or red fuming nitric acid.

PROPERTIES OF PRIORITY CONTAMINANTS

Xylidine (aminodimethylbenzene) is a pale yellow to brown liquid with a weak, aromatic, amine-like odour having an odor threshold of 0.0048-0.056 ppm. It is slightly soluble in water and is toxic by ingestion, inhalation and skin absorption. For example, the American Conference of Governmental Industrial Hygienists' (ACGIH) suggests a time-weighted average (TWA) of 0.5 ppm based on acceptable contaminant concentrations for a normal, 8-hour workday and 40-hour work week. The National Institute for Occupational Safety and Health's (NIOSH) immediately dangerous to life or health (IDLH) concentration is 150 ppm.

Red fuming nitric acid (RFNA) contains more than 85% nitric acid, approximately 6-15% NO_x (as nitrogen dioxide), and less than 5% water. It is a red fuming liquid with an acrid, suffocating odor having an odour threshold of 0.27 ppm. It is toxic by inhalation, corrosive to skin and mucous membranes. The ACGIH's TWA is 2 ppm



Environmental Centre of Excellence Project

Location Map for
Barta and Tasi, Latvia

Figure No 1

while its short-term exposure limit (STEL) is 4 ppm. The NIOSH IDLH is 100 ppm.

OBJECTIVES OF ESA DEMONSTRATION

An environmental assessment demonstration at two former Soviet military installations (Barta and Tasi), near the city of Liepaja, took place in August 1995. The purpose of the demonstration was four-fold : (1) to carry out site assessment activities at typical Soviet air defence missiles installations; (2) to provide an opportunity for the Latvians to obtain hands-on assessment training and experience on their own territory; (3) to familiarize the team with the current infrastructure in Latvia for undertaking environmental assessment and remediation activities; and (4) to establish the Chemical Technology Faculty of Riga Technical University as the Environmental Centre of Excellence in Latvia.

ESA DEMONSTRATION PROCEDURES

Background Research

Members of the team had visited Tasi in 1993 and 1994 and Barta in 1994. It was known that several spills had occurred at the former military installations. A member of the Latvian Border Guards also indicated that some buildings had radiation impacts. The relevant government agencies, local residents and media were briefed on planned activities, questioned whether they were aware of any environmental problems on the bases, and requested for assistance with logistical needs. This information assisted in planning the activities for the environmental site assessment.

Initial Visual Reconnaissance

An initial visual reconnaissance of the sites was conducted by the Canadian-Latvian team along with Latvian military and forestry personnel to identify the apparent zone of greatest contamination and site features that might control the movement of spilled fuel such as drainage ditches and ponds. The areas and features identified would be further investigated according to the plan which was developed.

Radiation and Air Quality Monitoring

Radiation and air quality monitoring were routinely carried out to ensure the health and safety of those working in the area. Air quality was monitored using a photoionization detector which measures total ionizable organic vapours while radiation exposure was monitored using badges and a meter. A health and safety plan was developed and implemented to address hazards of potential contaminants (e.g., xylidine, red fuming nitric acid), required protective equipment (e.g., respirators with organic cartridges) and clothing (e.g., tyvex and saranex suites), establishment of hot and cold zones, accident measures, etc.

Survey Grid and Documentation

A survey grid was established across the area of interest in both Barta and Tasi. All buildings and site features were located relative to this grid. Surface topography, the presence of water bodies, condition of surface vegetation, presence of staining on the ground, visual indicators of former fuel tanks and location of water wells were noted. Video recording and photographs were used as part of the documentation.

Soil Sampling, Monitoring Well Installation and Groundwater Sampling

A series of shallow soil samples were collected and analyzed for the presence of xylidine and nitrate in order to generally delineate the known or suspected spill areas. Based on the analytical results, boreholes were drilled and monitoring wells were installed in select locations. Subsurface soil samples were collected during well installation using a hand auger with a power auger used to advance the borehole. Each sample was logged and characterized according to its physical properties. Documentation also included any physical signs of contamination such as soil staining, discolouration, and/or odours. All soil samples were screened in the field for the presence of organic vapours by bag head space analysis using a portable photoionization detector. This vapour monitoring helped identify contaminated zones within the soil profile. The hand auger was decontaminated between collection of each sample using laboratory grade detergent and the power auger was similarly decontaminated between boreholes.

Ground water monitoring wells were installed once the water table was penetrated by about 1 m. The monitors were installed to verify the overall direction of ground water flow, determine horizontal and lateral hydraulic gradients, and permit collection of samples to characterize the ground water quality. The wells typically consisted of standpipes installed so that the screened section extended from above to below the water table. This configuration allowed the monitor to be used for a variety of purposes including: measurement of water level depths; checking for the presence and thickness of free product; checking for organic vapours in the unsaturated zone; collection of ground water or free product samples; and performing hydraulic conductivity tests.

The monitors consist of threaded 51 mm I.D. PVC pipe with a 1.5 m machine cut 10 slot screen. The monitor pipes were pre-cleaned and wrapped in a protective plastic wrap at the factory. The pipe and screen sections were pre-threaded with O-Ring seals. No glues or solvents were used to connect the pipe sections to ensure that foreign contaminants were not introduced to the borehole. A silica sand pack was placed around the screen and extended in most cases to about 0.5 m above the slotted interval. A pellet form of bentonite seal was placed above the sand pack.

All newly installed monitors were equipped with dedicated Waterra foot value pumping devices attached to dedicated lengths of 12.7 mm I.D. polyethylene tubing. The ground water monitors were purged to ensure that fresh formation ground water was entering the monitor and to clean out the fines from the sand pack as much as possible. Roughly three borehole volumes were removed from each well until representative formation waters flowed into the monitors and field measurements of pH and conductivity stabilized. Ground water samples were then collected and analyzed for the presence of xylidine and nitrate where appropriate.

The only exception to the use of PVC well pipes was at Barta wells MW1 and MW1A. This area was known to be highly contaminated with xylidine so stainless steel well points were drawn to the water table at these locations.

Water Level Measurements

All monitoring wells were surveyed to establish their relative elevations and were located with respect to site landmarks once the drilling program was completed. Ground and top of pipe elevations were measured with an accuracy of less than 0.01m error on closures.

Water levels were measured in the field to determine ground water level fluctuations and hydraulic gradients. Measurements of water levels and the testing for the presence of non-aqueous fluids in the monitors was performed using a dual interface probe. This instrument is specifically designed to detect both aqueous and non-aqueous fluids and is capable of detecting immiscible layers as thin as 1 mm in thickness. In order to limit potential for cross-contamination of ground water monitors the instrument was rinsed with laboratory grade detergent along with distilled water between each measurement. Organic vapour measurements were taken by inserting the probe of the photoionization detector into the monitor and covering the top of the monitor pipe. Readings were recorded as the instrument readings stabilized. Water level measurements along with product thickness measurements and vapour measurements were compiled in tabular format.

Hydraulic Conductivity of Soil

The hydraulic conductivity of the soil was determined by performing in-situ permeability tests where the rate of rise or fall of the water level in a well over time after a certain volume is removed or displaced is measured. Hydraulic conductivity was calculated using Hvorslev's (1951) method. The "Waterra pump" was used to perform the tests which are considered withdrawal tests. Some tests were repeated at certain locations as a QA/QC check.

Soil Vapour Survey

A soil vapour survey was conducted by augering a borehole to the water table and sniffing for organic vapours to further delineate the xylidine plume. A soil sample was also collected at the water table using the hand auger and analyzed for the presence of xylidine. Due to interferences with the power auger exhaust, vapour readings were considered erroneous and this delineation was based on the soil analyses.

Technical Seminar and Media Activities

Upon completion of the activities in Barta and Tasi, the scope of these activities and the preliminary results were transmitted to regional authorities and to the general public. The former audience was addressed at a technical seminar attended by government officials from Latvia, Lithuania and Estonia and a government consultant from Denmark. Presentations took place in English and Latvian with translation provided by the Project Coordinator. This was followed by a press conference for the print media and a tour of the team facilities and equipment at Cimdenieki and a visit to the Barta site for visual, audio and print media. This event took place on the first anniversary of the withdrawal of Soviet troops from Latvia and generated a great deal of interest throughout the country. It was covered on the program "Panorama" the most watched news and current affairs program in Latvia.

BARTA SITE SETTING

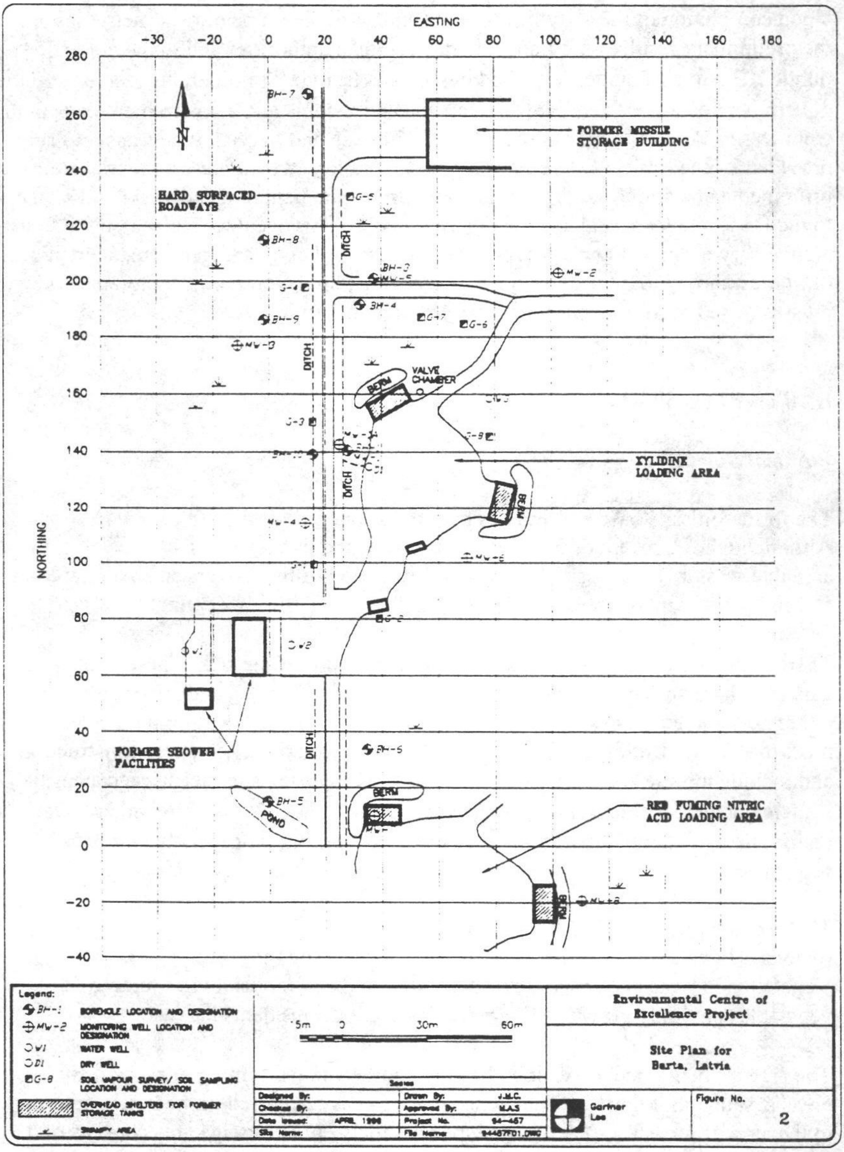
Physical Surroundings

The former missile base at Barta has been abandoned since the fall of 1994. Although the full extent of the lands occupied by the base exceeds 400 hectares, the area that was obviously used for missile storage and testing covers an area of at least 500 m by 1,000 m, or about 50 hectares.

There are numerous roads that lead to various portions of the site. These roads are generally hard surfaced (either asphalt or reinforced concrete), and are oriented in either north-south, or east-west directions. Drainage ditches exist on both sides of most roadways. Buildings occupying the site are primarily of concrete construction, and include missile and ammunition storage buildings, missile fuel storage areas, vehicle garages, barracks, kitchens, and an on-site sanitary sewage treatment plant. In many cases soil berms were built up against and over buildings, and planted with vegetation.

The site topography is flat, with swamps present in many areas. In many cases roadways have drainage culverts under them connecting the swampy areas. Vegetation is typically a mixture of deciduous and coniferous trees. Some wild vegetables naturally grow in this area which the local residents harvest.

The area in the immediate vicinity of the xylidine and red fuming nitric acid spill areas is shown in Figure 2. The spills appear to have occurred immediately adjacent to the storage areas for each of the respective fuels. Each storage area consists of a large open paved surface, with overhead shelters present for the storage tanks. The fuel tanks have since been removed; however, they were set in depressions in the soil beneath the overhead shelters. These depressions are still evident.


EASTING
-30
-20
0
20
40
60
80
100
120
140
160
180
NORTHING
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
N
BH-7
FORMER MISSILE STORAGE BUILDING
HARD SURFACED ROADWAYS
G-5
DITCH
BH-8
BH-3
MW-5
MW-2
G-4
BH-4
BH-9
G-7
G-6
MW-3
DITCH
BERM
VALVE CHAMBER
G-3
G-8
MW-1
BH-10
D1
XYLIDINE LOADING AREA
DITCH
BERM
MW-4
MW-6
G-1
G-2
W1
W2
FORMER SHOWER FACILITIES
DITCH
BH-6
BERM
BH-5
POND
RED FUMING NITRIC ACID LOADING AREA
BERM
MW-8
Legend:
BH-1 BOREHOLE LOCATION AND DESIGNATION
MW-2 MONITORING WELL LOCATION AND DESIGNATION
W1 WATER WELL
D1 DRY WELL
G-8 SOIL VAPOUR SURVEY/ SOIL SAMPLING LOCATION AND DESIGNATION
OVERHEAD SHELTERS FOR FORMER STORAGE TANKS
SWAMPY AREA
15m
0
30m
60m
Scales
Designed By:
Drawn By: J.M.C.
Checked By:
Approved By: M.A.S
Date Issued: APRIL 1996
Project No. 94-457
Site Name:
File Name: 94457F01.DWG
Environmental Centre of Excellence Project
Site Plan for Barta, Latvia
Gartner Lee
Figure No. 2

A total of three water wells were discovered in the vicinity of the spill areas. Two dug wells were located near the former shower building west of the xylidine loading area, and are shown in Figure 2 labelled W1 and W2. One drilled well was located northeast of the xylidine loading area and is labelled W3 on Figure 2.

The exact sequence of events leading up to the known xylidine spill is not known. However, it has been reported by local authorities that eleven tonnes of this material were spilled onto the paved surface at the xylidine loading area. It appears that the fuel spread westward following the slight westward slope of the paved surface, and some entered a drainage ditch. The northwest portion of the paved surface is stained with xylidine over about a 30 m by 30 m area. A circular concrete crib (about 0.9 m diameter) is situated at the west edge of the loading area, and is shown labelled as D1 on Figure 2. The crib does not have a solid bottom, and rests directly on unpaved ground. A 0.1 diameter steel pipe leads from the base of this crib northwards along the drainage ditch, to an outfall in a swampy area north of the loading area. It is possible that this crib/pipe was utilized as a dry well for the disposal of liquids or storm water into the swamp. This dry well crib contained "SAMIN" in a 1994 visit and was found to still be heavily stained with xylidine. Soils in the vicinity of the concrete crib, and also along the east side of the road and north of the loading area have been affected by xylidine.

As with the xylidine spill, details of the RFNA spill are not known. The only visually obvious indication of the spill is vegetation stress in the form of dying trees immediately east of the RFNA loading area. The visual stress zone appears to have dimensions of about 30 m by 20 m. The visual stress zone appears to correspond to the areas where low pH was measured in both soil and ground water, indicating the influence of the RFNA spillage.

Geological Setting

In the immediate vicinity of Barta, the soils generally consist of sand and gravel fill underlain by a fine sand to silty sand. At locations MW-3 and MW-4, the sand sequence thins (0.5 to 1.0 m) and fine glacial deposits (clayey silt till) are found just below the sand. The total depth of the till unit is unknown due to limitations of the available drilling equipment.

Ground Water Flow Directions

A total of nine ground water monitors were installed in the vicinity of the xylidine and RFNA spill areas to determine ground water elevations and flow directions, and to permit ground water sampling.

Six of the monitor locations were chosen to provide information specifically about the xylidine spill, as follows: upgradient at MW-2 and MW-6; downgradient at MW-3 and MW-4; cross-gradient at MW-5; and two ground water monitors close together in the "hot spot" at MW-1 and MW-1A.

For the RFNA spill, the following is relevant: MW-8 is in the source; MW-7 is a relatively close downgradient well; and MW-1 through MW-6 are also downgradient locations.

The small surface water pond that is west of the RFNA area is in a downgradient direction from the RFNA spill.

The locations of all monitors are shown in Figure 2. Only the shallow aquifer was investigated due to the limitations of the drilling equipment available for the site assessment work.

Shallow ground water exists about 1 m below grade during the dry season and generally flows in a northwest to west direction towards monitoring well locations MW-3 and MW-4. Figure 3 illustrates the localized ground water flow pattern. The shallow flow system is influenced by site features such as the compacted base for the concrete road running in a north-south direction and the low lying wet areas present on either side of the concrete road. This is evident as ground water mounding is present at monitoring well location MW-1A. The ground water table fluctuates rapidly during rain events during which ground water levels were observed at or near the surface.

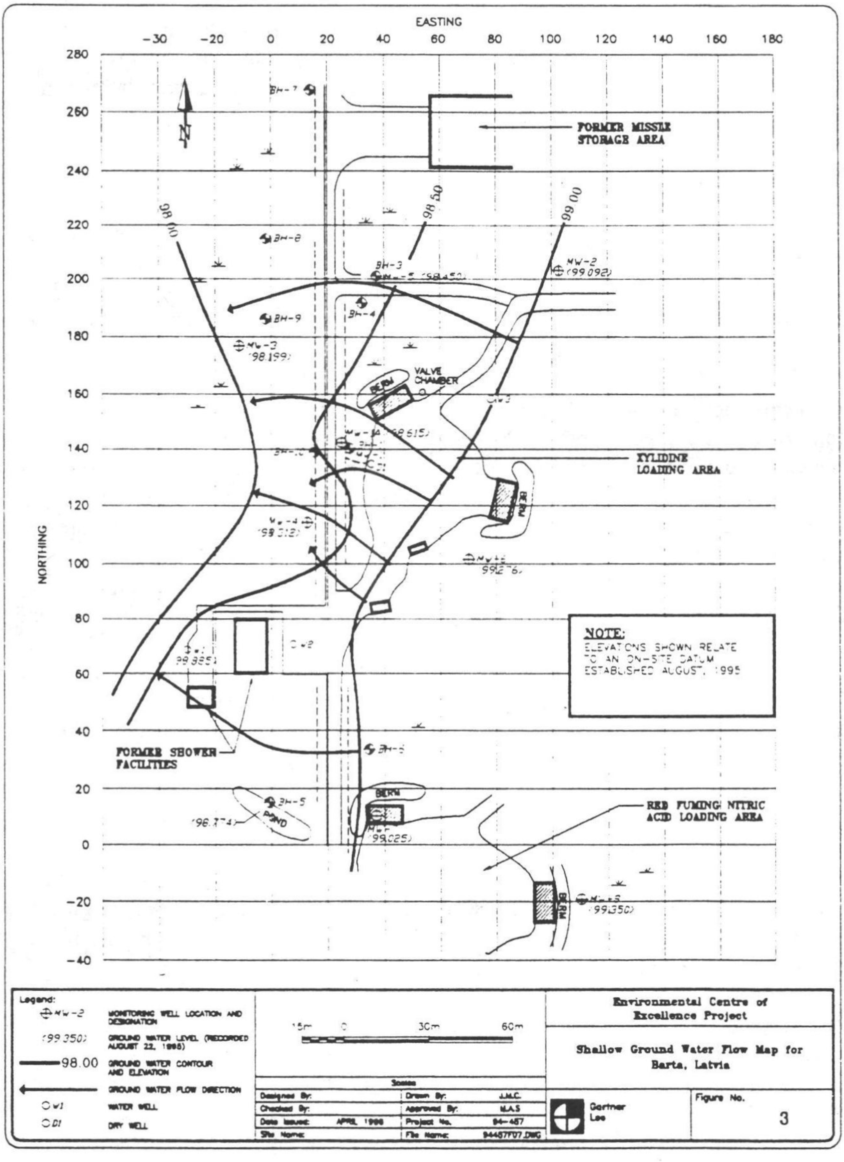
The hydraulic conductivity of the soils varies across the site, and appears to decrease westward across the study area. For example, at location MW-6 the soil permeability is 5.7×10^{-6} m/s and at location MW-3 the permeability of the soil is 3×10^{-7} m/s. The soil permeability is consistent with the geology in these areas, as finer grain soils are present west of the north-south road. Ground water velocity was estimated to be 5 m/yr in the vicinity of monitoring well MW-6 and 0.15 m/yr in the vicinity of monitoring well MW-3.

Surface Water Conditions

There is one known creek which flows in a north-south direction and is situated about 1 km west of the xylidine and RFNA spill areas. In the immediate vicinity of the study area, there are numerous drainage ditches along side the concrete roads which are interconnected via culverts. During rain events, flooding occurs with the ground water table rising close to or at the surface. The runoff is directed to the drainage ditches which flood the low lying areas on either side of the roadways.

Also, during rain events it was observed that local flooding in the vicinity of the concrete crib at the xylidine loading area had a distinctive black sheen on the water surface. It is therefore believed that this fluctuation in the ground water surface is a significant factor in the movement of xylidine contaminants.

There is a shallow pond located west of location MW7, which is likely a local ground water discharge zone.


EASTING
-30
-20
0
20
40
60
80
100
120
140
160
180
NORTHING
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
N
BH-7
FORMER MISSILE STORAGE AREA
98.00
98.50
99.00
BH-8
BH-3
MW-5 (98.450)
MW-2 (99.092)
BH-4
BH-9
MW-3 (98.199)
VALVE CHAMBER
BERM
MW-1A (98.615)
XYLIDINE LOADING AREA
BERM
MW-4 (98.012)
MW-6 (99.276)
W2
(99.885)
NOTE:
ELEVATIONS SHOWN RELATE TO AN ON-SITE DATUM ESTABLISHED AUGUST, 1995
FORMER SHOWER FACILITIES
BH-6
BH-5
POND
(98.774)
BERM
MW-1 (99.025)
RED FUMING NITRIC ACID LOADING AREA
BERM
MW-8 (99.350)
Legend:
MW-2 MONITORING WELL LOCATION AND DESIGNATION
(99.350) GROUND WATER LEVEL (RECORDED AUGUST 22, 1995)
98.00 GROUND WATER CONTOUR AND ELEVATION
GROUND WATER FLOW DIRECTION
W1 WATER WELL
D1 DRY WELL
15m
0
30m
60m
Scales
Designed By:
Drawn By: J.M.C.
Checked By:
Approved By: M.A.S.
Date Issued: APRIL 1996
Project No. 94-457
Site Name:
File Name: 94457F07.DWG
Environmental Centre of Excellence Project
Shallow Ground Water Flow Map for Barta, Latvia
Gartner Lee
Figure No.
3

EXTENT OF XYLIDINE AND RFNA CONTAMINATION AT BARTA

Soil Contamination

Laboratory analyses of the soils at Barta are tabulated and presented in Appendices A and B. The results are plotted on Figure 4. The majority of the analytical work carried out to date on samples from Barta was conducted by the Latvian chemists at the project laboratory at RTU or at EED's laboratory.

Xylidine Impacts

Soil sample collection to delineate xylidine impacts was carried out in three phases. The first phase included the collection of near surface samples using a hand auger. Ten sampling locations were chosen over in the area surrounding the xylidine spill zone to attempt to define the maximum extent of contamination. These locations are identified with the BH designation in Figure 4.

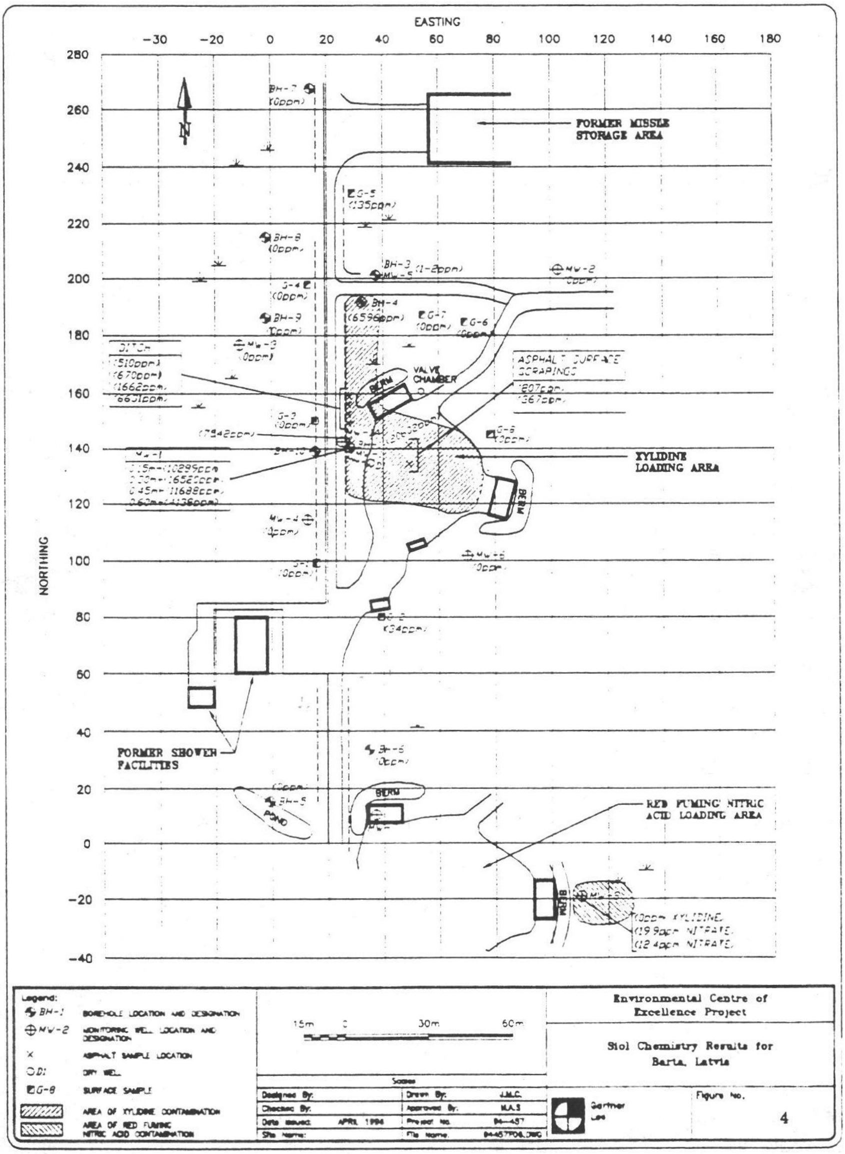
High concentrations of xylidine were detected in the vicinity of BH1 with concentrations of 20,602 ppm found at surface. A series of shallow grab samples were also obtained within the drainage ditch, immediately north of BH1, where xylidine staining was evident. Xylidine concentrations within these grab samples decreased from 6,631 ppm to 510 ppm northward (noted under "Ditch" in Figure 4). following the slope of the drainage ditch. Borehole BH4 is located in the swamp immediately north of the loading area, near the discharge of the drainage ditch. At this location a xylidine concentration of 6,596 ppm was found within 0.3 m of ground surface.

Xylidine was not detected at any other BH location, suggesting that the main migration pathway was via the drainage ditch east of the roadway. It is also likely that the roadway, consisting of reinforced concrete paving over a densely compacted granular base, serves as migration barrier, preventing migration westwards.

During the second phase of the soil collection, a power auger was used to advance the boreholes to permit hand-auger recovery of soils from depth. Monitoring wells were also installed in these boreholes. These are identified by the prefix MW on Figure 4. Xylidine was detected in the soils only at MW-1, at concentrations varying from 4,138 to 16,520 ppm, as shown on Figure 4.

The third phase of soil sample collection occurred as part of a soil vapour study carried out surrounding the xylidine loading area. A total of eight holes were advanced, and are designated by the prefix 'G' in Figure 4. In each of these boreholes one sample was collected at the water table interface and analyzed for the presence of xylidine. The site was in a relatively dry condition during collection of these samples, and the ground water level was about 1 m below ground.

Xylidine was detected at 34 ppm at location G-2, situated in the drainage ditch behind


EASTING
−30
−20
0
20
40
60
80
100
120
140
160
180
NORTHING
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
−20
−40
N
BH-7 (0ppm)
FORMER MISSLE STORAGE AREA
G-5 (135ppm)
BH-8 (0ppm)
BH-3 (1-2ppm)
MW-5
MW-2 (0ppm)
G-4 (0ppm)
BH-4 (6596ppm)
BH-9 (0ppm)
G-7 (0ppm)
G-6 (0ppm)
MW-3 (0ppm)
DITCH
(510ppm)
(670ppm)
(1662ppm)
(6601ppm)
ASPHALT SURFACE SCRAPINGS
(807ppm)
(367ppm)
VALVE CHAMBER
BERM
G-3 (0ppm)
(7942ppm)
(2000ppm)
G-8 (0ppm)
BH-10
MW-1
0.15m-(10289ppm)
0.30m-(16520ppm)
0.45m-(11688ppm)
0.60m-(4136ppm)
D1
XYLIDINE LOADING AREA
BERM
MW-4 (0ppm)
MW-6 (0ppm)
G-1 (0ppm)
G-2 (34ppm)
FORMER SHOWER FACILITIES
BH-6 (0ppm)
(0ppm)
BH-5
POND
BERM
RED FUMING NITRIC ACID LOADING AREA
BERM
MW-7
(0ppm XYLIDINE)
(19.9ppm NITRATE)
(12.4ppm NITRATE)
Legend:
BH-1 BOREHOLE LOCATION AND DESIGNATION
MW-2 MONITORING WELL LOCATION AND DESIGNATION
× ASPHALT SAMPLE LOCATION
D1 DRY WELL
G-8 SURFACE SAMPLE
AREA OF XYLIDINE CONTAMINATION
AREA OF RED FUMING NITRIC ACID CONTAMINATION
15m 0 30m 60m
Scales
Designed By:
Drawn By: J.M.C.
Checked By:
Approved By: M.A.S
Date issued: APRIL 1994
Project No. 94-457
Site Name:
File Name: 94457F06.DWG
Environmental Centre of Excellence Project
Siol Chemistry Results for Barta, Latvia
Gartner Lee
Figure No.
4

a former storage shed. This was to be expected since the original spill is believed to have occurred in the paved area and drained to the surrounding drainage ditches. Location G-5 is located in a low lying area to the north of the former fuel loading area, and xylidine was detected there at a concentration of 135 ppm. This, however, appears to be anomalous as no xylidine was detected in the soils at location MW-5 situated south of G-5 in the same low lying area. No xylidine was detected west of the north-south road, again indicating that the road is a temporary barrier for xylidine migration.

Asphalt scrapings were collected from the stained area to the east of the dry well (D1). The samples were impacted with xylidine at concentrations levels of 367 and 807 ppm.

RFNA Impacts

Soil samples at MW-7 and MW-8 were analyzed for the presence of nitrate, as part of the assessment for the effects of the RFNA spill. These samples were analysed by a member of the team at the Water Treatment Laboratory in Liepaja or at EED's laboratory.

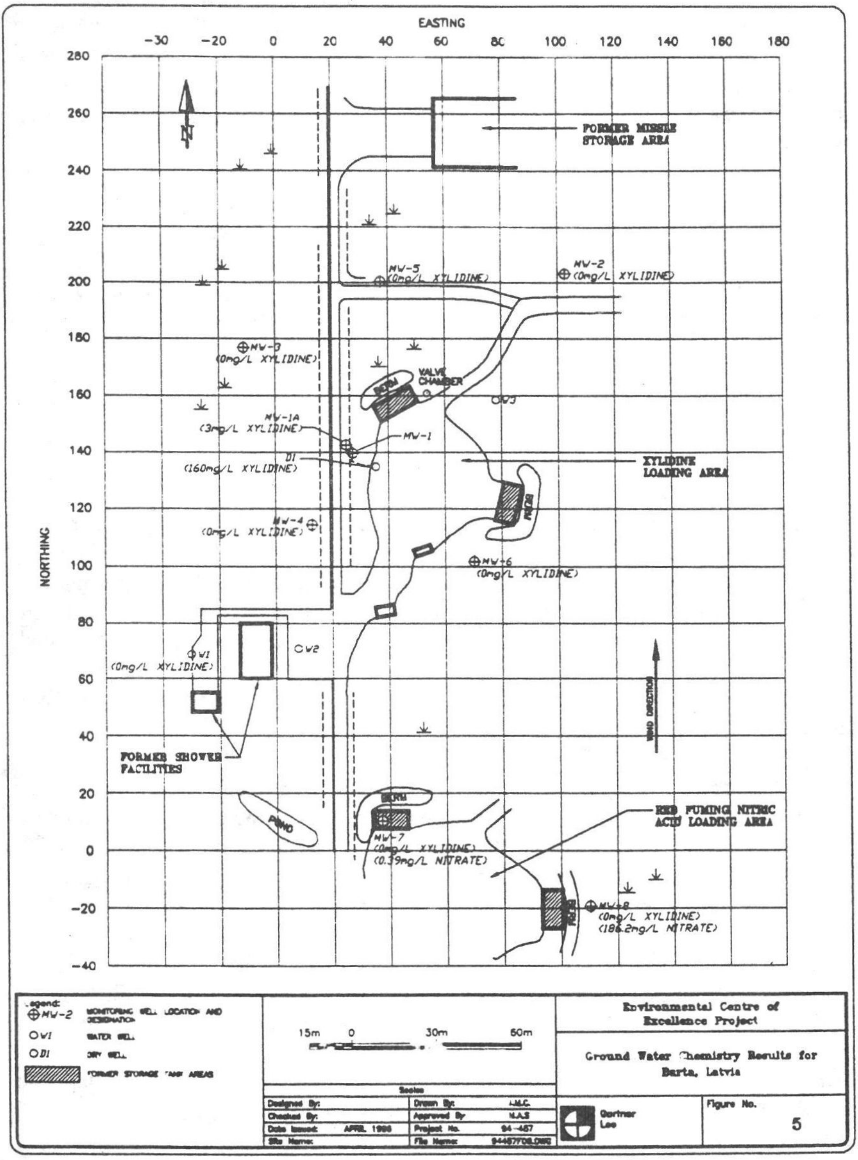
Nitrate concentrations of 19.9 and 12.4 ppm were found in the soils at location MW-8. Field pH of these soil samples, as measured at the time of sampling, varied between approximately 3 to 5.

Ground Water Quality

Laboratory analyses of ground water samples collected at Barta are tabulated and presented in Appendix C. The results are plotted on Figure 5.

Xylidine Impacts

Ground water impacts from xylidine appear to be confined to the source of the spill. Approximately 0.5 m of free phase xylidine was found in monitoring well MW-1. Xylidine has a specific gravity of 0.97 and, as such, remains just above the water table with some mixing of the natural ground water. It is noted that this monitoring well did not intercept the water table; therefore, monitoring well MW-1A was installed roughly 0.9 m west of MW-1. A xylidine concentration of 3 mg/L was detected in monitoring well MW-1A, and no free phase product was found at this location. The apparent discrepancy of these data have not yet been resolved. However, one possible cause is related to the materials that these wells are installed in. MW-1A was installed closer to the reinforced concrete road, and within fill materials that appeared to be densely compacted for the road construction. It is possible that the xylidine product may appear in this monitor within time; however, there was no mobilization of this product during the relatively short time frame of the August, 1995 site assessment.


EASTING
-30
-20
0
20
40
60
80
100
120
140
160
180
NORTHING
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20
-40
N
FORMER MISSILE STORAGE AREA
MW-5 (0mg/L XYLIDINE)
MW-2 (0mg/L XYLIDINE)
MW-3 (0mg/L XYLIDINE)
BERM
VALVE CHAMBER
W3
MW-1A (3mg/L XYLIDINE)
MW-1
D1 (160mg/L XYLIDINE)
XYLIDINE LOADING AREA
BERM
MW-4 (0mg/L XYLIDINE)
MW-6 (0mg/L XYLIDINE)
W1 (0mg/L XYLIDINE)
W2
WIND DIRECTION
FORMER SHOWER FACILITIES
POND
BERM
MW-7 (0mg/L XYLIDINE) (0.39mg/L NITRATE)
RED FUMING NITRIC ACID LOADING AREA
BERM
MW-8 (0mg/L XYLIDINE) (186.2mg/L NITRATE)
Legend:
MW-2 MONITORING WELL LOCATION AND DESIGNATION
W1 WATER WELL
D1 DRY WELL
FORMER STORAGE TANK AREAS
15m
0
30m
60m
Scales
Designed By:
Checked By:
Date Issued: APRIL 1996
Site Name:
Drawn By: J.M.C.
Approved By: N.A.S.
Project No. 94-457
File Name: 94457F05.DWG
Environmental Centre of Excellence Project
Ground Water Chemistry Results for Barta, Latvia
Gartner Lee
Figure No.
5

At the cross-gradient location MW-5 to the north of the loading area, only trace amounts of xylidine were present in the ground water at concentrations of 1 to 2 mg/L. The presence of contaminants at this location may be due to the flooding that occurs during rain events. Xylidine is only very slightly soluble in water and as such we anticipate limited movement in the ground water. However, at this site, due to flooding and mounding during rain events, the xylidine product is mobile. Flow is then influenced by the culverts that are set under the roadways, MW-5 is located north of one of the culverts. Xylidine was not detected at any of the other monitoring well locations.

During a rain event, it was noticed that the ground water rises to about surface level, creating flooding in the paved loading area. The dry well crib was partially full of water (ground water, rain water and xylidine residue). Water samples were collected from the dry well during the rain event and analyzed for xylidine. It was found that the water was impacted with xylidine at a concentration of 160 mg/L.

A surface water sample was collected from the small pond west of the RFNA area. Xylidine was not detected.

RFNA Impacts

The RFNA spill is believed to have occurred in the vicinity of MW-8, but it appears that the extent of the spill was small since only a small area of trees and vegetation appear to have been destroyed. It is unknown, however, whether any significant regrowth has occurred in this area. Ground water samples in this area were analyzed for nitrate as a general indicator for the presence of RFNA. Nitrate levels were found to be 186.2 mg/L at monitoring well location MW-8, with a corresponding pH value of 3. By comparison, Ontario's Drinking Water Objective for nitrate is 10 mg/L with a recommended pH range between 6-8.

MW-7 is located downgradient of the RFNA spill area, within a second former acid storage tank area. MW7 is slightly impacted from the nitric acid spill having a nitrate concentration of 0.39 mg/L and a pH value of 5.5. This may change as the slug of nitrate contamination flows from location MW-8 towards MW-7. It is also possible that the nitrate concentrations may be naturally attenuated prior to reaching MW-7.

The other ground water monitors (MW-1 to MW-6) are downgradient or cross gradient of the nitric acid spill and do not appear to be impacted from the RFNA. There were also no impacts from the xylidine spill in the nitric acid loading area. It is noted, however, that since the focus of the assessment was the xylidine spill the RFNA spill area was not addressed in detail. For example, no wells were installed to permit determination of a background nitrate level in ground water.

A surface water sample was collected from the small pond west of the RFNA area. Nitrate was not elevated, and the pond water had a neutral field pH.

SUMMARY OF BARTA

The results of the Barta ESA can be summarized as follows:

- relatively pure xylidine liquid exists as a 0.5 m thick layer floating on the shallow ground water table over an area of at least 15 m by 5 m;
- xylidine concentrations of up to about 20,602 ppm (2%) have been found in shallow soils;
- dissolved xylidine concentrations of up to about 160 ppm have been found in the ground water; and
- nitric acid spill was confined to a relatively small area and has likely self-remediated to a large degree.

SUMMARY OF TASI

During a site visit in October 1993, members of the team were informed of a RFNA spill that had occurred at a former oxidant loading point in Tasi which assisted in planning and focusing the activities for the preliminary environmental site assessment at Tasi.

Figure 6 shows the infrastructure (e.g., gravel pads, swamps) as well as the location and designation of boreholes, monitoring wells, water wells and surface soil sampling at Tasi. A total of three ground water monitors were installed and sixteen soil samples were taken to characterize the site during the period from August 24-28, 1995.

Table 1 shows the record and analysis of surface and subsurface soil samples. The CCME agriculture remediation criteria along with method detection limits are also noted on this table. The PID readings ranged from not detectable to 3.7 ppm; the concentration of xylidine was below the method detection limit of 1 ppm; and the concentration of nitrate in two surface samples were 80.1 ppm (S2) and 86.1 ppm (S3).

Table 2 shows the record and analysis of ground water and surface water samples. The CCME and Ontario drinking water criteria along with method detection limits are also noted on this table. The pH of the water samples ranged from 5.5 (Swamp #2) to 7.18 (BH3); the concentration of xylidine was below the method detection limit of 1 ppm; and the concentration of nitrate was below CCME and Ontario drinking water criteria.

The results of the Tasi ESA indicate that significant quantities of nitric acid were spilled although the extent of the spill is not yet known.

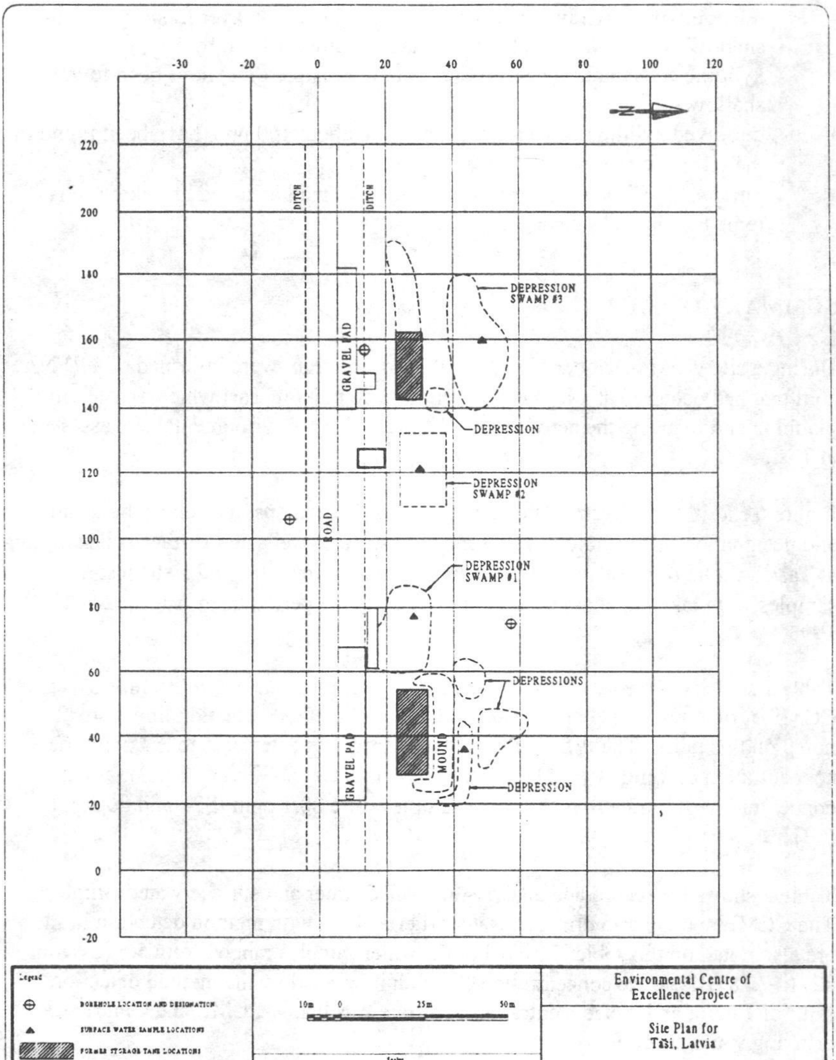

-30
-20
0
20
40
60
80
100
120
N
220
200
180
160
140
120
100
80
60
40
20
0
-20
DITCH
DITCH
ROAD
GRAVEL PAD
GRAVEL PAD
MOUND
DEPRESSION SWAMP #3
DEPRESSION
DEPRESSION SWAMP #2
DEPRESSION SWAMP #1
DEPRESSIONS
DEPRESSION
Legend
BOREHOLE LOCATION AND DESIGNATION
SURFACE WATER SAMPLE LOCATIONS
FORMER STORAGE TANK LOCATIONS
10m
0
25m
50m
Scales
Designed By
Checked By
Date Issued
APRIL 1994
Drawn By
J.M.C
Approved By
M.A.S
Project No
94-437
File Name
94437F04.DWG
Environmental Centre of Excellence Project
Site Plan for Tāši, Latvia
Gartner Lee
Figure No
6

TABLE 1. SOIL ANALYSIS AT TASI

Sampling location	Sample number	Sampling date	Depth (m)	PID (ppm)	xylidine (ppm)	pH	nitrate (mg/L)
CCME agriculture remediation criteria					n/a	6 to 8	n/a
Method detection limit (MDL)					1	0.1	
BH1	BH1-1	24-08-95	0-0.15		<MDL	6.57	
	BH1-2	24-08-95	0.60-0.80		<MDL	6.9	
	BH1-3	24-08-95	1.20-1.40		12	7.16	
	BH1-4	24-08-95	1.80-2.00		<MDL	7.33	
	BH1-5	24-08-95	2.55-2.75		<MDL		
	BH1-6	24-08-95	2.90-3.10		<MDL		
BH2	BH2-1	24-08-95	0.15-0.35	3.7	<MDL		
	BH2-2	24-08-95	0.60-0.80	ND	<MDL		
	BH2-3	24-08-95	1.20-1.40	ND	<MDL		
	BH2-4	24-08-95	1.90-2.00	ND	<MDL		
BH3	BH3-1	24-08-95	0-0.15	2.3	<MDL		
	BH3-2	24-08-95	0.91-1.06	2.1	<MDL		
	BH3-3	24-08-95	1.80-2.00	ND	<MDL		
TS1	S1	24-08-95	0-0.15		<MDL		
TS2	S2	24-08-95	0-0.15		<MDL		80.1
TS3	S3	24-08-95	0-0.15		<MDL		86.1

TABLE 2. WATER ANALYSIS AT TASI

Sampling location	Sampling date	Temperature (oC)	pH	Conductivity (uS)	xylidine (ppm)	nitrate (mg/L)
CCME drinking water criteria			6.5 to 8.5		n/a	45
Ontario drinking water criteria			6.5 to 8.5			10
Method detection limit (MDL)			0.1		1	
BH1	28-08-95	14.4	7.17	487	<MDL	
BH2	28-08-95	13.0	7.16	800	<MDL	
BH3	28-08-95	13.2	7.18	792	<MDL	
Swamp #1 (S1)			6.00		<MDL	0.13
Swamp #2 (S2)			5.50		<MDL	0.16
Swamp #3 (S3)			6.00		<MDL	0.19
Ditch-1					<MDL	0.22

CONCLUSIONS

The objectives of the environmental assessment demonstration were achieved as :

- The team became acquainted with the history, layout and environmental conditions of former Soviet Air Defence missile bases. The results confirmed the presence of severe environmental problems related to "SAMIN" missile fuel and/or MELANGE oxidant at Barta and Tasi.
- The Latvian team members had an opportunity to obtain hands-on assessment training and experience. They have become very proficient in recognizing and addressing health and safety issues; and surface and subsurface soil and water sampling and analysis. They are capable of continuing this work and transferring their newly acquired knowledge to others.
- The team became familiar with the current infrastructure and resources (e.g., sand, piping) in Latvia for undertaking environmental assessment and remediation activities.
- The Environmental Centre of Excellence is being established at the Chemical Technology Faculty of Riga Technical University in Latvia and will provide an excellent mechanism for continuing site assessment and remediation training.

RECOMMENDATIONS

The remediation of the xylidine contamination in the low-lying swampy area should be commenced as soon as possible to avoid its further migration. An evaluation of potential technologies for remediating xylidine and nitric acid contamination should be studied and implemented.

REFERENCES

Canadian Council of Ministers of the Environment, "Interim Canadian Environmental Quality Criteria for Contaminated Sites, Report CCME EPC-CS34, September 1991.

Emergencies Engineering Division, "Management Plan for the Latvian Centre of Excellence Project, Ottawa, Ontario, July 1995.

Gartner Lee Limited, Remedial Strategy and Health and Safety Plan for Xylidine Spill at Barta, Latvia (draft), prepared for Emergencies Engineering Division and Riga Technical University, Markham, Ontario, April 1996.

Ontario Ministry of Environment, "Ontario's Drinking Water Objectives", Summer 1992.

Sax, N.I. and R.J. Lewis, Jr., "Hawley's Condensed Chemical Dictionary", Eleventh

Edition, Van Reinhold Company, New York, USA, 1987.

ACKNOWLEDGEMENTS

The authors would like to thank Andrew Somers, Marina Vorobeca, Gunta Schneider for their field support; Shamil Cathum and Dario Velicogna for ongoing analytical support; and Sarma Valtere for logistics and coordination efforts.

APPENDIX A SUBSURFACE SOIL SAMPLE ANALYSIS AT BARTA

Sampling location	Sample number	Sampling date	Depth (m)	PID (ppm)	xylidine (ppm)	pH	nitrate
CCME agriculture remediation criteria					n/a	6 to 8	n/a
Method detection limit (MDL)					1	0.1	
MW1	S-1	17-08-95	0-0.15	0.2	10269		
	S-2	17-08-95	0.15-0.30		11886		
	S-3	17-08-95	0.30-0.45	2000	16520		
	S-4	17-08-95	0.45-0.60		11698		
	MW1-4	19-08-95			735.6		
	MW1-5	19-08-95			4138		
	MW1-5d	19-08-95			4098		
MW1A	S-5	19-08-95	0.75-0.90				
MW2	MW2-1	18-08-95	0-0.15	10	<MDL		
	MW2-2	18-08-95	0.20-0.50	4	<MDL		
	MW2-3	18-08-95	0.60-0.75	0.3	<MDL		
	MW2-4	18-08-95	0.90-1.15	9	<MDL		
	MW2-5	18-08-95	1.21-1.36	5	<MDL		
	MW2-6	18-05-95	1.52-1.61	2.3	<MDL		
	MW2-7	18-08-95	1.80-1.95	1.5	<MDL		
MW3	MW3-1	18-08-95	0-0.15	1.5	<MDL		
	MW3-2	18-08-95	0.30-0.50	0.3	<MDL		
	MW3-3	18-08-95	0.60-0.75	0.7	<MDL		
	MW3-4	18-08-95	0.90-1.06	2.5	<MDL		
	MW3-5	18-08-95	1.21-1.36	2.4	<MDL		
	MW3-6	18-08-95	1.52-1.67	0.6	<MDL		
	MW3-7	18-08-95	1.80-2.00	0.2	<MDL		
MW4	MW4-1	18-08-95	0-0.15	7.5	<MDL		
	MW4-2	18-08-95	0.60-0.75	4.5	<MDL		
	MW4-3	18-08-95	0.90-1.05	8.2	<MDL		
	MW4-4	18-08-95	1.20-1.35	2.1	<MDL		
	MW4-5	18-08-95	1.95-2.05	1.2	<MDL		
MW5	MW5-1	19-08-95	0-0.15	1.5	1		
	MW5-2	19-08-95	0.60-0.75	1	2		
	MW5-3	19-08-95	0.91-1.06	19.1	<MDL		
	MW5-4	19-08-95	1.21-1.36	4.9	<MDL		
	MW5-5	19-08-95	1.80-1.95	ND	<MDL		
MW6	MW6-1	21-08-95	0.15-0.30	ND	<MDL		
	MW6-2	21-08-95	0.60-0.75	ND	<MDL		
	MW6-3	21-08-95	1.20-1.35	ND	<MDL		
	MW6-4	21-08-95	1.80-1.95	ND	<MDL		
MW7	MW7-1	21-08-95	0.90-1.05	ND	<MDL		2.7
	MW7-2	21-08-95	1.20-1.40	ND	<MDL		
MW8	MW8-1	21-08-95	0.90-1.10	ND	<MDL	4.0	19.9
	MW8-2	21-08-95	1.20-1.40	ND	<MDL	3.5	12.4

APPENDIX B. SURFACE SOIL ANALYSIS AT BARTA

Sampling location	Sample number	Sampling date	Depth (m)	PID (ppm)	xylidine (ppm)	pH	nitrate
CCME agriculture remediation criteria					n/a	6 to 8	n/a
Method detection limit (MDL)					1		
BH1	BH1	17-08-95	0-0.15		20602		
BH3	BH3	17-08-95	0-0.15		<MDL		
BH4	BH4	17-08-95	0-0.15		6596		
BH5	BH5	17-08-95	0-0.15		<MDL		
BH6	BH6	17-08-95	0-0.15		<MDL		
BH7	BH7	17-08-95	0-0.15		<MDL		
BH8	BH8	17-08-95	0-0.15		<MDL		
BH9	BH9	17-08-95	0-0.15		<MDL		
BH10	BH10	17-08-95	0-0.15		<MDL		
Asphalt Surface Scrapings	PL1-1	19-08-95			807		
	PL1-2	19-08-95			367		
SD1-1	SD1-1	19-08-95	0-0.15		4392		
SD1-2	SD1-2	19-08-95	0.25-0.30		7542		
G1	G1-1	21-08-95	0.91-1.05		<MDL		
G1	G1-2	21-08-95	1.12-1.27		<MDL		
G2	G2-1	21-08-95	0.91-1.06		34		
G3	G3-1	21-08-95	0.91-1.06		<MDL		
G4	G4-1	21-08-95	0.60-0.80		<MDL		
G5	G5-1	21-08-95	0.50-0.70		135		
G6	G6-1	21-08-95	0.68-0.83		<MDL		
G7	G7-1	21-08-95	0.90-1.05		<MDL		
G8	G8-1	21-08-95	0.90-1.05		<MDL		
Ditch	1	29-08-95			6631		
	2	29-08-95			1662		
	3	29-08-95			671		
	4	29-08-95	0.30-0.60		510		

APPENDIX C. GROUNDWATER ANALYSIS AT BARTA

Sampling location	Sampling date	Temperature (oC)	pH	Conductivity (uS)	xylidine (ppm)	nitrate (mg/L)
CCME drinking water criteria			6.5 to 8.5		n/a	45
Ontario drinking water criteria			6.5 to 8.5			10
Method detection limit (MDL)			0.1	1	1	
MW1			5.0		3	
MW1A	22-08-95					
MW2	19-08-95		7.4	635	<MDL	
MW3	18-08-95		7.3	540	<MDL	
MW4	22-08-95	20.5	7.3	910	<MDL	
MW5	22-08-95	15.5	7.2	594	<MDL	
MW6	22-08-95	12.2	6.4	238	<MDL	
MW7	22-08-95	14.0	7.0	377	<MDL	0.39
MW8	22-08-95	18.0	3.4	>2000	<MDL	186.2
D1					160	