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THE EFFECT OF SALT TYPE AND CONCENTRATION ON LEAD REMOVAL FROM SOIL USING EDTA

by

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ABSTRACT

The removal of lead from highly contaminated soil from a smelting operation site was studied. Two salts, one monovalent (NaCl) and one divalent ($MgCl_2$), were used in experiments to determine their effect on lead removal from soil fines using the chelating agent EDTA. Tests were first conducted to determine the best pH for the experiments. Using aqueous HCl solutions in both the presence and absence of EDTA at pH levels of 1 to 5, pH 2 was found to provide the most promising results. In the absence of EDTA in solution, tests revealed that salt additions of 0.1, 0.5 and 1.0 N (equivalents based on ionic charge) of either NaCl or $MgCl_2$ at pH 2 decreased the removal of lead from soil but the decrease was more pronounced with $MgCl_2$. With EDTA in solution it was found that, at pH 2, NaCl at high concentrations increased the recovery of lead, while $MgCl_2$ at high concentrations decreased lead removal.

INTRODUCTION

Past research involving the remediation of heavy metal contaminated soils has focused on stabilizing the contaminants within the soil or removing them, for example, through soil washing processes [Lorusso, 1992]. Increasing emphasis has been placed upon soil washing procedures due to the reusability of the soil after treatment and the potential recovery and recycling of the contaminants from the soil washing solution.

The soil used in this study was sampled from Longue Pointe Garrison, a 1.2 km^2 industrial site located in east Montreal, leased out by the Department of National Defense to private smelter operators in the 1960's and 1970's. The smelting operations, which involved the manual recovery of lead electrodes from spent lead acid batteries and the smelting of these electrodes, resulted in the contamination of approximately 50 000 m^3 of soil with scattered lead casings and lead dust deposits from the smelter smoke stack. The contamination ranges from 1 to 12% lead by weight of soil [Garand and Normand, 1994]. The average contamination of the soil fines used for this study was 89 000 ppm or 8.9% lead. Twenty-five percent of the total lead was contained in the soil fines.

EDTA is commonly used to remediate lead contaminated soils due to the strength of the EDTA-Pb complex. Removal of lead by EDTA has shown to be highly dependent upon pH [Tuin and Tels, 1990, Farrah and Pickering, 1978] and less dependent on the concentration of EDTA in solution [Yu and Klarup, 1994]. Inorganic substances such as salts have been investigated due to their ability to promote ion exchange [Brown and Elliot, 1992]. EDTA, pH, salt type and concentration are the four test parameters of importance in this study.

EXPERIMENTAL PROCEDURES

Preparation of Soil Fines

The soil was initially left to air dry, sieved down to 104 µm and put through a mixing and splitting procedure to increase the homogeneity of the soil fines. The procedure involved pouring the soil fines through a splitter, mixing the two piles formed and re-splitting them. After mixing, the soil was split repeatedly until the resultant piles were approximately 30 g in weight. These 30 g piles represented the individual soil samples used in the soil washing tests.

Soil Washing Tests

The solution to soil ratio for the tests was 30:1. A 1:1 ratio EDTA:Pb was used and the pH was adjusted using a dilute solution of HCl. Salt concentrations used were 0.1, 0.5 and 1.0 N with the equivalents based upon ionic charge. For each of the tests, 10 g of soil was weighed into 600 mL beakers and 300 mL of the appropriate soil washing solution was added. The sample was then placed under a multiple stirrer which was maintained at a speed of approximately 200 rpm. A sample run time of two hours was used, with 10 mL samples of the solution/soil slurry taken at 15, 30, 60, 90 and 120 minutes using large 20 cc syringes. The samples were centrifuged and the supernatants separated. The supernatants were drawn off, diluted and analyzed by atomic absorption spectrophotometry (AAS).

Initial Lead Level in the Soil

The measure of lead removal from soil using a particular soil washing solution was based upon the lead levels found in the supernatants compared to the initial levels of lead in the soil. Initial lead levels were determined using a standard aqua regia digestion procedure.

Prior to digestion, a sample of the soil used in the soil washing tests was placed in a muffle furnace for four hours at 600°C to eliminate organic matter. After cooling, 0.1 g of soil was weighed into digestion tubes and 6 mL of aqua regia (4.5 mL of HCl, 1.5 mL HNO_3) was added. The mixtures were gently refluxed over low heat for approximately 2 hours. Once nearly all the acid had evaporated, 1 mL of deionized water and 1 mL of HNO_3 were added and the mixture was reheated for approximately half an hour. After cooling, deionized water was added to bring the sample up to 25 mL, then the samples were vortexed and left to settle overnight. The samples were then diluted and analyzed by AAS.

MINERALOGICAL STUDY

Samples of the Longue Pointe Garrison soils were sent to Canada Centre for Mineral and Energy Technology (CANMET) for a mineralogical study in order to determine the speciation of the lead compounds in the soil. The results were as follows [Laflamme, 1994]:

- approximately 66 % of the lead existed as cerussite or $PbCO_3$ and 60% of the $PbCO_3$ existed as liberated particles,
- the balance of lead consisted of Pb oxide(s), metallic Pb and angelsite ($PbSO_4$) found in approximately equal proportions,
- lead-bearing iron oxide is a lead carrier of some importance due to its ability to carry up to 19% wt Pb, and
- Pb was also found in low concentrations in carbonaceous matter.

RESULTS AND DISCUSSION

pH Tests

Figures 1 and 2 show the results of aqueous HCl tests at pH levels of 1 to 5 with and without EDTA in solution. In the absence of EDTA in solution, lead recovery was higher at low pH levels. This could be attributable to dissolution of contaminants such as lead carbonate and lead oxide by the acid and thus the liberation of Pb ions to solution [Tuin and Tels, 1990]. Competition for soil binding sites by the higher concentration of H^+ ions at low pH levels may have also contributed to the liberation of lead.

With EDTA in solution (Figure 2), lead recoveries were increased at all pH levels but the effect of EDTA was more significant at high pH levels, such as pH 5. This is due to the larger concentration of deprotonated EDTA at higher pH levels available to complex with lead. Also, evidence exists that EDTA helps to dissolve oxide layers which may have further contributed to the solubilization of lead ions [Yu and Klarup, 1994].

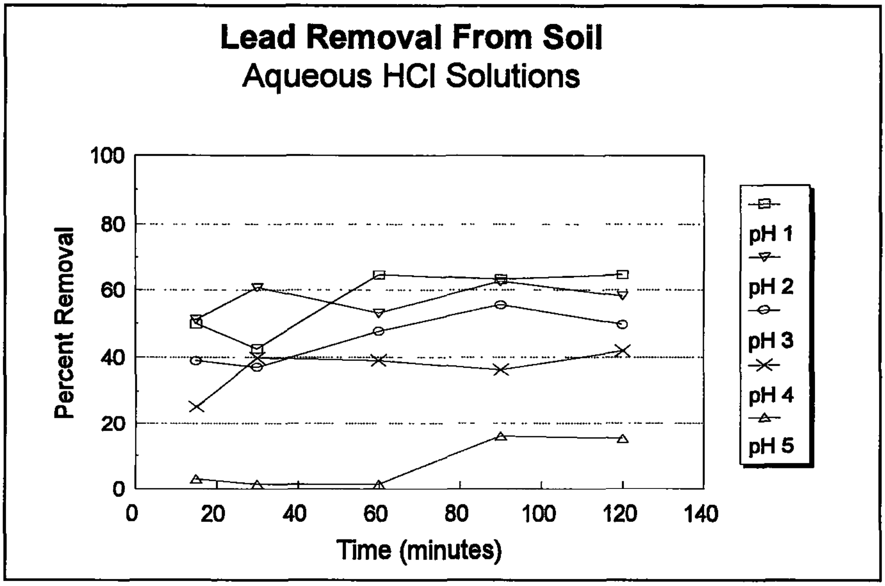

Figure 1

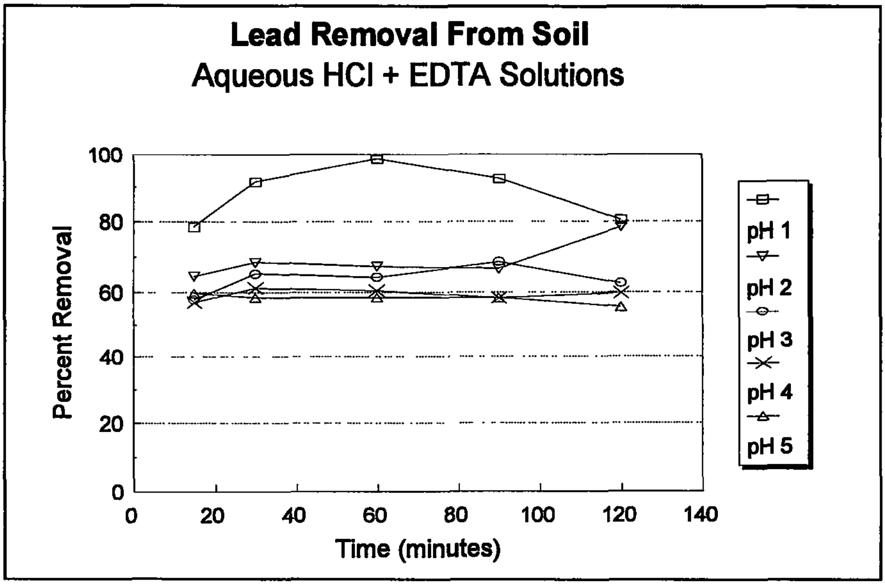

Figure 2

Based on the pH test results, the best pH level was chosen for the remaining tests. Lead removal was highest at pH 1, however pH 2 was chosen due to the risk of precipitation of EDTA at the lower pH. Also, in terms of percent removal of lead there was a larger window available to see the effect of the salt additions to the EDTA solutions at pH 2.

Salt Tests

Figures 3 and 4 show the results of additions of NaCl and $MgCl_2$ in concentrations of 0.1, 0.5 and 1.0 N to aqueous HCl solutions at pH 2. Because the concentrations are based upon ionic strength, twice as much NaCl on a molar basis was used in comparison with $MgCl_2$. Both figures show that the salts at all concentrations decrease lead removal. The decrease may be due to lead's higher affinity for the contaminant compounds such as carbonate in comparison with Pb chloride which may be formed. The solubility products of these compounds supports this suggestion as Ksp ($PbCl_2$) = 1.17×10^{-5} and Ksp ($PbCO_3$) = 1.46×10^{-13} [Lide, 1992]. Another reason may be activity coefficient effects. As the ionic strength of a solution is increased i.e. by the addition of salts to solution, the activity coefficient of Pb^{2+} is decreased. The activity coefficient is directly related to the concentration of free lead ions in solution and thus the Pb^{2+} concentration decreases [Skoog *et al.*, 1988].

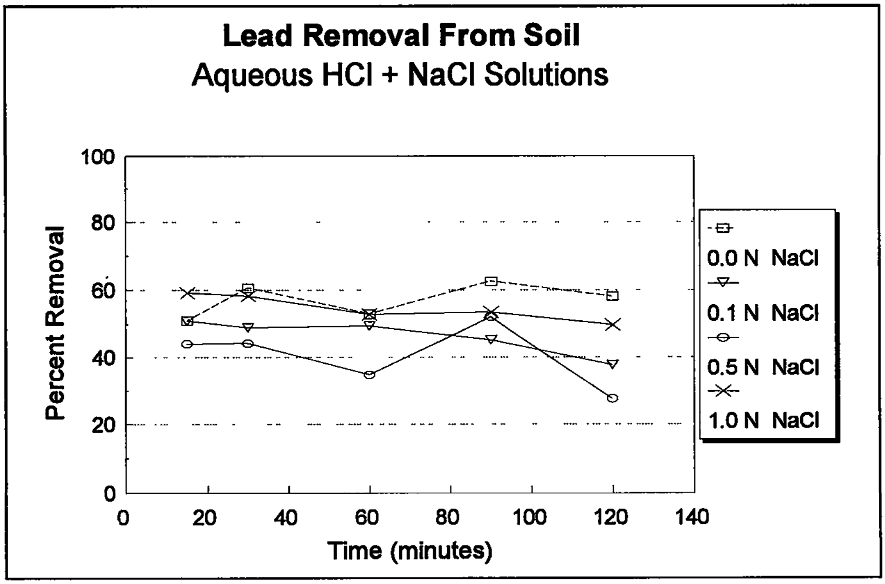

Figure 3

Based on Figures 3 and 4, sodium chloride has less of a negative effect on lead removal compared to magnesium chloride. This behaviour may be contributed to the mobilization of organic matter by NaCl [Amrheln *et al.*, 1992] while $MgCl_2$ has shown not to contribute to the mobilization of organic matter [Tessier *et al.*, 1979]. The organic matter content in the soil was found to be significant based upon the weight loss of samples placed in the muffle furnace. The weight loss was found to be 20% organic matter and moisture by weight of soil. Organic matter was found to greatly increase the strength of lead bound to soils [Sheppard and Thibault, 1992] thus its mobilization helps to liberate the lead.

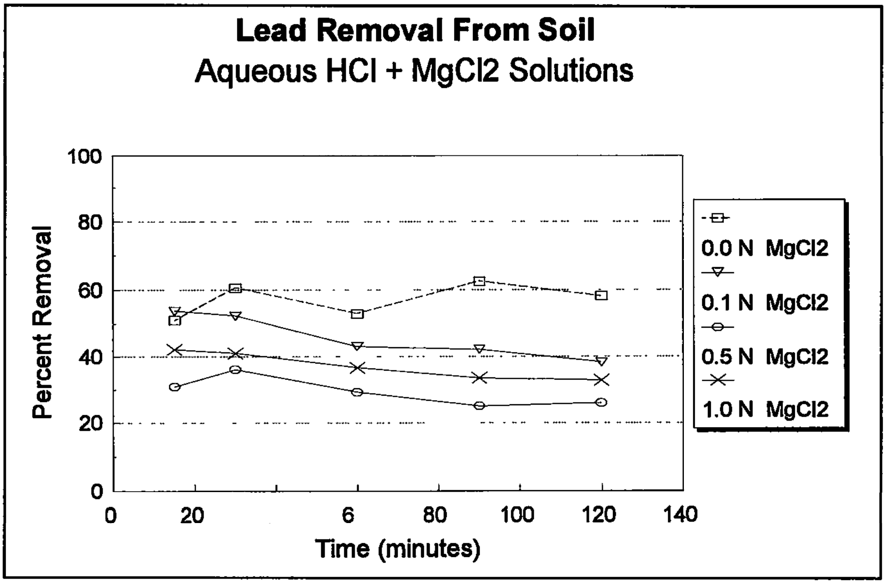

Figure 4

Evidence exists that divalent ions have a higher affinity for soil binding sites compared to monovalent ions but evidence also exists that as the ionic strength of a solution increases, the ratio of divalent to monovalent ions on binding sites decreases [Brown and Elliot, 1992]. Since twice as many monovalent ions are present in the sodium chloride solution compared to the divalent ions in the magnesium chloride solution, we see less of a negative affect on lead removal with NaCl.

Salt Tests with EDTA at pH 2

Figures 5 and 6 show the results of NaCl and $MgCl_2$ additions to EDTA at pH 2. It was found that at high concentrations, sodium ions enhance lead recovery while at high concentrations, magnesium ions decrease lead recovery. This effect may be explained by the higher competition of magnesium for EDTA. Sodium ions are not strong competitors for EDTA thus they increase recovery by competing for binding sites or increasing the mobility of organic matter.

Calculations were carried out to determine the extent of competition of Na^+ and Mg^{2+} for EDTA at pH 2. The following ratios resulted;

$$RATIO = \frac{[PbY^{2-}]}{[NaY^{3-}]} = \frac{5.01\times10^{13}}{[Na^{+}]} ,$$

$$RATIO = \frac{[PbY^{2-}]}{[MgY^{2-}]} = \frac{4.67\times10^{6}}{[Mg^{2+}]} .$$

These ratios illustrate the amount of deprotonated EDTA, $[Y^{4-}]$, bound to Pb^{2+} over the amount of EDTA bound to Na^+, $[NaY^{3-}]$ or Mg^{2+}, $[MgY^{2-}]$ as a function of the concentration of free competing alkali metal in solution. The ratios show that the amount of lead bound to EDTA will be higher for both cases but magnesium's affinity for EDTA is approximately 7 orders of magnitude higher than that of sodium. Thus, the competition of magnesium for EDTA may decrease lead removal by EDTA as seen in Figure 6.

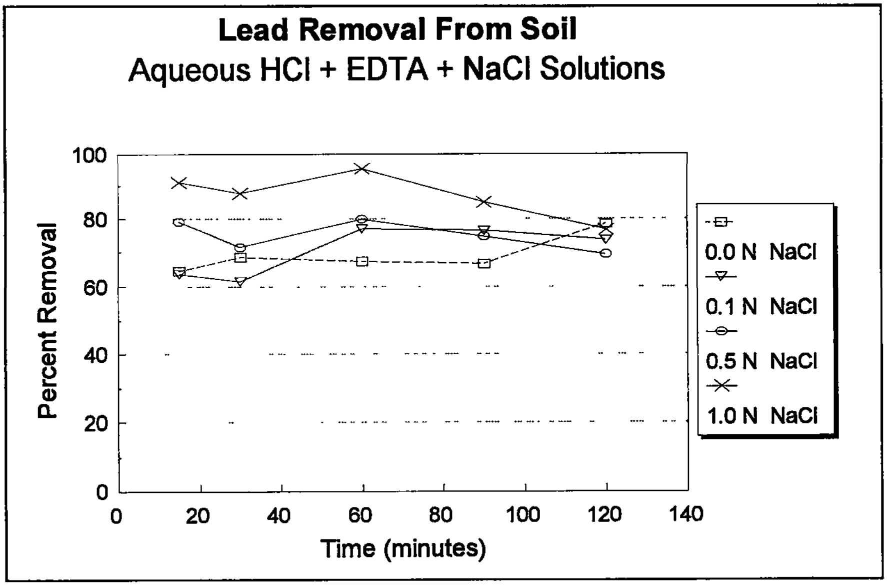

Figure 5

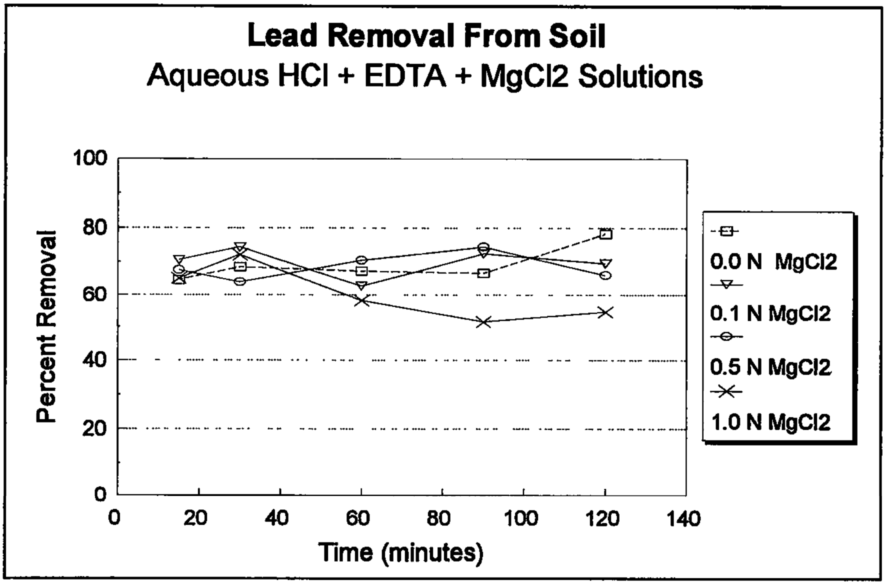

Figure 6

CONCLUSIONS

Based on the results of the tests involving the test parameter pH, it was found that low pH levels increased the removal of lead, as documented in numerous other studies. With the addition of EDTA to solution, low pH levels remained the most effective but EDTA greatly increased lead removal at high pH levels. This was due to the larger concentration of deprotonated EDTA in solution at higher pH levels.

The salt tests without EDTA showed that salt additions at pH 2 at any concentration decreased lead removal but the decrease was more pronounced with the divalent ion magnesium.

The salt and EDTA tests at pH 2 showed that at high concentrations, sodium enhances the recovery of lead while magnesium decreases recovery. The decrease may be contributed to magnesium's higher affinity for EDTA compared to sodium.

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COMPARISON OF TWO MEMBRANE PROCESSES FOR TOXIC METAL REMOVAL

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ABSTRACT

Two membrane processes using the principle of ion exchange to remove toxic metals such as arsenic from contaminated water were investigated. The first system involved the recirculation of a polymer solution in a closed loop containing a plate and frame membrane module, while the second system consisted of a magnetically stirred batch-test cell containing a polymeric solution. The results indicate that the first system involving the plate and frame module is more promising for industrial applications reaching 96% and <99.9% retention using 1,000 ppm PEI. In the second system, arsenic retentions of 57%, 87%, 88% and 92% were achieved using PEI concentrations of 1,000 ppm, 5,000 ppm, 5,000 and 10,000 ppm respectively. The data collected showed that concentration polarization occurs at the surface of the membrane in the recirculation system, significantly increasing the retention of toxic metals with time.

INTRODUCTION

The disposal of arsenic and chromium wastewater solutions are common industrial problems. A literature review found many proposed methods of treatment, illlustrating the magnitude of these toxic metal waste problems. However, none of these arsenic removal techniques allow the discharge limit of 25 ppb set by the Canadian government to be reached [Canadian Council of Ministers of the Environment, 1992]. Additional methods have shown some promise in resolving the waste water situation. It was stipulated that the combined method using a binding agent and membrane process was efficient in treating heavy metals from aqueous solutions [Japan patent, 1977]. Various efficiency were achieved using this technique. The results from previous research has demonstrated that the removal of arsenic from contaminated groundwater is affected by various factors such as the salinity, the initial arsenic concentration, the pH of the solution, as well as the type of polymer and the concentration of polymer used [Legault et al, 1993]. In later studies, it was demonstrated that the retention of arsenic was directly proportional to the polymer concentration. Therefore, the rejection of the contaminant can be increased by varying the initial polymeric concentration when poly(ethylenimine) was used [Legault and Tremblay, 1994]. Based on these results, two new processes were developed involving ion exchange principle. In both cases, a water soluble polymer was used as a binding agent. The first system involved the recirculation of a polymer solution in a closed loop containing a plate and frame membrane module, while the second consisted of a magnetically stirred batch-test cell containing the polymeric solution.

ANALYSIS FOR ARSENIC AND CHROMIUM SOLUTIONS

The analysis of arsenic and chromium were achieved using an atomic absorption equipment, model 3100, manufactured by Perkin Elmer (Norwalk, U.S.A.). For the arsenic analysis, the equipment was combined with a mercury/hydride generator, model MHS-10 supplied by the same manufacturer. The detection limit of the analytical equipment was improved from 1 ppm to 1 ppb using the hydride generator. The generator reduces interference when analyzing arsenic which is a result of the wavelength used to detect arsenic being close to that of visible light. The atomic absorption system was used manually. The reagent used was 1.5 % HCl and the gas pressure used was 275 kPa (40 psi). An initial solution of 0.1 μg of As/ml was used to calibrate the equipment. For the chromium analysis, atomic absorption equipment without the mercury/hydride generator was used.

EXPERIMENTAL

Synthetic groundwater was produced for all the experiments by preparing solutions containing specific quantity of pentavalent arsenic solution (Na_2HAsO_4) or chromium trioxyde (CrO3). All the tests were performed at room temperature. Twenty minutes was allowed for the system to reach steady state, after which the permeate solution was remixed with the feed solution. An initial feed sample of 5 ml was taken after discarding the first 5 ml collected. For all trials, all samples were refrigerated until they were analyzed. Each test was performed using standard ultrafiltration equipment. Bioken polyethersulphone membranes with a molecular weight (M.W.) cut-off of 10,000 Daltons were employed for the arsenic trials while a Desal membrane having a M.W. cut-off of 1,000 Daltons was used for the chromium experiment. The retention of heavy metals on the high pressure side (feed) of the membrane (R_{As}) was used to characterize the efficiency of the metals removal [Volchek et al, 1992] using equation (1):

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

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

The first series of experiments involved a new system containing two initial solutions. The first solution referred to as feed #1 had 300 ml for the arsenic trials and 5 litres for the chromium one, and contained either 0.1 or 0.3 ppm of arsenic or 12 ppm of chromium, 1,000 ppm NaCl, and 1,000 ppm of polymer. The second solution referred to as feed #2 had 6 litres or 3.5 litres of synthetic water for the arsenic trials, and 8 litres of synthetic water for the chromium one. This solution was composed of a fixed concentration of contaminant, and 1,000 NaCl. The first solution was recirculated within the membrane system at a constant pressure of 275 kPa (40 psi). This first solution was added to the recirculation loop at a flowrate equal to the rate of collection of the permeate. That same system was also used to study chromium rejection. The first chromium solution contained 12 ppm, and 3,000 ppm of polymer. No salt was added to the solution due to the incompatibility with the membrane. The second chromium solution was made of 12 ppm of chromium and water only. All the runs were performed using poly(ethylenimine) (PEI) as the binding agent.

The second series of experiments used a magnetically stirred batch-cell containing the polymeric solution. This test system was composed with a standard Amicon stirred-cell (Bervely, U.S.A.) and a feed pump. The feed pump supplied synthetic groundwater to the stirred-cell. It was computer controlled to maintain a constant pressure in the stirred-cell. The total stirred-cell volume was 0.075 liters. Initially, the stirred-cell was loaded with a synthetic groundwater solution containing various concentrations of PEI. Two types of membranes were used, Bioken (Norwood, U.S.A.) polyethersulphone membranes with a molecular cut-off of 10,000 Daltons and Osmonics (Minnetonka, U.S.A) cellulose acetate membranes with 1,000-5,000 Daltons molecular weight cut-off. Samples of permeate were collected at regular intervals, refrigerated and then analyzed. Two solutions were used with this system. The first one of 75.34 ml composed of 0.3 ppm of arsenic, 1,000 ppm of salt and a fixed concentration of PEI either 1,000 ppm, 5,000 ppm or 10,000 ppm. The second solution of 4 litres contained 0.3 ppm of arsenic, and 1,000 ppm of salt. Two tests of two runs each have been performed. A total of 4 liters of water permeated through the stirred-cell. The pressure inside the cell was maintained at 275 kPa (40 psi). New membranes were used for all tests and two membrane types were studied. The agitation speed within the cell was maintained at 364 rpm.

No pH adjustments were made to any of the solutions, and the pH of the solution was approximately 6.5. The permeate and concentrate streams were sampled at a specific volume to encounter the change occurring in the feed solution. The time and the volume was recorded at each sample.

RESULTS AND DISCUSSION

The first series of tests involved the application of the polymeric binding/membrane separation method in a continuous process. Figure 1 shows the flow diagram for this process.

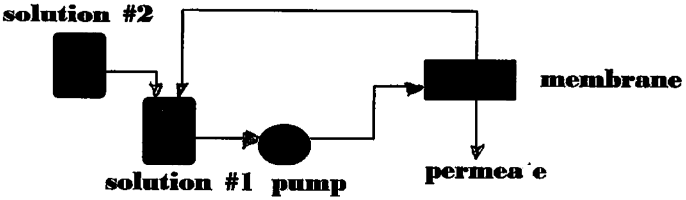

Figure 1 Recirculation Using a Plate and Frame Process.

This system is composed of two different solutions. The polymer is present in solution #1, and is used until the polymer reaches saturation. At that point, the contaminant is retrieved from the system and the solution is treated to regenerate the polymer. The results of the runs are reported in Figure 2 as B1000 #1 and B1000#2 respectively. The graph shows the Vp/Vc as a function of the retention of arsenic (%), where Vp is the volume of permeate collected and Vc is the dead volume of the experimental system. Based on the data obtained from this study, the system was proven to be very efficient with a 96.0 % retention for the run and above 99.9 % for the second one. Retention above 99.9% was also achieved using chromium in this system which confirmed the efficiency of this system. The results are presented in Table 1.

During the first arsenic run, the retention increased from 71.7 % to 96.0 % after the treatment of 6 litres of contaminated solution. The results demonstrated that the permeate concentration diminished from 0.033 ppm to 0.005 ppm of arsenic during the treatment, resulting in an increase in the arsenic retention of 24.3 %. During the second arsenic run, the same phenomenon was observed where the arsenic concentration in the permeate decrease from 0.020 ppm to less than 0.001 ppm resulting in over 99.9 % retention by the membrane following the treatment of 3.5 litres of contaminated solution. In the same manner, the experiment using the chromium showed the same behavior starting with a lower chromium removal to finish with more than 99.9% rejection. These observations could possibly be explained by the formation of a polymeric gel at the surface of the membrane. As the experiments proceed, the polymer being recirculated accumulates at the surface of the membrane, increasing its local concentration. It is this local concentration of the polymer which increases the likelihood of the contaminant to contact and bind to the polymer resulting in an increase in the contaminant removal. As well, from the results obtained using arsenic, it was noticed that a higher removal was achieved using higher initial arsenic concentration. The literature sited very few studies using low arsenic concentrations. In this experiment, an arsenic retention of 96.0 % was achieved at 0.1 ppm of arsenic compared to >99.9 % at an initial arsenic concentration of 0.3 ppm.

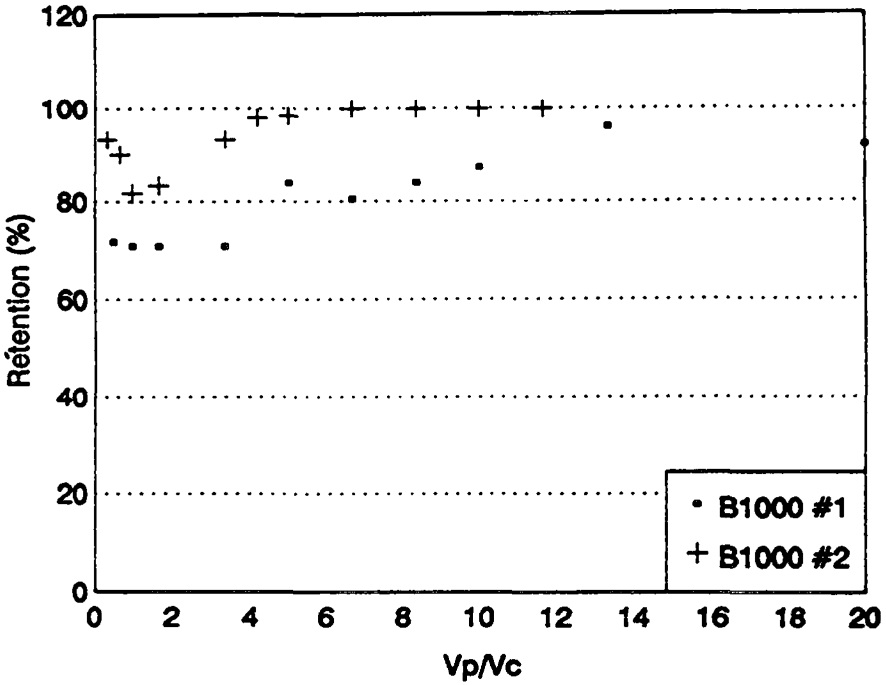

Figure 2 Arsenic Retention Using The Recirculation Plate and Frame Process using 1,000 ppm of PEI, and 1,000 ppm of NaCl Solution.

Table 1 Chromium Retention Using 12 ppm of Chromium and 3,000 ppm of PEI

TIME (hrs)	Permeate Concentration (ppm)	% REJECTION
1.00	0.195	98.38
2.00	3.920	67.47
4.14	5.000	58.51
6.11	3.160	73.78
22.32	2.265	81.20
24.00	0.660	94.52
26.30	0.168	98.61
27.26	0.110	99.09
28.06	0.140	98.84
29.30	0.113	99.06
30.30	0.093	99.23
76.22	0.025	99.79
78.30	0.005	99.59
83.41	<0.001	>99.99

The second system involved a magnetically stirred batch test cell. Figure 3 shows the flow diagram of the process. Table 2 lists the molecular weight cut-off and type of membrane, the concentration of polymer in the test cell, the initial arsenic retention, and the final arsenic retention after 4 liters of arsenic-contaminated water had permeated through the stirred-cell.

The lower separations compared to those observed with the recirculation experiment can be explained by the effect of concentration polarization, since the mass transfer at the surface of the membrane in the stirred-cell was much better than that of the flow-through cell. Results indicate that arsenic retention does not drop as severely with the Bioken membrane as it does with the Osmonics membrane. The Bioken membrane was produced from polyethersulphone whereas the Osmonics membrane was produced from cellulose acetate and has a special surface treatment to reduce membrane fouling. However, in this application the surface-treated cellulose acetate membrane seemed to foul more readily than the polyethersulphone membrane.

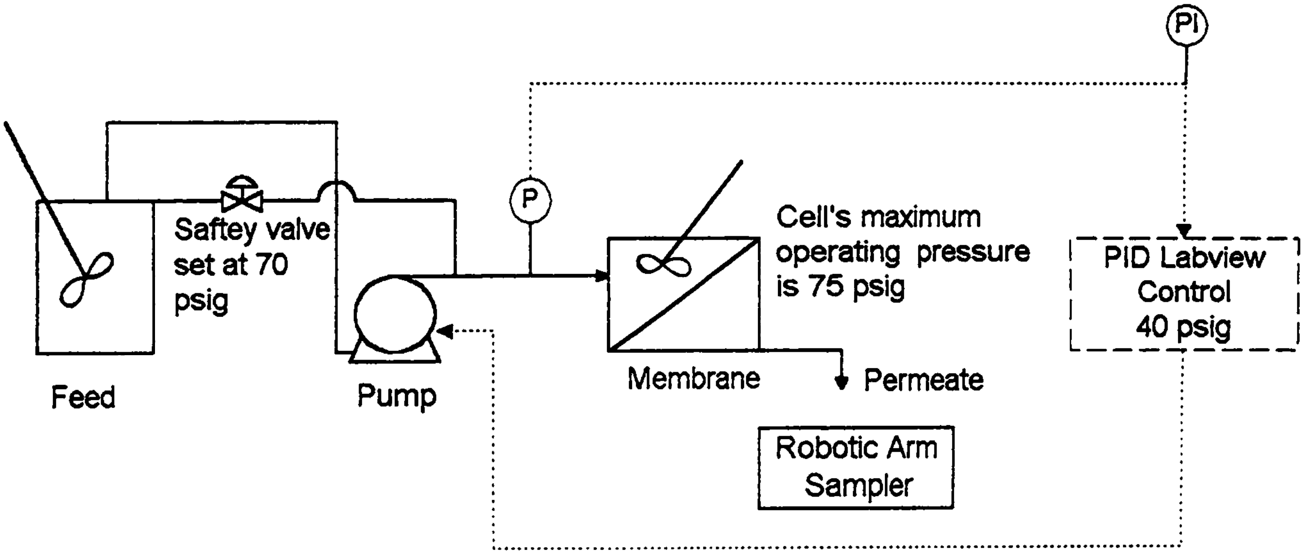

Figure 3 Magnetically batch stirred-cell.

Table 2. Results of the stirred-cell experiments using 0.3 ppm of arsenic, 1,000 ppm of NaCl and two types of membranes having different molecular weight cut-off.

Membrane	Molecular Weight Cut-off (Daltons)	PEI Concentration (ppm)	Initial Permeate Flowrate (cc/cm^2/s)	Final Permeate Flowrate (cc/cm^2/s)	Initial Arsenic Retention R_{As} (%)	Final Arsenic Retention R_{As} (%)
Bioken	10,000	1,000	0.68E-3	0.73E-3	57	30
Bioken	10,000	5,000	0.65E-3	0.72E-3	87	40
Osmonics	1,000-5,000	5,000	1.05E-3	1.22E-3	89	20
Osmonics	1,000-5,000	10,000	0.83E-3	0.96E-3	92	<1

CONCLUSIONS

1. The polymeric/membrane separation is an effective technique for the removal of toxic metals from aqueous solution;
2. The recirculation process involving a plate and frame module is more promising for industrial application than the batch stirred-cell;
3. Formation of a polymeric gel occured at the surface of the membrane using the recirculation process and,
4. Lower contaminant concentrations are more difficult to remove.

RECOMMENDATIONS

1. Studies should be performed using "real" contaminated samples to check for detrimental effects of naturally occuring salts and organic contaminants on the process;
2. The recirculation process should be implemented at a larger scale to determine its feasibility;
3. Additional investigation should be carried-out using chromium as a contaminant;
4. New membranes should developed to remove heavy metals from aqueous solutions;
5. Removal of other heavy metals should be determined using the recirculation system and,
6. Further investigation should take place on the polymeric gel production.

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AN ADVANCED PROCESS FOR THE REMOVAL OF ARSENIC FROM EFFLUENTS

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ABSTRACT

A novel process was developed to effectively remove arsenic from wastewater and contaminated water. The process consists of three major steps: adsorption of arsenic on finely dispersed activated alumina, membrane filtration to separate particulates from liquid phase, and regeneration of the adsorbent. The effect of process parameters such as pH, residence time, and adsorbent characteristics were studied and the process was optimized with respect to these parameters. A number of commercially available aluminas were characterized and tested.

INTRODUCTION

Arsenic contamination of water is a serious problem that many communities in Canada and around the world are faced with. The seriousness of the problem, due to high toxicity of arsenic and its health hazards, makes the development of efficient and cost effective technologies for treatment of arsenic contaminated water and soil a high priority task particularly if increasingly stringent effluent discharge and water quality criteria are to be met.

The Emergencies Engineering Division of Environment Canada and ZENON Environmental Inc. have developed an effective technique for the removal of arsenic from contaminated water and wastewater streams. This technology can handle high concentrations of arsenic while being economically competitive with the conventional methods such as activated alumina packed column adsorption.

MATERIALS AND METHODS

Water Samples

Different spiked water samples as well as actual contaminated water were used in the experiments. The contaminated water samples were obtained from Deloro Water Treatment Plant (Deloro, Ontario). The samples obtained were water contaminated by mining effluent discharge. Table 1 shows the level of different ions in the water samples used in this study.

Table 1.
Composition of spiked water and actual contaminated water sample.

Component	Untreated groundwater (ppm)	Spiked water (ppm)
Cl^-	73.4	-
CO_3^{2-}	4.8	-
HCO_3^-	222	-
NO_3^-	less than 0.1	-
SO_4^{2-}	114	-
Arsenic	~60[1]	2-50

EXPERIMENTAL PROCEDURE

Adsorption Tests

The following experimental procedure was followed for all adsorption tests:

- samples of alumina were activated at 250°C overnight and cooled for subsequent use,
- 400 mL arsenic solution of desired concentration and pH was put into 600 mL beakers and placed under a multiple stirrer,

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[1] The value changes with season.

- at time zero the activated alumina was added to the stirring arsenic solution,
- 3 mL samples were taken at the desired time intervals using a plastic syringe and filtered into a sample vial using a syringe filter. 5 μL of concentrated nitric acid was added to each sample,
- pH of the system was adjusted between samples using a 0.1 M nitric acid, and
- samples were analyzed using flame atomic adsorption/hydride generator equipped with electric discharge lamp.

Membrane Filtration Tests

In order to evaluate different options of membrane separation, bench scale tests were carried out using two different types of commercial microfiltration membranes:

- tubular membrane manufactured by ENKA with an average pore diameter of 0.2 μm and filtration area of 0.036 sq.m, and
- hollow fibre membrane ZeeWeed™ manufactured by ZENON Environmental Inc. with an average pore diameter of 0.1 μm and filtration area of 0.5 sq.m.

For both types of membranes, a model suspension was prepared by dispersing different amounts of activated alumina CP-1.5 in deionized water. No arsenic was added to the suspension. Permeate quality was monitored by periodical sampling and analyzing the permeate turbidity. The rejection of alumina particles by the membrane was calculated based on the concentrate and permeate turbidities. Permeate flux was measured periodically and adjusted to 25°C.

RESULTS AND DISCUSSION

Characterization of Activated Alumina Samples

Adsorption characteristics of the samples of activated alumina were determined using nitrogen sorption porosimetry. The alumina samples were degased under vacuum at 350°C for a minimum of four hours prior to determination. Table 2 illustrates the results of the adsorbent characterizations.

Table 2.
Adsorption characteristics of activated alumina samples
used in the adsorption study

Alumina	Manufacturer	Surface Area, m^2/g	Pore vol. cc/g
50-212um, 60A, Basic	Scientific Adsorbents	89.7002	0.453
HTC-100	Alcoa	378.74	0.6375
F1-100	Alcoa	823.34	2.0579
CG-20	Alcoa	148.25	0.3514
CPN-100	Alcoa	402.38	0.8887
CPN-325	Alcoa	803.35	1.9640
CP-1.5	Alcoa	458.45	0.8605
CP-5	Alcoa	447.63	1.0700
CP-100	Alcoa	180.54	0.3568

Determination of an Optimum pH

A pH range of 1 to 8 was investigated using two types of activated alumina supplied by two different manufacturers (50-212μm particle size, basic by Scientific Adsorbents Inc. and CPN-325 by Aluminum Company of America). All activated aluminas used in this study were of γ type with identical surface chemistry; therefore, the results obtained can be extended to all γ type activated alumina. The pH is one of the most important factors determining the extent of adsorption and the overall rate of the process. Just as the charge on the surface of the adsorbent varies with pH, the adsorbate might also become more or less charged by going through protonation or deprotonation.

Using 50-212 μm basic alumina, adsorption tests were carried out at pH 1, 3, 4, 6, 7, and 8 at a 3 g/L alumina concentration. The initial arsenic concentration was approximately 26 ppm and the pH was kept constant throughout the experiment. The data are presented in Figure 1. The data show that the best arsenic removal was obtained at pH 3. To better illustrate this, the percentage of arsenic removal was plotted against pH after contact time of 10 minutes (Figure 2). It can clearly be seen that pH 3 yields at least 30% higher arsenic removal than other pHs after 10 minutes of contact between adsorbent and adsorbate.

In a second set of experiments, the range of pH was narrowed down to between pH 2 to 4 in order to determine the optimum pH more precisely. The results showed that the highest degree of arsenic removal and lowest residual arsenic concentrations were obtained at pH 3. Similar results were obtained with commercially available aluminas.

Screening of Industrial Activated Alumina

In order to identify the most effective commercial alumina for the removal of arsenic from water, eight samples of industrial activated alumina, supplied by Alcoa, were tested. A set of adsorption experiments were performed under similar conditions with respect to initial arsenic concentration, pH, contact time, and alumina concentration. Figure 3 shows the results of these experiments. Figure 3 illustrates that the best sample of alumina for the adsorption process was CPN-325. The order of performance of the tested samples was found to be as follows:

CPN-325 > CP-5 > CP-1.5 > HTC-100 > CPN-100 > F1-100 > CP-100 > CG-20

When CPN-325 was used the arsenic concentration decreased from 38 ppm to 0.02 ppm in less than 10 minutes. Close examination of adsorption characteristics of these alumina samples in Table 2 shows that the samples that performed better had a higher pore volume and a larger specific surface area. The only exception was F1-100 which had a larger particle size than the rest of the samples. The larger particle size of F1-100 explains the lower arsenic removals achieved with this sample.

Effect of Competing Ion on Adsorption

The presence of competing ions can strongly affect the efficiency of the adsorption process. The effect of the presence of sulphate ion on the adsorption process was studied since sulphate is one of the most important competing ions for arsenic adsorption. In order to determine the effect of sulphate competition on arsenic adsorption onto activated alumina, spiked samples of arsenic contaminated water with different sulphate concentrations were prepared and adsorption tests were performed at pH 3, initial arsenic concentration of 46 ppm, and using CPN-325 at 3 g/L. An additional test using actual arsenic contaminated water was conducted and compared against a spiked water sample.

Figure 4 shows that in the absence of sulphate > 99% removal was achieved. The removal efficiency was not significantly affected with sulphate concentrations of up to 50 ppm. The effects were more noticeable at sulphate concentrations of 100 ppm and higher. Significant decrease in the removal efficiency was observed at 300 and 600 ppm and the removal of arsenic dropped by as much as about 20%. Table 3 shows the initial rate of arsenic removal in terms of *μg As/min*, and *mg As/min/g alumina* at different sulphate concentrations.

Figure 5 illustrates the results of the adsorption test on an actual contaminated water (from Deloro, Ontario) as well as spiked water sample. The figure shows that with the Deloro sample the removal was less than the spiked sample by about 20%. This decrease in arsenic removal might have been due to the presence of sulphate and perhaps the presence of other ions and also the fact that a fraction of total arsenic in surface and ground waters is in the form of As (III) which is poorly adsorbed under the test conditions.

Table 3.
Initial arsenic removal rate at different concentrations of sulphate.

[Sulphate] ppm	Initial rate µg As/min As	Initial rate mg As/min/g AA
0	9.14	3.05
10	9.12	3.04
30	9.14	3.05
50	9.1	3.03
100	8.68	2.89
300	7.82	2.61
600	7.36	2.45

Adsorbent Regeneration

Feasibility of the regeneration and reuse of activated alumina was investigated to determine the extent to which the used alumina's adsorption capacity can be regenerated. In order to regenerate the activated alumina, the samples should be placed under conditions that would cause arsenic to desorb from the surface sites. This is achieved by changing the pH to a value that would change the speciation of the adsorbed arsenic anion and reducing the affinity of the adsorbent surface to arsenic. An increase in pH would also result in an increase in dissociative adsorption of water molecules which will force arsenic anions off the surface. Another available option would be to introduce a competing ion that has a higher affinity towards the surface of the alumina, hence replacing arsenic. When selecting a competing species it should be kept in mind that the affinity of the competing ion introduced should be high enough that at high concentrations it would replace arsenic but also arsenic would be able to replace it in the presence of high arsenic concentrations.

As previously mentioned the choices available for regeneration were: pH increase using sodium hydroxide, application of phosphate solution, and use of a sulphate solution. Use of phosphate was rejected because of the strict discharge criteria for phosphate in water. The feasibility of the application of sulphate was investigated by performing adsorption experiments using an alumina sample that was exposed to a 100 g/L sodium sulphate solution for three days and comparison of its performance with a fresh alumina sample. The test showed that with sulphate already adsorbed onto the alumina surface, arsenic cannot easily replace it. There was an approximate initial 40% loss in arsenic removal which rendered the use of sulphate unfeasible (Figure 6).

The option of pH increase with sodium hydroxide was investigated. The regeneration was performed in the same reactor without removing any liquid or change in the volume of the reactor contents. After 24 hours of adsorption at pH 3, the pH was adjusted to pH 11, 12, and 13 in three different experiments and samples were taken every 10 to 20 minutes. Samples were also taken in order to determine aluminum loss due to hydrolysis. Figures 7 and 8 show the results. It can be seen that the degree of arsenic desorption was very close at pH 12 and 13, while the loss of alumina at pH 12 was approximately half as much at pH 13.

Membrane Separation Experiments

Two types of microfiltration membranes were selected for this study: a) tubular membranes manufactured by ENKA, and b) hollow fibre membranes manufactured by ZENON Environmental Inc. Tubular microfiltration membranes, particularly ENKA membranes, are most frequently used for the separation of suspensions so that the choice to test one of such membranes was justified.

At the same time, hollow fibre microfiltration membrane modules had a very limited application in industry for the separation of suspensions, because they are highly sensitive to fouling. However, one of ZENON's recent membrane products, namely ZeeWeed^{TM}, demonstrated remarkably good performance in a series of applications where various suspensions had to be treated. Based on these facts, it was decided to evaluate the applicability of ZeeWeed^{TM} modules to the adsorption/microfiltration process.

ENKA Flux Data

Initially, ENKA membrane was tested using deionized water, i.e. a permeate from reverse osmosis (RO). RO water flux through the membrane was found to be extremely high - more than 2,500 gfd at 25°C and 5 gpm of the feed flow. When activated alumina was added to the system to make a 10g/L slurry, permeate flux suddenly dropped to 384 gfd (almost 75% decline) and continued declining. Two hours later, permeate flux reached a level of 132 gfd (95% decline). This indicated that under the test conditions, the membrane experienced severe fouling.

Based on test results it was concluded that the performance of the ENKA membrane was unsatisfactory with respect to its possible incorporation into adsorption/microfiltration process. This membrane experienced a severe flux decline and required frequent cleaning to recover the flux, but even after cleaning, the flux could not be completely recovered.

ZeeWeed^{TM} Flux Data

As opposed to the ENKA membrane, permeate flux of the ZeeWeed^{TM} membrane was remarkably stable. Even though the initial RO water flux of the ZeeWeed^{TM} was much lower than that of the ENKA membrane, (attributable to significant differences in physico-chemical and mechanical characteristics of these two membranes), it changed only slightly in time. The flux could easily be recovered by using so-called "relaxation cleaning", i.e. aerating the membrane for approximately 5 to 10 minutes without applying the vacuum.

As the concentration of alumina in the slurry rose from 3 g/L to 60 g/L, permeate flux remained practically constant. A decline in flux was observed only at alumina concentrations higher than 60 g/L. This was a very important finding. The higher the alumina concentration in the slurry, the higher the adsorption capacity, and the longer the regeneration cycles.

In addition to the stable permeate flux, the rejection of alumina particles by the membrane was higher than 99.99%. Based on positive test results it was concluded that the ZeeWeed™ membrane could be incorporated into the adsorption/microfiltration process.

CONCLUSIONS

Based on the results of the experiments carried out in this study the following conclusions and recommendations were made:

- An advanced technology for the removal of arsenic from mining effluents and other aqueous streams was developed. This technology incorporates adsorption of arsenic on finely dispersed activated alumina, microfiltration, and adsorbent regeneration.

- It was demonstrated that rapid adsorption occurs when pH is kept constant at about 3 and alumina particle size is in the range of several microns. As a result, the concentration of arsenic in the effluent could be reduced to 0.02 ppm or less within ten minutes.

- It was found that commercially available activated aluminas could successfully be used in the process. Examples of such aluminas are CP-1.5 and CPN-325 manufactured by Aluminum Company of America (ALCOA).

- It was demonstrated that both a small particle size and a large pore volume are important factors for fast adsorption. Among aluminas with a given particle size range preference should be given to the alumina with the largest pore volume.

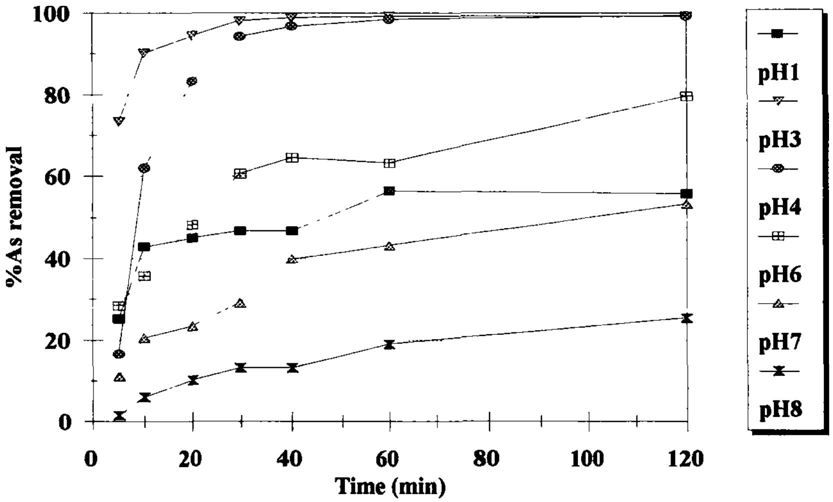
- Test results revealed that pH 3 was the best pH for adsorption; however, pH 2.5 to 4.0 is still acceptable. This finding is of a great importance for the treatment of mining effluents; most effluents have pH in this range; therefore, pH adjustment and related expenditures would be minimized.

- Results of microfiltration tests, carried out on tubular and hollow fibre membranes, revealed that a very high (more than 99.98%) rejection of alumina particles could be achieved for both types of membranes. Hollow fibre membrane module ZeeWeed™ demonstrated a very stable permeate flux whereas the flux of the tubular ENKA module rapidly and irreversibly declined. It was therefore concluded that ZeeWeed™ membrane modules are the best choice of membranes for the adsorption/microfiltration process.

- An effective regeneration of alumina from arsenic could be achieved by desorbing the adsorbed arsenic with a solution of sodium hydroxide (pH 12 to 13). Due to small adsorbent particle size the rate of desorption was as fast as the rate of adsorption. Activated alumina losses due to its partial dissolution did not exceed 3%.

Figure 1

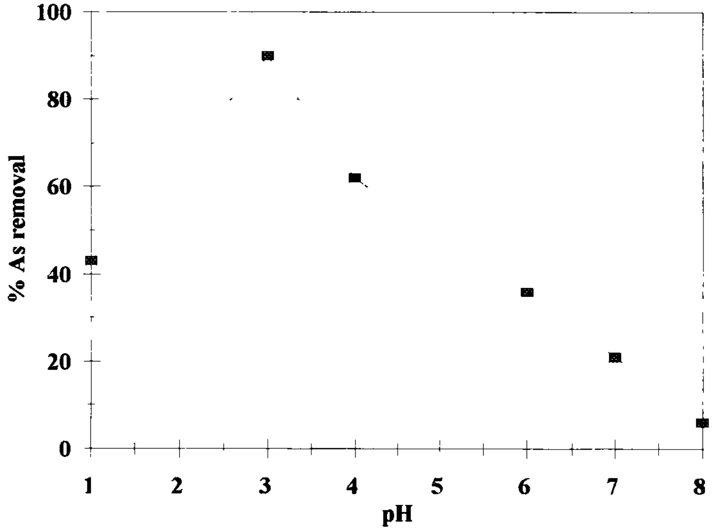
Arsenic removal vs Time at different pH s



Initial [As]=26 ppm
Activated Alumina Concentration = 3 g/L, 50-212 um basic

Figure 2

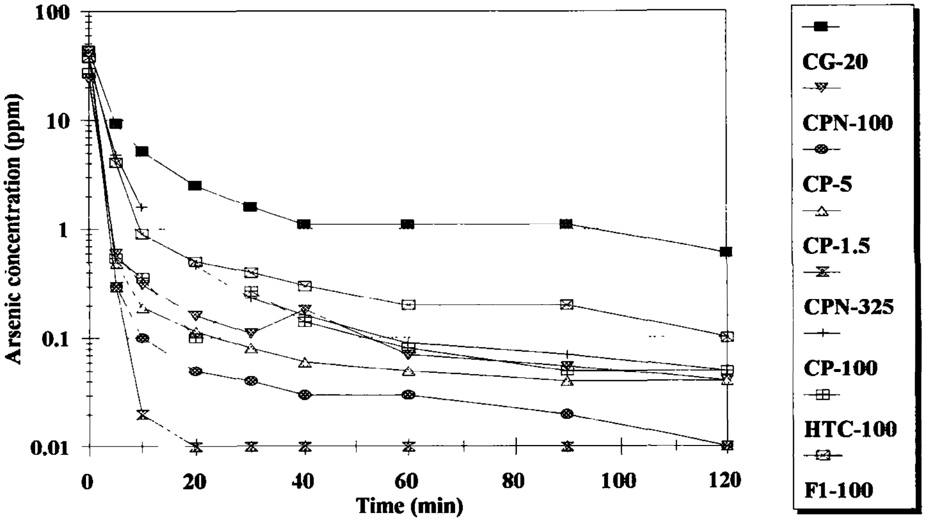
Arsenic removal vs pH, for specialty alumina



Contact Time = 10 min
Initial [As] = 26 ppm
Activated alumina concentration = 3 g/L, 50-212 um basic

Figure 3

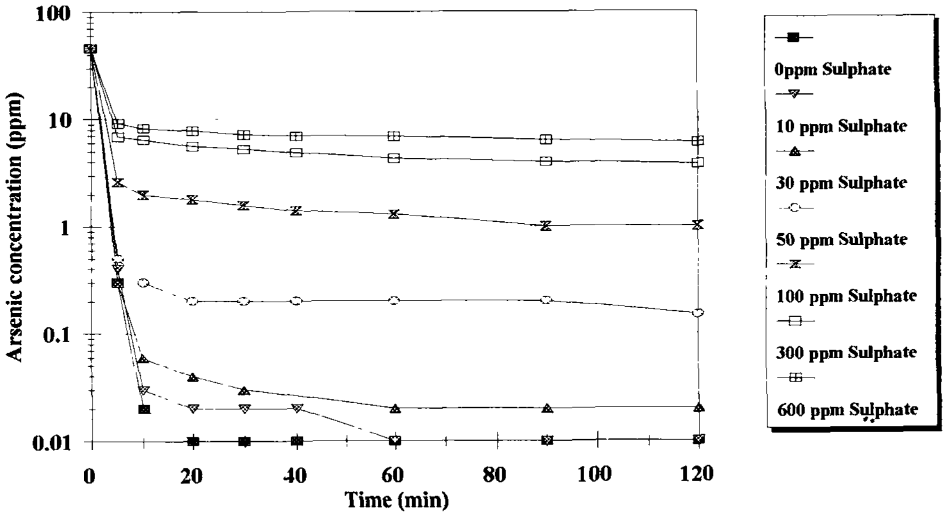
Arsenic concentration vs Time
for commercially available alumina



pH=3
Average Initial [As] = 38 ppm
Activated alumina concentration = 3 g/L
MDL for As = 0.01 ppm

Figure 4

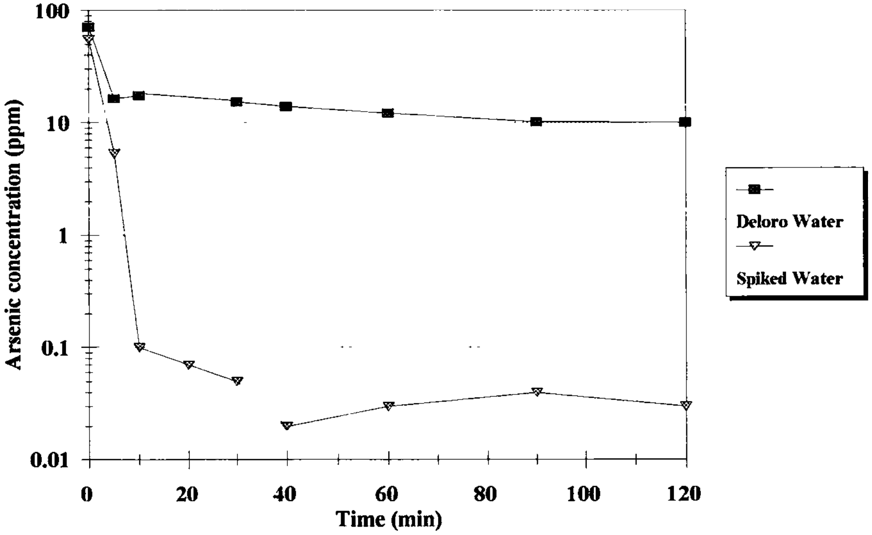
Effect of Sulphate on Arsenic removal vs Time



pH = 3
Initial arsenic concentration = 46 ppm
Activated alumina concentration = 3 g/L, CPN-325

Figure 5

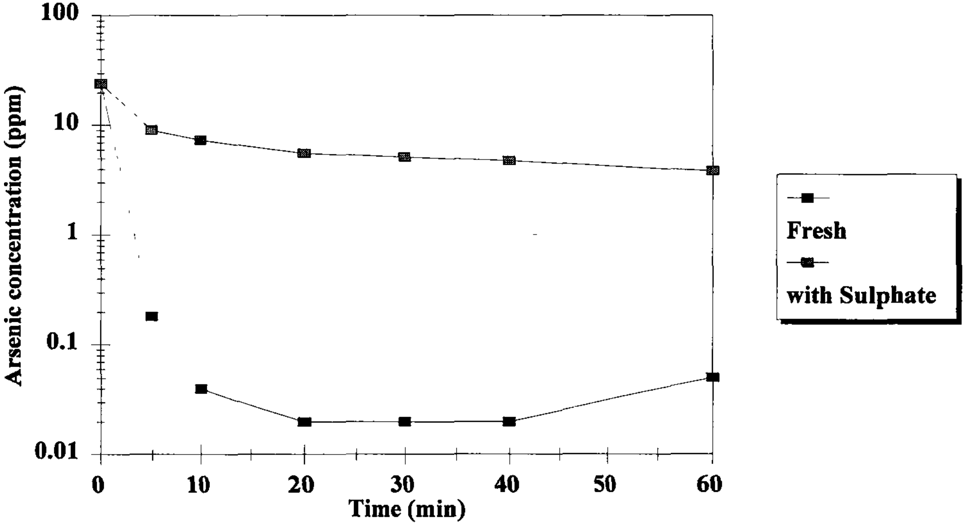
Arsenic concentration vs Time for synthetic vs actual wastewater



pH = 3
Initial [As] = 63 ppm
Activated alumina concentration = 3 g/L, CPN-325

Figure 6

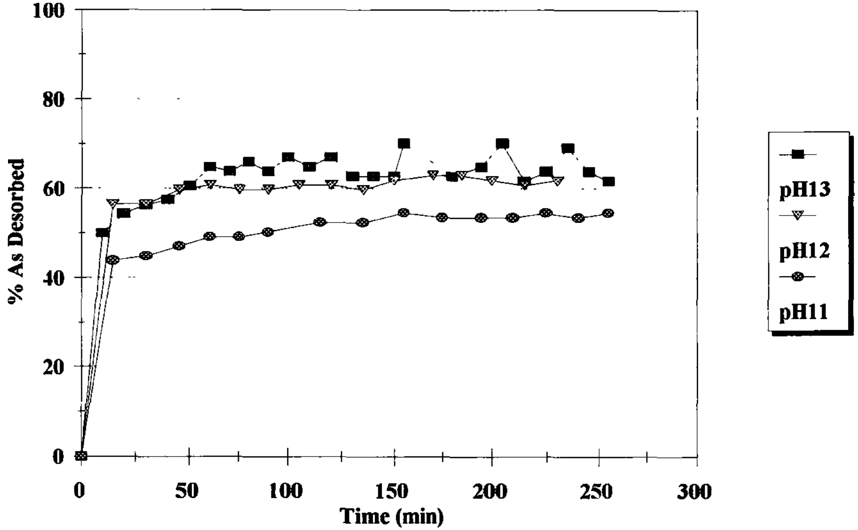
Regeneration test
Fresh vs Sulphate loaded alumina



pH = 3
Initial [As] = 24 ppm
Activated alumina concentration = 3 g/L, 20-30 um, 300A

Figure 7

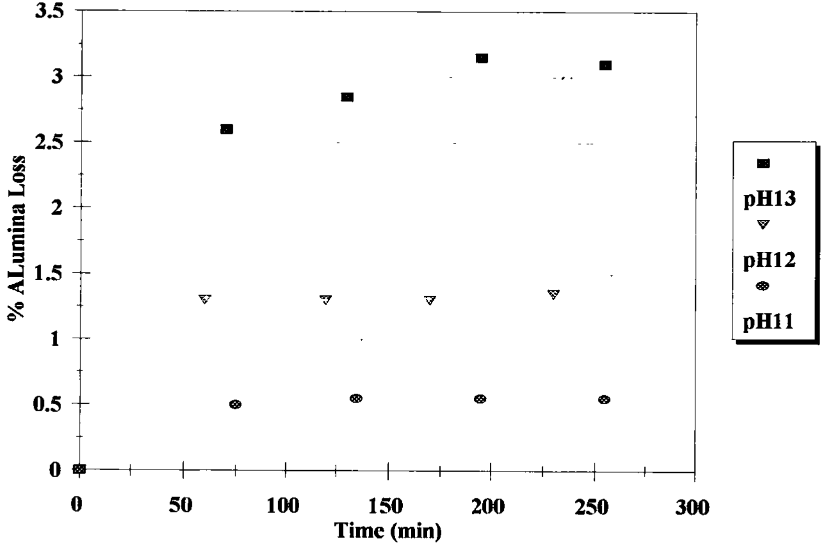
Arsenic desorbed vs Time during regeneration



pH = 3
Initial [As] = 43 -50 ppm
Activated alumina concentration = 20 g/L, HTC-100
Alumina sample was not separated from pH3 solution prior to

Figure 8

Alumina losses during regeneration process



ELECTROLYTIC DECOMPOSITION OF N-NITROSODIMETHYLAMINE IN WATER

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Abstract

A series of benchscale tests were carried out in order to study the feasibility of electrolytically reducing N-nitrosodimethylamine (NDMA) in aqueous solutions. The experiments were performed using inexpensive carbon, stainless steel, and nickel electrodes. Besides electrode materials, the solution pH and the voltage were the variables studied in this work. A higher rate of decomposition of NDMA was achieved in acidic conditions, using a relatively high potential applied to the electrodes. The results of our study are summarized and recommendations for future work are presented.

Background

The Emergencies Engineering Division (EED) of Environment Canada is actively involved in a program of environmental assistance to the countries of Eastern Europe. One of the main objectives of this program, which is sponsored by Environment Canada, Department of Foreign Affairs and International Trade, and Canadian private sector companies, is to develop and transfer remediation technologies for contaminated soil and water at former nuclear missile sites.

Hydrazine and its methylated derivatives, namely monomethylhydrazine (MMH) and unsymmetrical dimethylhydrazine (UDMH), have been extensively used as missile fuels by the former Soviet Army. Accidental leaks which often occurred during missile operations led to the pollution of surrounding areas. Hydrazine, MMH, and UDMH are not stable when exposed to direct sunlight or brought in contact with metal ions in the soil (Judeikis and Damschen, 1992); however, some products of their natural degradation are more stable and far more toxic and carcinogenic than the original compounds. N-Nitrosodimethylamine (NDMA) represents one such product of degradation. It should be mentioned here that the presence of nitrosamines in soil and groundwater is not only associated with missile fuels. Nitrosamines also find their way into environment as a result of the use of pesticides and other chemicals. They frequently occur in waste waters from rubber, tanning, and metal-working industries. However, in missile sites NDMA may be present in much higher concentrations (up to hundreds of milligrams per litre of groundwater) than in cases where its presence was caused by industrial or agricultural activities.

NDMA has long been the focus of a number of researchers who evaluated and applied different treatment technologies for contaminated soil and water (Davis, 1982; Castegnaro, et al, 1982; Burgess and Lavanish, 1964; Polo and Chow, 1976; Cooper and Keller, 1993; Solarchem, 1993), due to high toxicity and carcinogenity of NDMA. These technologies, however, were only feasible for lab scale as they required expensive reagents or equipment, or only applicable to low concentrations of NDMA (below 1 ppm), or were associated with secondary contamination caused by the decontamination itself. Optimization of existing treatment technologies for NDMA and a search for new ones, is therefore an environmental necessity.

The electrolytic reduction of NDMA in aqueous medium was reported to be successful in transforming NDMA into less toxic products such as amines, ammonia, and UDMH (Whitnack et al, 1963). The work however was done on a laboratory scale, using a rotating pool of mercury and platinum electrodes. These conditions cannot be applied to large-scale field operations due to the associated high operating and capital cost.

Work Objective

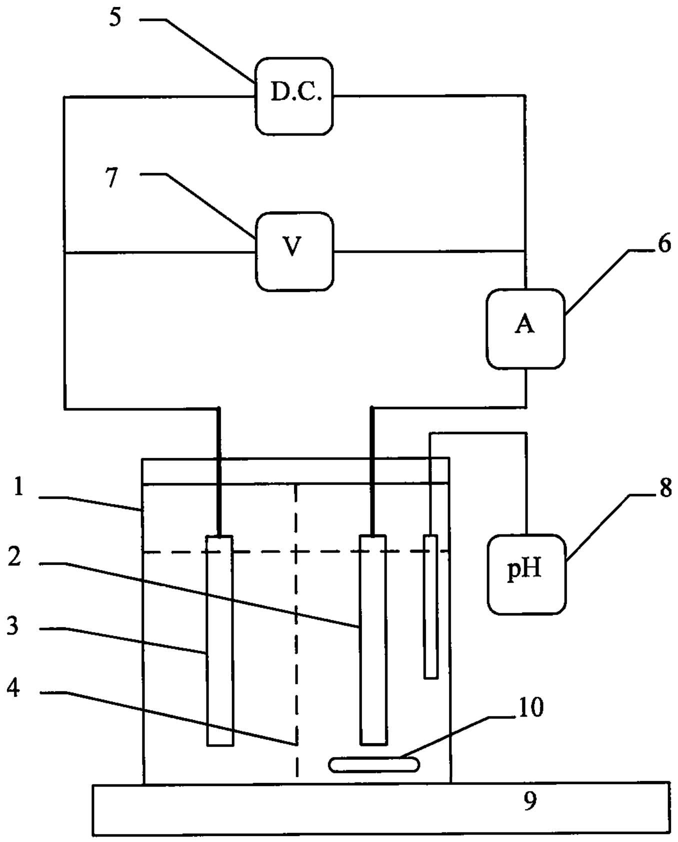
The objective of this work was to evaluate the applicability of electrolytic reduction of NDMA to field conditions, using inexpensive materials. It should be mentioned here that this paper reports only preliminary results. A substantial amount of work has yet to be done to optimize treatment conditions and evaluate the technical and economical feasibility of the process.

Methodology

All experiments were carried out using a two-electrode cell with replaceable electrodes, as shown in Figure 1. The cathode and the anode compartments were separated by a porous glass wall to minimize the diffusion of NDMA and minimize possible simultaneous reduction and oxidation processes. A constant voltage in a range of 0.5 to 3.5 volts was applied to the electrodes, using a direct current (DC) power generator.

At the beginning of each test, 225 ml of a solution containing 100 ppm of NDMA and specific concentrations of supporting electrolyte (sulphuric acid and/or sodium sulphate) was placed into the cathode compartment. The anode compartment was filled with 225 ml of a similar solution of the supporting electrolyte which, however, did not contain NDMA. Test solutions were prepared using deionized and degassed water. Deoxygenation was achieved by bubbling dry nitrogen through the electrolyte for 10 minutes.

Figure 1
Electrochemical test system



1 - test cell; 2 - cathode; 3 - anode; 4 - porous glass wall; 5 - DC generator; 6 - ampermeter; 7 - voltmeter; 8 - pH-meter; 9 - magnetic stirrer; 10 - magnetic bar.

Sulphuric (H_2SO_4)acid was used to adjust the pH of test solutions because of its low cost; in addition, unlike hydrochloric and nitric acids, sulphuric acid would not cause the formation of toxic by-products. In the tests, the pH was varied in the range of 0.5 to 11. When sodium sulphate was used as an electrolyte, its concentration was 1,000 ppm. When necessary, sodium hydroxide was also used for pH adjustment.

Samples from both the anode and the cathode compartments were taken at specific time intervals (normally, after one, two, three, and four hours) and analyzed for NDMA using UV-VIS spectrophotometry and gas chromatography with mass spectroscope as a detector. Standard procedures described in literature were used for sample preparation and analysis.

In some tests, samples were analyzed for UDMH which was expected to be one of the major products of NDMA reduction. The analysis were performed using methodics reported by Pinkerton et al., 1963.

Results and Discussion

Material of Electrodes

In the first set of tests, three different types of electrodes, made of carbon, stainless steel, and nickel, were tested. All electrodes had the same rectangular shape. Experimental results revealed that in acidic solutions, both the stainless steel and the nickel electrodes were subject to a rapid corrosion. This corrosion accelerated as the voltage applied increased. As a result, the test solution became contaminated with nickel and iron ions. This meant that after NDMA is removed, the treated water would also require metals removal, prior to its discharge into environment. It was decided therefore to use carbon electrodes in all subsequent tests.

There was no visible corrosion of carbon electrodes in either acidic or alkaline solutions; however, their surface became pitted when a voltage higher than 2.5 volts was applied. This partial disintegration of the electrode material was apparently caused by the failure of a binding compound used in the electrodes.

Supporting Electrolyte

Sodium sulphate and sulphuric acid were used as supporting electrolytes, to increase the conductivity of test solutions. It was found that, at the same concentration, sulphuric acid provided a much higher conductivity, compared with sodium sulphate. The addition of H_2SO_4 was also found to be beneficial for the reduction of NDMA; therefore, sulphuric acid was subsequently used as the supporting electrolyte of choice.

Solution pH and Applied Voltage

In the first set of tests, the solution pH was maintained in a range of 4 to 11 and the voltage was in a range of 2.5 to 3.5 volts. In these conditions, no decrease in the NDMA concentration was observed during the four hours of electrolysis. The observed current was low, suggesting a high resistance of the solution medium. Our results did not agree with the data published by Whitnack et al., 1963, who reported the reduction of NDMA in a broad range of pH (from less than 1 to 11.5). Whitnack et al. did not mention, however, an actual rate of reduction and the time required to achieve this rate. It is difficult, therefore, to compare our results with the data published by these authors.

In subsequent tests, the pH was maintained in the range of 0.5 to 3. This change in experimental conditions resulted in a drastic improvement in reduction. Tables 1 and 2 and Figure 2 illustrate the results.

As evident from the illustrations, both a decrease in solution's pH and an increase in the applied voltage dramatically improved the rate of reduction and resulted in lower residual concentrations of NDMA. More than 90% of the initial NDMA could be reduced within four hours of electrolysis at pH 1 and a voltage higher than 2.5 V.

Residual concentrations of NDMA are still too high for the water to be discharged to the environment. A further optimization of process parameters appears to be necessary to decrease residual concentrations of this toxic compound. Nonetheless, there are alternative technologies of NDMA destruction, such as advanced oxidation (Solarchem, 1993), which are technically and economically feasible at NDMA levels of several ppm and lower. Therefore, electrolytic reduction of NDMA may potentially be considered as a first step of treatment to remove a majority of the contaminant; this could be followed by a polishing step which would bring NDMA concentration down to environmentally acceptable limits.

A pH of 1 would require substantial quantities of sulphuric acid to be added to the water; accordingly, substantial quantities of a neutralizing agent should be added to the treated waste as it could not be discharged to the environment at such low pH. A substantial NDMA reduction was also achieved at pH 2. From the view point of economics, it might be more feasible to operate the system at a higher pH thus saving on reagents and adding less salinity to the treated water.

Table 1
NDMA reduction*
at a constant pH of 1 and varying voltage

Time (h)	NDMA Reduction (%)		
	U = 2 V	U = 2.5 V	U = 3 V
0	0	0	0
1	16.4	48.6	52.1
2	22.1	74.2	85.2
3	23.5	89.7	89.8
4	34.3	88.9	92.0

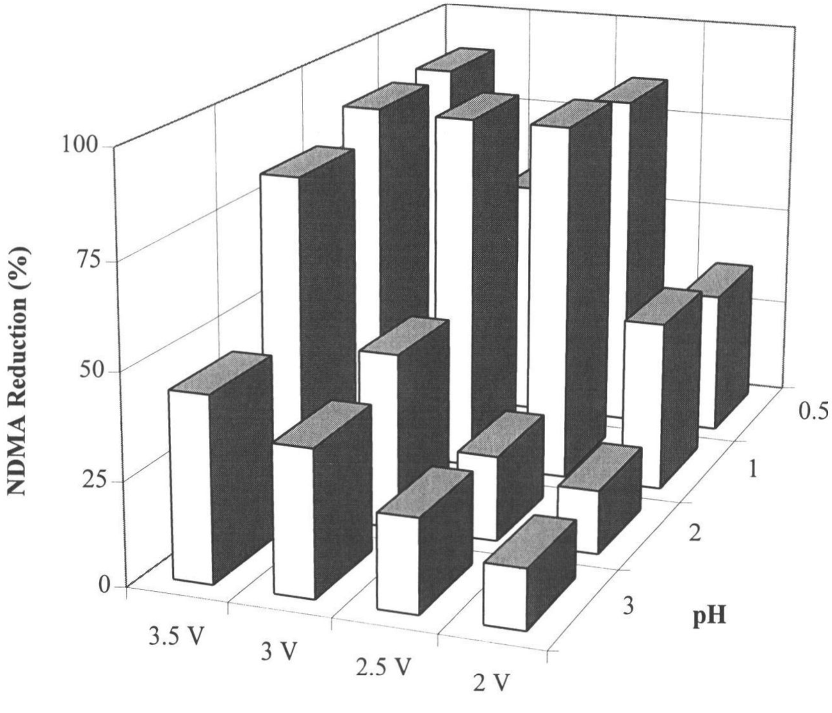
Table 2
NDMA Reduction*
at a constant voltage of 3.5 and varying pH

Time (h)	NDMA Reduction (%)		
	pH = 1	pH = 2	pH = 3
0	0	0	0
1	66.3	36.6	9.6
2	85.4	56.4	27.2
3	93.4	76.1	48.7
4	94.1	83.9	53.9

* Test conditions:

- Carbon electrodes;
- Supporting electrolyte: sulfuric acid
- Initial NDMA concentration: 100 ppm
- Temperature: 20 - 22 C

Figure 2
Average values of NDMA reduction
after four hours of electrolysis
(for test conditions, refer to Tables 1 and 2)



According to Whitnack et at., 1963, UDMH is one of the major products of NDMA reduction. Samples were analyzed for UDMH in approximately 30% of our tests. The presence of UDMH was detected in some samples, although the concentration could not be determined quantitatively. A further study should be done to determine and minimize the yield of UDMH.

Conclusions and Recommendations

Based on the results of bench scale study, the following conclusions were drawn:

- Electrolytic reduction of NDMA in water could be achieved using inexpensive carbon electrodes and a simple two-electrode cell. This setting makes the process potentially applicable for the treatment of contaminated surface and ground water in field conditions.

- Acidic conditions and a voltage higher than 2 were required to achieve a fast decomposition of NDMA. The best results occurred at a pH of 1 and a potential difference of 3 to 3.5 V. Sulphuric acid could be used to adjust the pH to a desired level.

- UDMH was formed in some tests as one of the products of NDMA reduction. To avoid the presence of UDMH in the treated water, the conditions of reduction should be modified in a way to exclude the formation of UDMH. Alternatively, the process of NDMA reduction should be followed by a process for UDMH destruction. One of such processes is currently being investigated by EED.

- Operation at higher voltages (3 V and higher) led to a partial disintegration of carbon electrodes, apparently because the failure of a binding compound used in the electrodes. To extend the life of the electrodes, it appears to be necessary to test carbon materials with different binding compounds.

This paper presents results of preliminary tests only. Certain data must be verified and test conditions optimized. In addition to the variables studied in this work, the following important factors must be evaluated:

- the chemical composition of test solutions, including inorganic and organic components, and its influence on the rate of NDMA degradation;

- the presence of products and by-products of NDMA reduction in the treated solution, their toxicity and carcinogenic properties;

- the porosity of the wall used to separate the cathode and anode compartments. The porosity must be high enough to allow for a substantial electric current, while minimizing the diffusion of NDMA across the wall;

- modification of electrode configurations.

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The Destruction of Hydrazine fuels by Electrolysis

by
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Abstract

This paper summarizes studies using electrolysis for the destruction of Hydrazine (HZ) and 1,1-dimethylhydrazine (UDMH) in aqueous solutions. The investigation was performed using an electrolytical cell with a stainless steel cathode and a carbon, lead, or nickel anode. The concentrations of HZ and UDMH were in the range of 100 to 800 ppm and disodium hydrogen phosphate (Na_2HPO_4) was used as the electrolyte to increase the conductivity of the cell. The pH of the solution was achieved by the addition of phosphoric acid.

The destruction efficiency of HZ and UDMH was found to be more than 99%. The results from the work show that this new process is a viable solution to reduce HZ and UDMH contamination of aqueous solutions.

Introduction

HZ and UDMH are widely used as propellants in the aerospace industry. The utilization of hydrazine propellants in space and missile programs can lead to accidental environmental releases of these fuels during transport, transfer, or storage. These fuels are highly toxic, and as a result of fundamental studies (Shank, 1974, NIOSH, 1977), the American Conference of Governmental Industrial Hygienists (ACGIH) and the National Institute if Occupational Safety and Health (NIOSH) have listed these compounds among the industrial substances suspected of being human carcinogens. The nature of the health threat posed depends not only on the quantity of the material released, the nature of the release (gas or liquid), the environmental conditions at the time of the release, but also on the chemistry that can occur in the environment.

The hydrazines (HZ and UDMH) are very strong reductants, and therefore the main reactions in the environment are the oxidation of these compounds. Of all the reactions involving HZ, the autooxidation by atmospheric oxygen assumes a most important role. This process can lead to the degradation of HZ into innocuous materials such as nitrogen and water. Thanks to this rapid autooxidation, HZ is not a very persistent environmental contaminant. The autooxidation of UDMH on the other hand leads to the formation of formaldehyde dimethyl hydrazone (FDH), N-nitrosodimethylamine (NDMA), formaldehyde, ammonia, dimethylamine, nitrous oxide, nitrogen, methane, carbon dioxide, and water. NDMA is considered to be among the most potent of all chemical carcinogens, and there are no permissible exposure limits for it (National Safety News, 1977). The FDH has been determined to have the same relative magnitude of toxicity as NDMA (Keller, 1980). The aforementioned shows UDMH to be a very hazardous environmental contaminant. Therefore, numerous studies have been carried out to determine the rates, products, conditions, and reagents for the destruction of hydrazines. The yield of the UDMH oxidation products is strongly dependent upon the conditions employed , and may produce a variety of products including NDMA, FDH, tetramethylhydrazine, formaldehyde, dimethylamine, and 1,5,5-trimethylformazan (McBride, et al., 1957, Urry et al., 1965, Boehm et al., 1975, Banerjee et al.,1984).

This indicates that a novel method for the destruction of hydrazines should be determined in which the formation of toxic byproducts will be avoided. This paper contains the results of the electrochemical destruction of HZ and UDMH without the formation of NDMA.

Methods of analysis of HZ and UDMH solutions

The changes in HZ concentrations during electrolysis were monitored by colorimetric determination of HZ with p-dimethylaminobenzaldehyde according to the Standard Test Method for Hydrazine in Water (ASTM: D1385-88) using a Perkin Elmer Lambda 2 UV/Visible spectrophotometer. The concentration of UDMH was determined colorimetrically using trisodium pentacyanoamino ferroate (TPF) as the reagent (Pinkerton, 1963). The UV spectra analysis was carried out to monitor and define the pathway of electrolysis. Concurrent analysis of the end products of electrolysis was carried out by GC/MS and GC Purge and Trap.

Experimental

HZ and UDMH were obtained from the Fluka chemical company and were used without additional purification. The power supply for the electrolysis was a Protek DC power supply, model 3003. A stainless steel cathode and interchangeable graphite, nickel, or lead anodes were used in the electrolytic cell. The electrolyte was produced by preparing solutions containing 100 to 800 ppm of HZ or UDMH. The concentrations of Na_2HPO_4 and H_3PO_4 were dependent on the desired pH of the solution for the experiment. The electrolytical destruction of HZ is a one step process with a current density of $i = 0.0075$ A/cm^2. The electrolytical destruction of UDMH involves three steps. First, the oxidation at the anode at pH 7 with a low current density to avoid the evolution oxygen from water. The second step involves adjusting the pH to 2 and treating the solution with NaNO2 to produce nitroso intermediates. The final step is electrolysis with a current density $i = 0.03$ A/cm2, which leads to the complete destruction of the intermediates in solution. The duration of the process to completion depends upon the initial concentration of UDMH. For a 800 ppm content of UDMH the destruction takes approximately four hours.

Results and Discussion

Results 1

A total of 15 electrolytical oxidation runs of the simulated waste waters were performed with varying HZ concentrations, different anodes, and with different currents. Hydrazine is a strong reducing agent and its standard redox potentials:

$$N_2H_4 + 4\ OH^- - 4e^- \rightarrow N_2 + 4\ H_2O \qquad E^\circ = 1.16\ V \qquad (1)$$

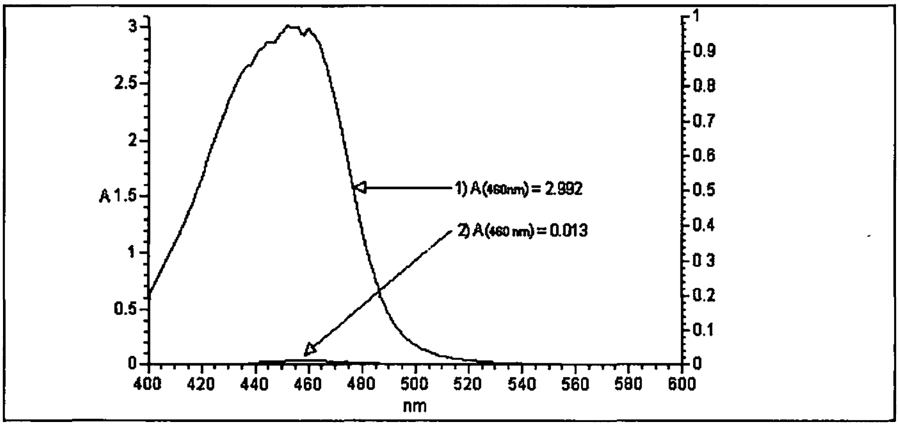
and

$$N_2H_5^+ - 4e^- \rightarrow N_2 + 5\ H^+ \qquad E^\circ = 0.23\ V \qquad (2)$$

indicate that hydrazine is a better reducing agent in an alkaline solution than in acidic solutions. If the electrolysis is carried out with a potential difference in which the oxidation of water does not occur, then the destruction of hydrazine may go as follows:

$$3\ N_2H_4 - 6e^- \rightarrow [\ 3\ HN{=}NH\ ] \rightarrow 2\ N_2 + 2\ NH_4^+ = 4H^+ \qquad (3)$$

During the electrolysis the decrease in hydrazine concentration was monitored spectrophotometrically by using p-dimethylaminobezaldehyde. As can be seen from Figure 1, the destruction of hydrazine is complete up to the detection limit (5.0 μg/L) (ASTM: D1385-88).



1) Before Electrolysis
2) After Electrolysis

Figure 1: Absorption Spectra of p-dimethylaminobenzaldazine.

Results 2

A total of 50 electrochemical oxidation experiments were performed on simulated UDMH wastewaters combining different UDMH concentrations, pH, anodes, and current. The analysis of voltamperometric and cyclic voltammetric curves shows that UDMH has two anodic waves. The half wave potentials are -0.08 and 0.16 Volts. This process involves the loss of two electrons and a proton (Cauquis, 1972). This shows UDMH to be a strong reducing agent. We achieved similar results with our cyclic voltametric measurements of the UDMH solutions. Depending on the pH of the solutions, the reactions could be as follows:

$$(CH_3)_2NNH_2 - 2e^- \rightarrow (CH_3)_2N^+{=}N^- + 2H^+ \qquad (4)$$

or

$$(CH_3)_2N^+HNH_2 - 2e^- \rightarrow (CH_3)_2N^+{=}NH + 2H^+ \qquad (5)$$

If the oxidation is carried out in the presence of oxygen, or oxygen containing oxidants, the reaction pathway is different:

$$(CH_3)_2NNH_2 \xrightarrow{O_2} (CH_3)_2N\text{-}NHOOH \rightarrow \underset{\text{NDMA}}{(CH_3)_2N\text{-}NO} \qquad (6)$$

The product, NDMA, is very toxic. Not only is NDMA a UDMH autooxidation product, but it is also a chemical oxidation product as well. This indicates that the electrolysis must be performed with a current and voltage without the evolution of oxygen from the water on the anode. This first step in the UDMH destruction was found to be more efficient at a pH of 7 using a graphite anode and low current in order to prevent oxygen evolution. In this case the diazine, $(CH_3)_2N^+{=}N^-$, is formed as the initial product via reaction (4). This produces a pink colour to the solution. The dimethyldiazene is very reactive and unstable and escapes quickly by the formation of tetramethyltetrazene. This produces two absorption maxima in the UV range, λ_1 = 240 nm and λ_2 = 274 nm. This is in very good agreement with previous investigators (McBride, 1957). Another strong absorption is found at λ_3 = 359 nm. When the solution is acidified to a pH of 2, the peaks at 240 and 274 nm disappear, and a new peak at λ = 234 (236) nm appears. (Figure 2) According to McBride, this absorbance is indicative of a conjugated acid of tetramethyltetrazene. If this step is carried out in a high current, a large amount of NDMA is formed (λ = 227 nm). According to the preceding, a possible mechanism for the first step reaction could be:

$$(CH_3)_2NNH_2 \rightarrow (CH_3)N^+{=}N^- \rightarrow (CH_3)_2N\text{-}N{=}N\text{-}N(CH_3)_2 \qquad (7)$$

$$(CH_3)_2N\text{-}N{=}N\text{-}N(CH_3)_2 \xrightarrow{H^+} (CH_3)_2N^+H\text{-}N{=}N\text{-}N^+H(CH_3)_2 \qquad (8)$$

The main question in this step is what substance gives an absorbance at λ = 359 nm? According to the results obtained by S. Banerjee (1984), and J.R. Bohem (1975) and our own observations, this substance is 1,5,5-trimethylformazan. In the formation of formazan, a formaldehyde-dimethylhydrazene intermediate may be formed. This could be the result of tetrazene hydrolysis or it could be formed via the following reaction:

$$(CH_3)_2N\text{-}NH_2 + H_2O \rightarrow CH_2O + CH_3NH\text{-}NH_2 \qquad (9)$$

$$CH_2O + CH_3NH\text{-}NH_2 \rightarrow (CH_3)_2N\text{-}N{=}CH_2 + H_2O \qquad (10)$$

Any attempt to identify formaldehyde with the chromatropic acid test (Feigl, 1966) during the first step were unsuccessful. Probably reactions (9) and (10) occur too quickly to identify the intermediates.

If these considerations are true, then the formation of formazan is easy to explain. The process is even more simplified at low pH values (Figure 2) and it could be as follows:

$$(CH_3)_2N\text{-}N{=}CH_2 + (CH_3)_2N^+{=}NH \rightarrow (CH_3)_2N\text{-}NH\text{-}CH_2\text{-}N{=}N^+(CH_3)_2 \rightarrow$$

$$(CH_3)_2N^+{=}N\text{-}CH{=}N\text{-}N(CH_3)_2 \rightarrow CH_3\text{-}N{=}N\text{-}CH{=}N\text{-}N(CH_3)_2 \qquad (11)$$

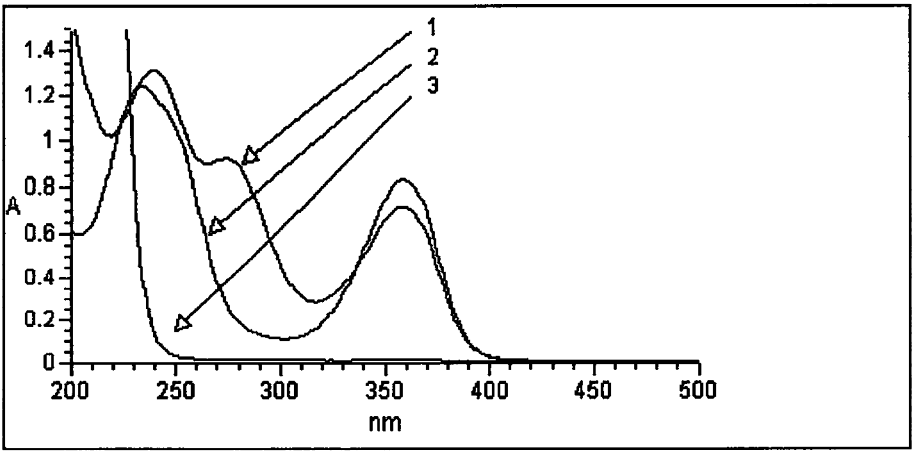
The second step in the destruction mechanism is to treat the solution (pH 2) with an appropriate amount of $NaNO_2$. After this step the solution becomes a deep yellow orange. It seems that some nitroso derivatives are formed since the solution may contain protonated tetrazene, protonated dimethylhydrazone, and some other secondary amine-like compounds. Formazan does not tend to undergo nitrosation.

The chemistry of the second step is not well understood and needs further investigation.

The third step involves electrolysis under higher current conditions. During this process the decrease in concentration of intermediate was monitored by UV spectroscopy. At the end of the process no absorbance at $\lambda = 234$ or $\lambda = 359$ nm were observed (Figure 2). The initial concentration of UDMH was adequately determined by using trisodium pentacyanoamino ferroate (TPF). This very sensitive reagent forms a red colour with UDMH, with an absorption maxima of $\lambda = 500$ nm. Unfortunately TPF cannot be used to monitor the decrease in the concentration of UDMH during the electrolysis due to the presence of interfering intermediates. At the end of the electrolysis a sample of the solution was treated with TPF and no absorbance was recorded at $\lambda = 500$ nm. This indicates a concentration of less than 0.6 μg / L (Feigl, 1966).

The presence of dimethyl amine was determined by GC purge and trap, and by GC/MS. The Merk ammonia test showed approximately 60 ppm of ammonia, while the chromatropic acid test showed a small amount of formaldehyde present in the end solution. We can therefore say that in the third step, the reduction on the cathode and the oxidation on the anode take place at the same time. Note that the electrolysis was carried out without a membrane between the anode and the cathode.

The end products of the UDMH destruction are: Nitrogen, nitrous oxide, formaldehyde, and dimethylamine. These results are only preliminary and more study must be carried out.



1) After step 1 at pH7.
2) After step 1 at pH2.
3) After step 3.

Figure 2. Absorption spectra of UDMH destruction pathways.

Results 3

In these experiments the autooxidation of UDMH was carried out. A solution of UDMH at 98% purity from Fluka was exposed to open air. The substance became brown. This brown substance was diluted to 200 ppm in water and analyzed by GC/MS and UV/VIS spectroscopy. The presence of NDMA and other intermediates, mentioned in results 2, were found. Then the three step electrolytical destruction process was carried out on this autooxidized solution. The analysis of the end products showed the presence of dimethylamine, but no NDMA.

Conclusions

The results obtained during the present investigation indicate that:

1. Electrochemical oxidation is an effective method to treat groundwater contaminated with Hydrazines.

2. The three step electrolytical destruction is a promising method to treat groundwater contaminated with UDMH and UDMH autooxidation products as well.

Acknowledgments

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Impact of New Jersey's Discharge Prevention Rules on the Frequency and Severity of Spills

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In September, 1991, New Jersey's Department of Environmental Protection adopted revised and updated administrative rules concerning the prevention, mitigation, and reporting of chemical spills. These rules require that major facilities meet standards in regard to spill prevention, cleanup and planning. A major facility is defined as any facility having a storage capacity of at least 20,000 gallons of designated hazardous substances.

After an initial increase in reported spills, the number has decreased over the past three years. Since the implementation of the revised rules, there has been no large spills reported. The rules have been successful in reducing the number and severity of spills that occur in New Jersey.

INTRODUCTION

The State of New Jersey first enacted the Spill Compensation and Control Act (the Spill Act) (N.J.S.A. 58:10-23.11) in 1977. The Spill Act required any person responsible for causing a discharge to report it to the Department of Environmental Protection (the Department). It also required the owner or operator of any facility with a storage capacity of 400,000 gallons or more of hazardous substances to prepare and submit to the Department Discharge Prevention, Containment and Countermeasure (DPCC) and Discharge Cleanup and Removal (DCR) plans. Litigation by the regulated community following promulgation of administrative rules under the Spill Act delayed implementation of those rules until 1980.

In 1979, the Spill Act was amended. Any facility with a storage capacity of 400,000 gallons of hazardous substances of all kinds or 50,000 of hazardous substances other than petroleum or petroleum products were now required to have DPCC and DCR plans. Who is required to report a discharge was also revised. Now any person who may be subject to liability for a discharge must report the discharge to the Department. In addition, discharges that occurred prior to the effective date of the Spill Act are required to be reported.

In the early 1980s, the discharge prevention program was relatively active, receiving and reviewing DPCC and DCR plans from the regulated community. However, during the late 1980s, due to lack of funding and interest, the program languished and was eventually reduced to one full-time employee.

Then, in 1989, the Exxon Valdez spill in Alaska brought national attention to the problem of discharges. In New Jersey, several spill events in early 1990 galvanized the State Legislature. A series of six bills were enacted in June 1990 revamping the requirements for DPCC and DCR plans and providing a source of funding for the discharge prevention program. These changes to the Spill Act, along with others passed in the intervening years, were incorporated into revised administrative rules which became effective in September 1991.

At the present time, facilities having a storage capacity of 200,000 gallons for all hazardous substances or 20,000 gallons for hazardous substances other than petroleum and petroleum products, termed major facilities, must have DPCC and DCR plans. The list of hazardous substances encompasses approximately 1,200 chemicals and chemical mixtures. There are nearly 500 facilities in New Jersey that are classified as major and are therefore required to prepare and submit DPCC and DCR plans to the Department.

PLANNING REQUIREMENTS

Under the discharge prevention rules (N.J.A.C. 7:1E), major facilities must meet standards that apply to equipment commonly used in the transfer, storage or handling of hazardous substances. Areas where hazardous substances are stored, transferred or handled must have adequate secondary containment. Aboveground storage tanks must have high level and high high level alarms and be integrity tested periodically. In-facility pipes must be labeled as to the hazardous substances that are transferred through them. Marine transfer areas must be illuminated and booms put in place before certain transfers begin. Leak detection devices are required in certain instances. Equipment that holds hazardous substances or is used to prevent a discharge must be properly maintained and leaks must be cleaned up in a timely fashion.

The rules do not overlook human beings as a cause of discharges. Employees must be properly trained in the handling of hazardous substances. Owners or operators must ensure that contractors that do work at the facility have properly trained employees. Standard operating procedures on all processes involving hazardous substances must be available to all employees at the facility. The site must have security in place to discourage vandalism.

However, even the most thorough planning to prevent discharges is not always successful. Therefore, contingency planning in the event of a discharge is also required of major facilities. They must indicate in their DCR plan what equipment and trained personnel is available to them, either on-site or through a contractor. They must also have a plan for deploying employees and equipment to protect human health and safety and the environment. A discharge cleanup organization can be utilized. A response coordinator must be appointed by all major facilities.

Both of these plans, the DPCC plan and the DCR plan, must be submitted to the Department for review and approval. As part of the DPCC plan, the owner or operator of a major facility may propose an upgrade schedule for complying with standards not currently met at the facility. An owner or operator may also propose alternative methods of compliance. The Department then works with the owner or operator to finalize a mutually agreeable means and timeframe for compliance. The plans may need to be amended over time to reflect changes at the facility. They must be renewed every three years.

The final deadline for submission of plans for existing facilities under the September 1991 rules was August 1, 1994. To date, the Department has received plans covering 482 facilities. 455 of these have been approved. Through inspections of suspected major facilities, additional facilities that are subject to the rules are being identified. Also, changes at an existing major facility may result in a reduced storage capacity that is below the regulated threshold, removing the facility from the program.

REPORTING REQUIREMENTS

Subchapter 5 of the rules requires that all discharges be reported to the Department. This includes discharges that come from sources other than those at major facilities and historical discharges, that is discharges that occurred before the effective date of the Spill Act or of the revised rules. There is no de minimis quantity below which discharges need not be reported. Historical discharges can be reported in writing. All other discharges are to be reported to the Department's 24-hour environmental hotline. These telephone notifications must be followed up within 30 days with a written confirmation report on the incident.

The initial notification must include information about the person reporting the discharge, where the discharge is or has occurred, what the discharge consists of, an estimated quantity, when the discharge started and whether it has ceased, and what actions will be taken to clean up and remove the discharge. This notification must be made within 15 minutes of the time the person responsible knew or should have known of the discharge. The rules do allow for a justification of delay for cases where vital response actions to protect human life, or similar actions, are performed before notification of the Department.

DISCHARGE FREQUENCY AT MAJOR FACILITIES

Prior to the adoption of the revised rules in September 1991, no one within the Department kept track of those discharges associated with major facilities. However, the Bureau of Communications and Support Services tracks the total number of notifications, regardless of source, made to the environmental hotline. Data for the years 1989 through 1991 are shown in Table 1.

TABLE 1
Environmental Hotline Notifications

YEAR	TOTAL	HAZARDOUS SUBSTANCES	NONHAZARD. SUBSTANCES	OTHER
1989	14,658	5,893	7,927	838
1990	17,306	10,231	5,835	1,240
1991	20,326	11,307	7,270	1,749

The classification of "OTHER" includes notifications where the substance discharged was unknown. This data indicates that there was an overall increase in discharge notifications, with an 18% per year increase in the total and a nearly 100% increase in hazardous substance notifications in 1990 over 1989. The amendments to the Spill Act, increasing the number of substances on the list, were enacted in 1990.

Since January 1992, the Bureau of Discharge Prevention (Bureau) has been tracking the number of discharges reported at major facilities in New Jersey. This has been done through the confirmation reports that must be submitted. Table 2 shows the number of discharge confirmation reports received each quarter (Q) since January 1, 1992.

TABLE 2
Confirmation Reports Received

	1992	1993	1994	1995
1Q	152	219	182	184
2Q	326	216	180	
3Q	281	134	184	
4Q	209	175	163	
Totals	978	744	709	184

The data shows an initial increase from the first quarter (1Q) of 1992 to the second. This is most likely due to the learning curve, as more facilities determined that they are major and are required to submit confirmation reports. In addition, there is a one to two month lag between the initial notification and receipt of the confirmation report. After the high in the 3Q of 1992, the number of discharges per quarter has dropped and has remained around an average of 180 per quarter. There was a 14% drop in discharges between 2Q and 3Q 1992, and another drop of 26% percent between 3Q and 4Q 1992. From 4Q 1992 to the present average, an additional drop of 17% occurred, for an overall reduction of 44% per quarter in discharges from major facilities.

The primary cause of this reduction in discharges is the use of secondary containment. Releases that are held in an impermeable secondary containment area or are diverted to a holding area are not considered discharges. Thus, the requirement that major facilities have secondary containment for those areas that are most likely to experience a release, such as storage areas and truck transfer areas, greatly reduces the sections of a facility where a discharge can occur. There have been instances of aboveground storage tanks leaking into secondary containment, but they have not resulted in a release to the environment. This is the one of the desired outcomes of the adoption of N.J.A.C. 7:1E.

DISCHARGE SEVERITY AT MAJOR FACILITIES

The information contained in the discharge confirmation reports received from major facilities was analyzed to determine the distribution of the discharges with regard to size. Five classifications were used: over 10,000 gallons ($>$10,000); 1,000 to 10,000 gallons ($\geq$1,000); 100 to 1,000 gallons ($\geq$100); 10 to 100 gallons ($\geq$10); and less than 10 gallons ($<$10). Table 3A shows the number of discharges recorded for each category for each calendar year.

TABLE 3A
Distribution of Discharges by Size

	1992	1993	1994	1995*
> 10,000	0	1	4	0
≥1,000	31	23	30	16
≥100	98	87	82	47
≥10	268	211	188	35
< 10	581	422	405	86
Totals	978	744	709	184

*through 3/31/95

While Table 3A is useful in showing the absolute number of the discharges in each size category, it does not tell the whole story of impact on the environment. For example, the five discharges that fall into the largest category all consisted of water containing trace amounts of hazardous substances. So, although the 1993 discharge was 30,000 gallons, it consisted of cooling water with 0.5 parts per million cupric nitrate. Without a de minimis quantity or concentration for reporting, discharges of this type must be reported. This is because, depending upon the area where the discharge occurred, such a discharge could have a significant impact on the environment.

Another way to look at the distribution of discharges is as a percentage of the whole. This makes it easier to compare years even though the total number of discharges has been dropping each year. Table 3B shows the percentage of discharges that fall into each category for each calendar year.

TABLE 3B
Percentage of Discharges of a Given Size

	1992	1993	1994	1995*
> 10,000	0	0.1	0.5	0
≥1,000	3.2	3.1	4.3	8.5
≥100	10.0	11.7	11.6	25.5
≥10	27.4	28.3	26.5	19.1
< 10	59.3	56.5	56.5	46.8

*through 3/31/95

The data in Table 3B shows that although the total number of discharges has gone down, the distribution has remained fairly constant. There has not been a catastrophic discharge from a major facility since the implementation of revised N.J.A.C. 7:1E.

The majority ot discharges at major facilities are of quantities under 10 gallons. Over 80% are under 100 gallons. Many of these are discharges from mobile equipment, such as breaks in hydraulic systems, or discharges from in-facility pipes, such as gasket leaks. These types of discharges are difficult to prevent, but can be mitigated with rapid responses. The data appear to indicate that major facilities are making quick responses and are keeping many discharges under 10 gallons in size.

There is also other, anecdotal, evidence that discharges have been reduced or mitigated. The Bureau receives reports from facilities indicating that hazardous substances have leaked into secondary containment areas and not been released to the environment. There is at least one case where the requirement that booms be deployed around ships prior to the commencement of a transfer has kept a discharge from a vessel from being a serious incident. In general, these anecdotal reports are to be preferred over discharge ntoifcations and confirmation reports.

CONCLUSIONS

Since the inception of the present discharge prevention program in September 1991, the regulated community has been doing a good job of preventing and mitigating discharges. N.J.A.C. 7:1E appears to be having the desired effect of reducing or eliminating discharges. There have been no catastrophic discharges from a major facility in the period January 1, 1992 through December 31, 1994.

As time passes and owners and operators of major facilities in New Jersey complete any necessary upgrades to meet the standards in N.J.A.C. 7:1E, the number of large discharges (10,000) should further decrease. Once all storage, transfer and process areas have secondary containment, this will eliminate most sources of large discharges at major facilities. The overall size of discharges should also begin to shrink as the training and standard operating procedure requirements make responses to discharges at major facilities more efficient and effective.

In summary, the discharge prevention program has been successful in working with the regulated community to reduce the impact of discharges of hazardous substances on the environment. The Department hopes to continue this fruitful relationship with major facilities in New Jersey.

ENVIRONMENTAL IMPACT OF POLYCHLORINATED BIPHENYLS (PCBs) SPILLS AND FIRES

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ABSTRACT

First developed and synthesized in 1881, and commercially introduced in 1929, PCBs were manufactured in response to the North American electrical industry's urgent need for a more stable and effective transformer and capacitor fluid. Unfortunately, their chemical and physical stability have also led to widespread environmental contamination problem as a result of which their further import and use were banned in Canada in 1977. They are very persistent and they also bioaccummulate.

Because efficient destruction technology was lacking in the late seventies and early eighties the obvious means of control was one of containment. PCBs and PCBs-contaminated materials were kept in temporary warehouses and special storage facilities. As of December 1993, there were 11,505 tonnes (net weight) of askarel still in use in transformers and capacitors, 15,247 tonnes (gross weight) of waste askarel and askarel equipment, 2,161 tonnes (net weight) of in-use PCB contaminated mineral oil, 3,787 tonnes (net weight) of waste PCB-contaminated mineral oil, and 107,991 tonnes (gross weight) of other PCBs waste consisting of soil, fluorescent lamp ballasts, drained equipment etc.

There were over 150 PCBs spills and fires last year some of which could have been very well prevented. Of these, 41 could be considered as major. PCBs enter the environment through leaks in piping systems, tanks, storage containers, routine disposals and manufacturing facilities when it was being produced and fires. The danger with PCBs fires is the formation of more toxic substances such as polychlorinated dibenzodioxins and polychlorinated dibenzofurans. Two case histories will also be described.

Of the various effects that have been noted in animal test systems, so far, only the dermatological effects like chloracne have been conclusively demonstrated in humans. Some scientists are of the opinion that PCBs are not as great a threat to human health as was once thought.

INTRODUCTION

The introduction of PCBs in electric transformers and capacitors in 1929 represented a major breakthrough in the history and technology of dielectric fluids

(Durfee et al., 1976). Essentially, PCBs were employed as a fire safety measure by virtue of their good dielectric characteristics, chemical and physical stability, and inertness which unfortunately have also contributed to their persistence and bioaccummulation in the environment (Jensen, 1986; Holmes et al., 1967.; Risebrough et al., 1969). As a group, PCBs may contain from 1 to 10 chlorine atoms attached to the biphenyl rings in 209 different ways or 209 isomers. As the number of chlorine atoms increase, so does the degree of bioaccummulation and persistence.

Pure PCBs are white crystalline solids but often liquid because of impurities. Because of the need for this dielectric fluid to transfer heat, PCBs were often diluted with chlorinated benzenes to yield askarels which are less viscous (Durfee et al., 1976; Miller, 1982). PCBs fluids are no longer manufactured but continue to be released into the environment through the use and disposal of the large quantities already in use or storage.

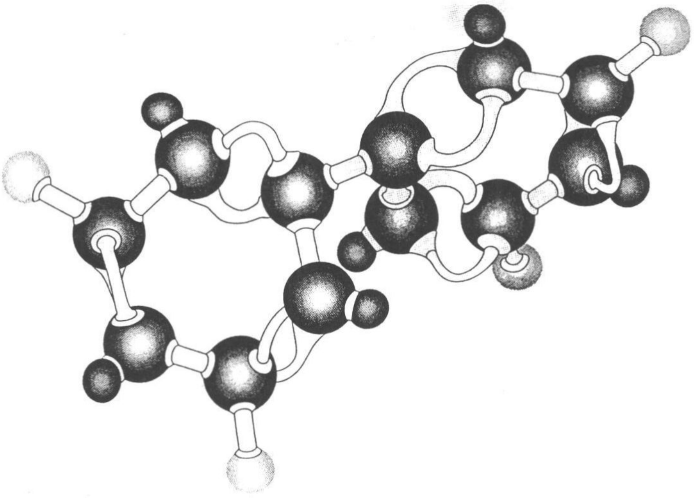


FIGURE 1: THE PCB MOLECULE

Spill Profile

For unknown reasons PCB spills are a politically sensitive issue and this substance has become identified in the public mind as one of the most hazardous compounds on earth. One probable reason is that they are ubiquitous and man-made, and aside from two incidents in Japan, not much is known about their long term effects on exposure at low levels. Of all the various toxic effects demonstrated in animals, only one or two has been clearly shown in humans. Because of several government and industry initiatives and public awareness the frequency of PCB spills has gone down dramatically. In 1977 the Canadian government banned further production and import of PCBs into Canada.There are still large quatities of PCBs in Canada. As of December 1993, according to the national inventory there were 11,505 tonnes (net weight) of askarel still in use in transformers and capacitors, 15,247 tonnes (gross weight) of waste askarel and askarel equipment, 2,161 tonnes (net weight) of in-use PCB contaminated mineral oil, 3,787 tonnes (net weight) of waste PCB-contaminated mineral oil, and 107,991 tonnes (gross weight) of other PCBs waste consisting of soil, fluorescent lamp ballasts, drained equipment etc (Environment Canada, National Inventory, 1995). There were about 41 major PCB spills last year some of which could have been very well prevented (NATES, 1995). See figure 2. Other minor ones (109) are not included in the chart.

Most spills occur at stationary situations, from leaking pipes, leaking transformers and capacitors and during retrofitting. Such electrical equipment may occasionally fail resulting in fluid release. Spills can also occur sometimes as a result of accidental damage from vehicle accidents and human error (NATES, 1995). Some spills have also been reported during normal maintenance of large tranformers and other equipment involving dielectric fluid such as retrofilling, bushing repair, and topping up.Yet others occur through unlawful disposal.

Table 1 below shows how PCBs are placed in an investigation researched by our branch six years ago. Our main goal then was to determine the minimum number of hazardous chemicals 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 and persistence. PCBs came fifth in the study. Figure 2 below shows the annual frequency of PCBs spills for the last decade. The graph shows progressive decrease in the frequency of spills since 1988. Figure 3 shows how the spill frequency of PCBs compare with other commercial chemicals during transportation only. The graph is not surprising since PCBs are not often transported in Canada.

TABLE 1: PRIORITY LIST RANKING OF PCBs

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

FIGURE 2: SPILL PROFILE OF PCBs 1984-94. ANNUAL SPILL FREQUENCY

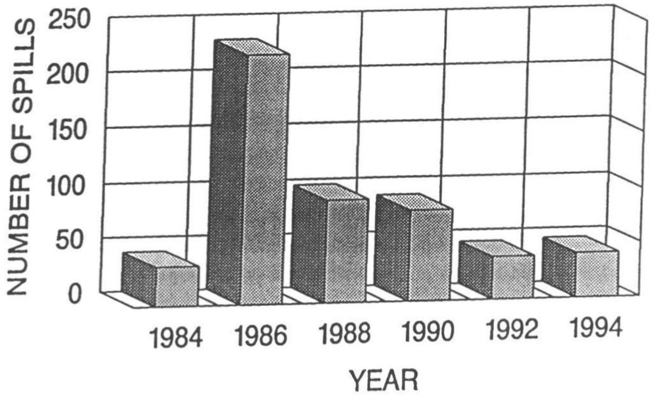
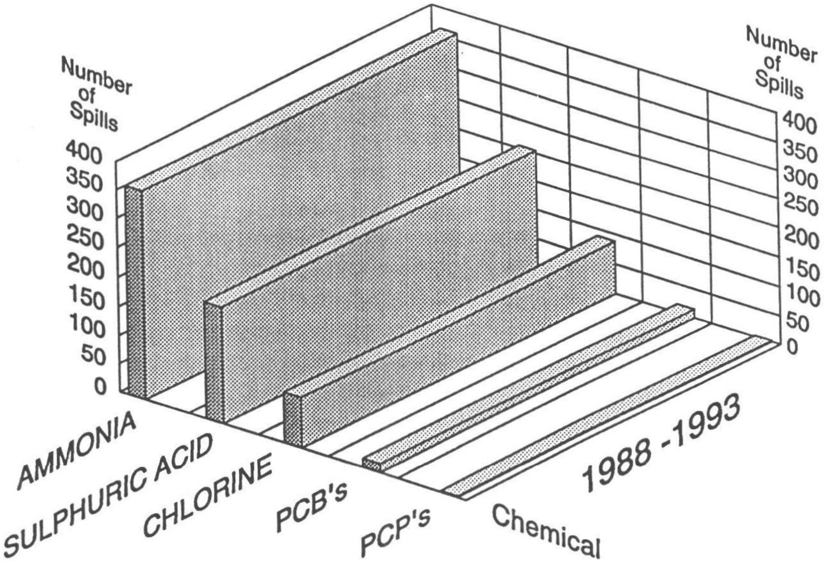


FIGURE 3: THE SPILL PROFILE OF PCBs 1988-93. TOP 5 PRIORITY CHEMICALS COMPARED (TRANSPORTATION BY RAIL AND ROAD).



Behaviour and Environmental Fate During a Spill

There are no known natural sources of PCBs. Sources are mainly anthropogenic. PCBs were prepared commercially by the chlorination of biphenyl with anhydrous chlorine in the presence of catalysts, followed by some purification. Usually, the more time is spent on the purification step, the more chlorine substitution takes place on the rings.

"Behaviour" includes all the visible characteristics displayed by a chemical. PCB is a viscous to mobile, colourless to brown liquid that slowly spreads when spilled depending on the ambient temperature and formulation. Indoor spills usually occur in small quantities on concrete and its vapour will adsorb onto walls, carpeting, drapery, and metal objects. All forms of exposure should be avoided and the airborn concentration carefully monitored.On the other hand, outdoor spills could range from few drops from transformers to full trailer-tanks. It can take place on land or water. Knowledge about the behaviour and environmental fate of PCBs is rather fragmentary and still muddled.

From an environmental impact standpoint, the four most important physical properties of PCBs are very low water solubility, very low vapour pressure, high octanol-water partition coefficients and stability or persistence. There are five possible mechanisms by which PCBs can be transported in the soil a) as a dissolved material in the water b) by sorption c) as an emulsion with water d) as an immiscible oily liquid phase and e) as a discrete fluid. PCBs fluids are generally insoluble in water, and when spilled on the soil usually settle first as a pool on the ground surface before infiltration and downward movement through multi-layered soil, water and soil gases. The liquid fills the pores at the soil surface and begin to penetrate downward. Some evaporation of the lighter components will occur. The downward transport of oils and immiscible liquids has been extensively reviewed (Greenkorn, 1983). The downward penetration of PCBs fluid through the soil or a porous medium has been shown to obey Darcy's Law. Darcy's Law states:

$$Q = KIA$$

where
Q is the vertical rate of flow of the fluid through the soil
I is the hydraulic gradient
A is the total cross-sectional area of soil penetrated
and
K is the coefficient of permeability, it embodies such things as coarseness, porosity, type of soil etc.
The equation may not be applicable to liquids that will react with the soil components, such as mineral acids and strong bases.

The different stages of PCBs fluid penetration through the soil is shown below:
1) Spill occurs.
2) Soil penetration commences.
3) Spill pool is dissipated
4) Saturated plug continues to move downward, leaving behind a constant residual saturation in the soil.
5) Saturated slug exhausted as residual saturation, downward movement ceases to occur
6) Light PCB oils form a pan cake and float on the water table
7) Heavy PCBs oils sink into the water table.

Extensive soil and water sampling will be necessary to determine the nature and extent of contamination when a spill occurs. Soil sampling should always be directed first at determining the presence of PCBs. Several quick tests are now available. Once the qualitative results are known, then the quantitative measurements can be made. One can also determine if a water table has been contaminated after a PCBs spill from a knowledge of the elapsed time, stratigraphy of the soil, the permeability coefficient, and the penetration depth. The area of the spill pool will increase with time and depth of soil penetration for a given location. Soil penetration is also dependent on the length of time that the spill pool has existed for the location. The maximum soil penetration will occur generally at the origin of the spill.

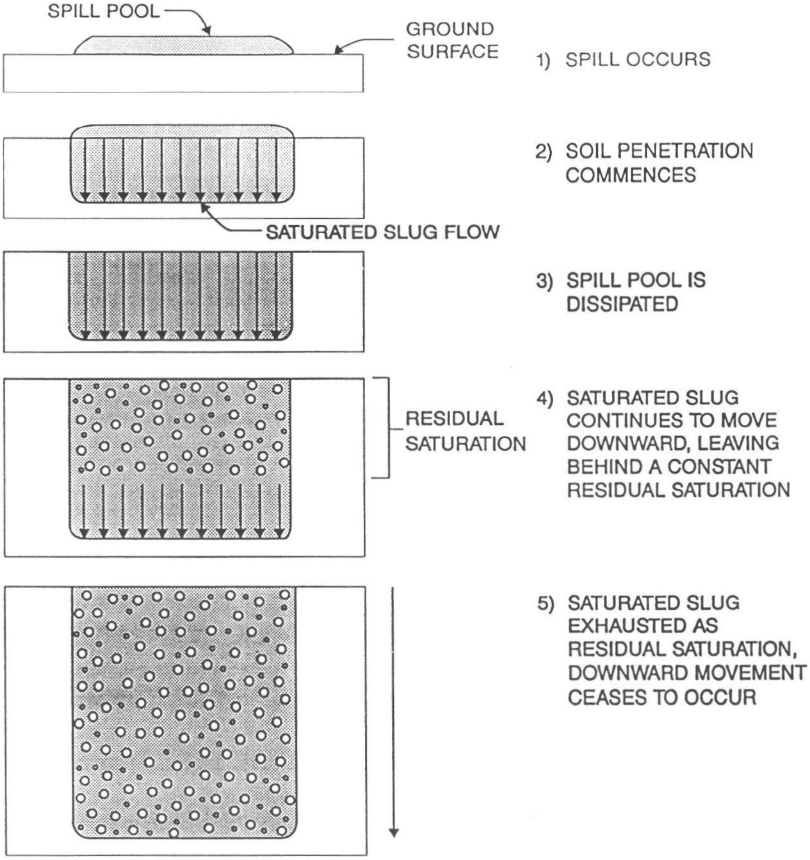


FIGURE 4: SUBSURFACE PENETRATION AND MOVEMENT OF PCBs

Spills on Water

PCBs fluids less dense than water (density of water=1,000 kg/m^3 ; average density of PCBs = 1,500 kg/m^3) such as contaminated mineral oils will float and assume a round or pancake type shape. It will subsequently be broken down into globules due to turbulence or action of the waves. On the other hand, PCBs fluids heavier than water will sink and will adhere to the sediments where it will be taken up by aquatic organisms. As for the PCBs fluids that float, even though not very volatile, some evaporation into the atmosphere may occur depending on the windspeed, temperature, atmospheric stability, and type of fluid. When human exposures are likely, protective respiratory equipment should be used. Table 2 below shows the distribution and fate of an Aroclor 1248 spill after 30 days. It is interesting to note that for spills on land, most of the Askarel ends up in the soil, while in the case of spills on water, the bulk of the askarel will eventually be adsorbed on to the sediments.

Table 2. DISTRIBUTION OF SPILLED AROCLOR 1248, 30 DAYS AFTER SPILL.

Medium	% PCB REMAINING LAND SPILL	% PCB REMAINING WATER SPILL
Air	0.005	0.4
Soil	96.3	0.04
Water	0.001	0.4
Bottom Sediment	0.001	90.1
Ground Water	0.003	0

Fires

The PCB molecule has two benzene rings or 12 carbon atoms as well as some chlorine atoms and therefore will burn when ignited. The main danger from a PCB fire is not the PCB itself, but the formation of extremely toxic by-products of combustion such as polychlorinated dibenzo dioxins, polychlorinated dibenzo furans and hydrogen chloride gas which often produces immediate respiratory effect. The formation of dioxins and furans from thermal degradation of PCBs has been reviewed (Choudhry and Hutzinger, 1983; Erickson, 1984b). The reaction is shown in the equation below.

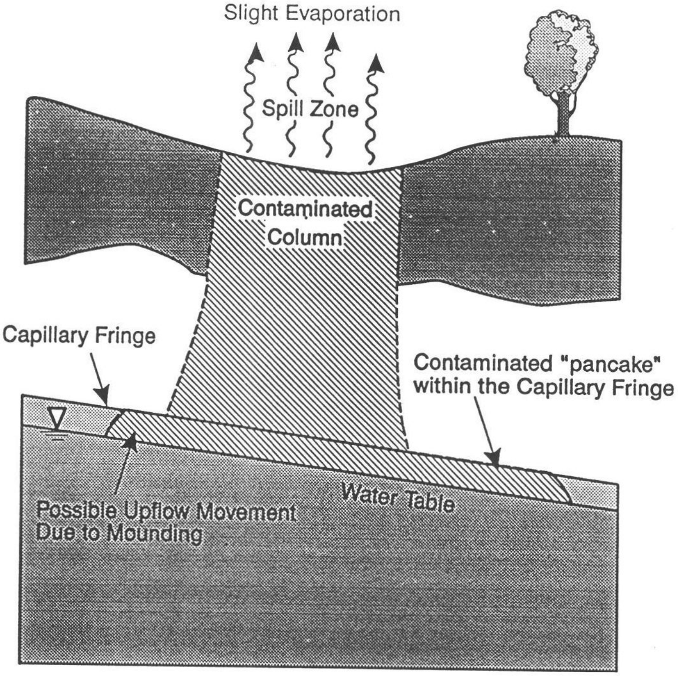


FIGURE 5: SUBSURFACE TRANSPORT OF PCBs LIGHTER THAN WATER

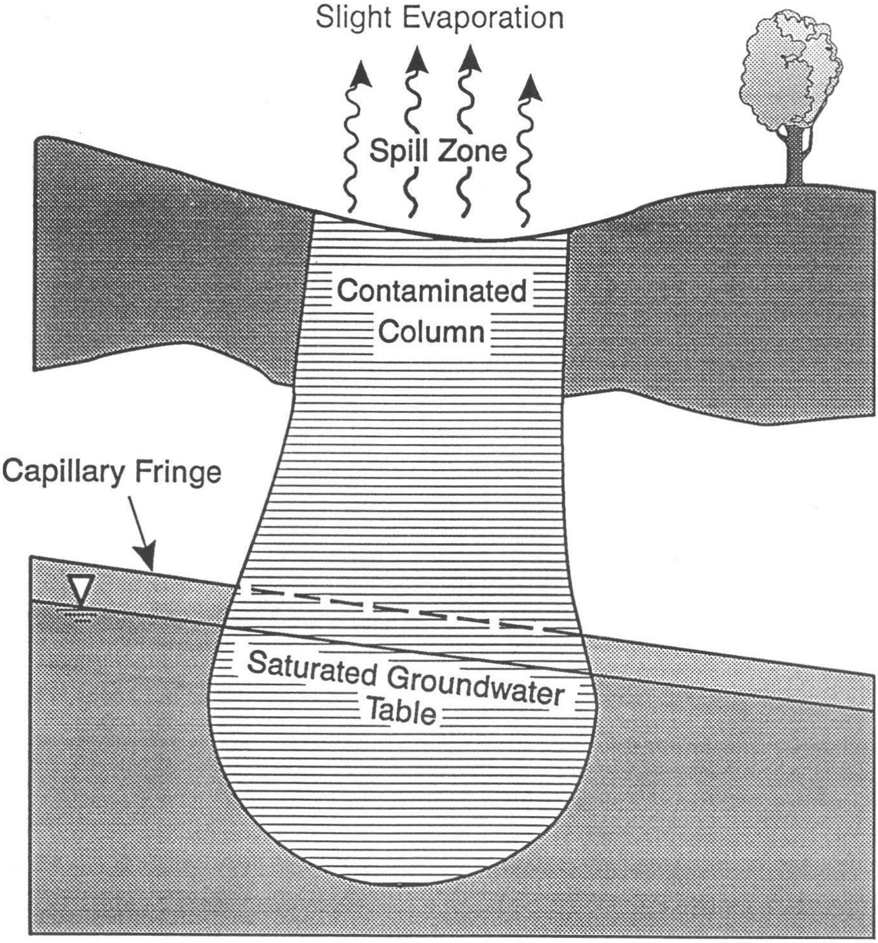


FIGURE 6: SUBSURFACE TRANSPORT OF PCBs DENSER THAN WATER

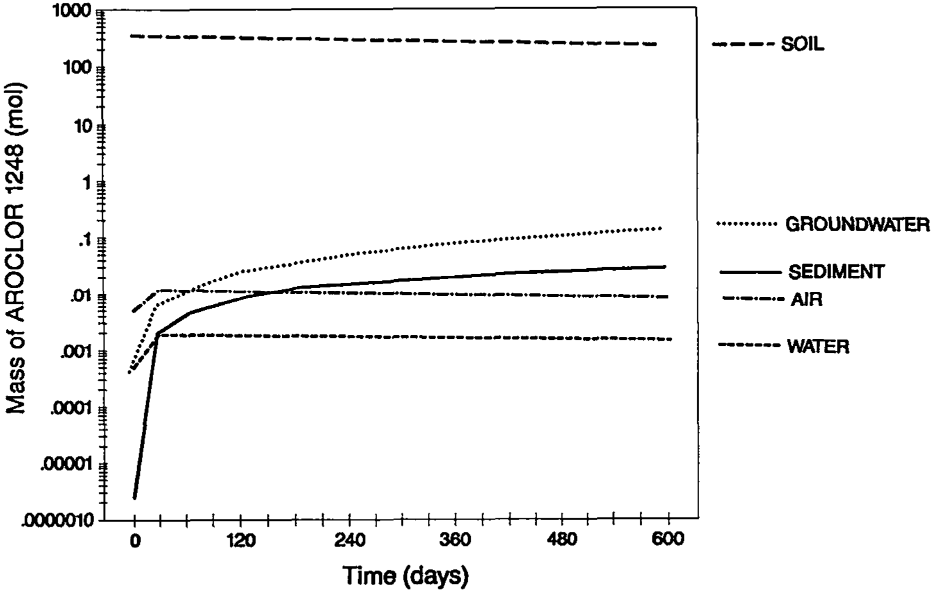


FIGURE 7: AROCLOR 1248 DISTRIBUTION AS A FUNCTION OF TIME FOR A LAND SPILL

Dioxins are frequently formed during thermal breakdown as a result of molecular rearrangement of chlorinated organic compounds and trace metals during inceneration. The actual formation of dioxins takes place after flue gases, fly ash, and other by-products have begun to cool down and condense at about 300 °C. While the formation of furans only requires oxygen insertion into the PCB molecule, the formation of dioxins would require extensive bond breaking, molecular rearrangement, presence of chlorobenzene or similar organochlorine compounds, and inorganic chlorine ions. Incomplete combustion of PCB usually produces furans. Its synthesis often takes place during the post-combustion phase. Generally, PCDDs in soot from fires involving PCBs range from non-detectable to 19 ppm. There are three current theories about dioxins and furans presence after a PCB fire:

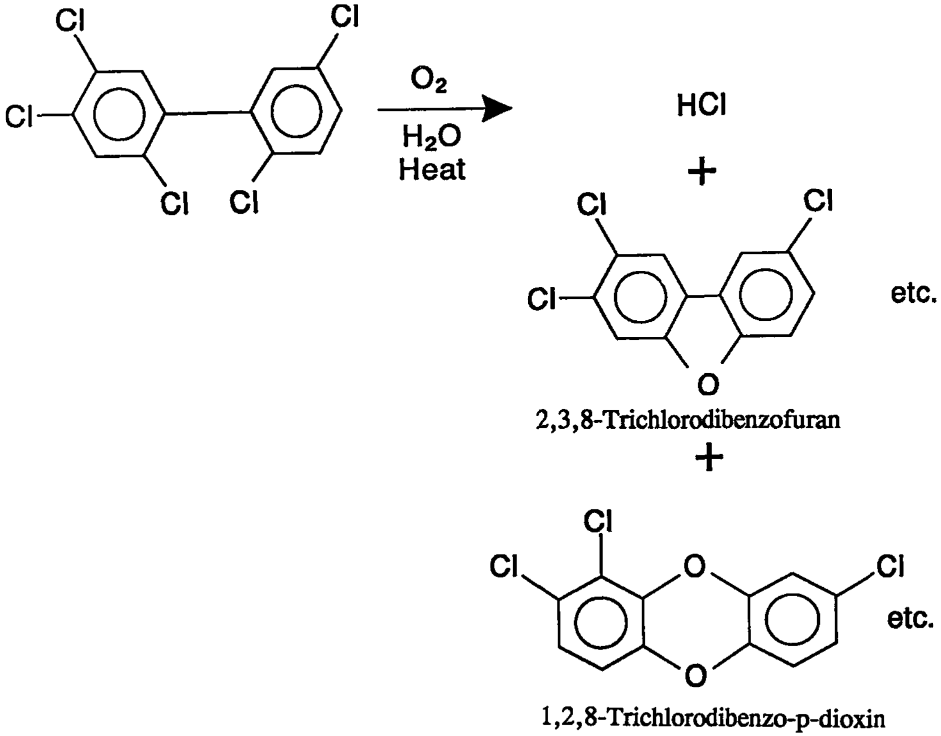
1) That dioxins and furans were present all along and they were able to survive the thermal stress.
2) That dioxins and furans were formed as a result of thermal breakdown and molecular rearrangement of the starting materials to form precursors very similar to dioxins and furans. Such intermediates found are: chlorinated phenols, polychlorinated biphenyls, and chlorinated benzenes.
3) That dioxins and furans are formed from precursors that bear no resemblance to these products. For example burning of different non-precursor substances such as cellulose, lignin, chlorinated plastics, hydrogen chloride gas, and other petroleum products have produced dioxins.

Environmental Fate and Transport

The predominating factors in terms of the environmental fate of a chemical when spilled are its physico-chemical properties as well as the location and weather conditions. Environmental transport of PCBs is rather global. PCBs are tranported by air, water, insects, fish, birds, humans and also deposited by rain, snow, and dry fallout. Polychlorinated biphenyls have been detected in all corners of the globe and in almost every media including soil, air, sediment, water, human milk, fish,sea gulls, meat, and even polar bear. While very low concentrations have been found in the air and water, extremely high levels have been reported in soils, sediments, and aquatic biota. This is not surprising given the persistence of these chemicals and the various forms of transport involved. The ultimate sink for PCBs spills are the sediments. There are various types of models which have been used to predict the environmental long-term fate of spilled chemicals. In fate and transport studies, four types of chemical releases are possible, these are volatilization, run-off, leaching to ground water, and fugitive dust emissions.

Volatilization

Even though the vapour pressure of PCBs is very low, small amounts of spilled PCBs will slowly evaporate into the overlying air (evaporation rate is about 4.8×10^{-4} to 7.8×10^{-5} g/m^2/h). This can happen for both spills on water and soils. Calculations of average mass losses through evaporation could be computed for many spills. As for PCBs mixtures that contain chlorobenzenes and mineral oils, the lighter components



THERMAL DEGRADATION OF PCBs

consisting mainly of chlorobenzenes and mineral oils will evaporate first, leaving behind the much less thicker PCBs. The evaporation rate is dependent on the windspeed and temperature. However, the net result of volatilization is the removal or transference of PCBs from one environmental compartment to another without any net loss from the environment.

Run-off

In the case of spills that occur near coastlines or water bodies, transport of PCBs to receiving surface waters can occur through run-off of surface soil from the spill site. The amount of run-off will depend on the properties of the surface soil, the location, slope or proximity to the shoreline, and the nature of vegetation. Rough estimations of the mass of PCBs that is lost from a site have been made from the average concentration in surface soil, the amount of run-off and soil erosion.

Leaching to Ground Water

The potential for leaching into ground water of very small spills that were often encountered (about 1-2 L) is very small because of the strong adsorptive and relatively immiscible nature of PCBs in the soil. As for large spills, migration through the soil to shallow ground water is possible. Soil penetration is enhanced by rainfall that infiltrates through the soil downward to the water table as already discussed above. Some leaching can also occur through water movement as a result partitioning of PCBs, but this is not considered to be a major mechanism as the partitioning coefficient of PCBs is very low. Some estimations of distribution of a spilled aroclor 1248, thirty days after the spilled event is shown below for land and water.

Fugitive Dust Emissions

Stirring up of fine dusts contaminated with PCBs at spill and station sites can occur during heavy construction and blowing winds. Particles of smaller sizes can travel much longer distances than those of larger sizes. Hence it is not surprising to find PCBs in the Arctic as well as the Antarctic. PCBs are transported physically by air, water, human, animals, fish, birds and micro-organisms. Precipitation from air can also occur by rain, snow, vapour condensation and dry fall-out.

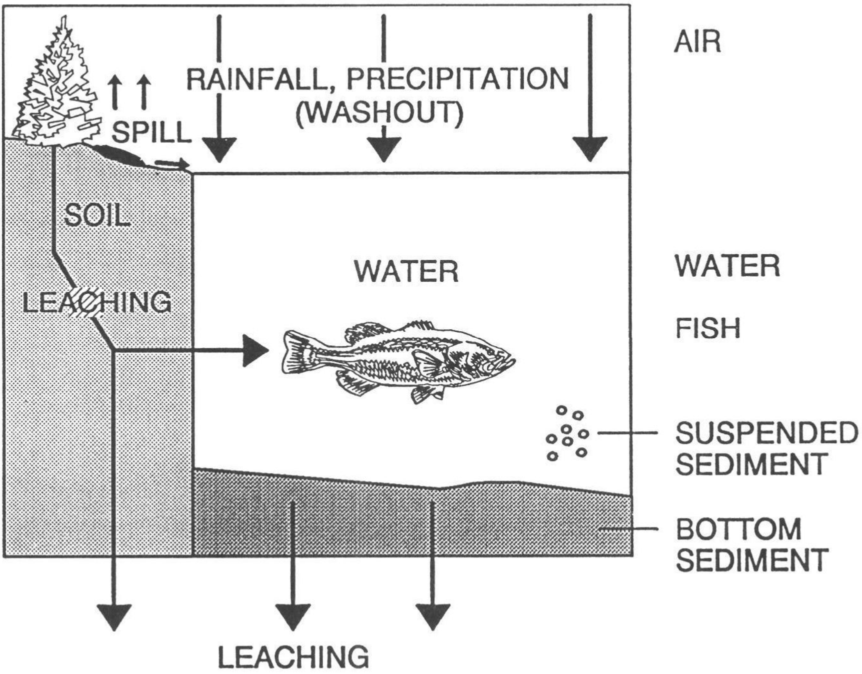
Destruction and Degradation

Abiotic Degradation

Incineration is the most common method of destroying PCBs. This method is carefully regulated to ensure that PCBs are completely destroyed since incomplete destruction can lead to more toxic products such as polychlorinated dibenzo furans and dioxins which are often detected during fires, use or aging of askarels. The destruction efficiency for incinerators has been determined to be 99.9999% for emissions of all PCBs incineration and can be achieved with high heat, long residence time, constant agitation, and various pollution control systems. High efficiency boilers have also been approved for PCBs combustion (Hunt et al., 1984).

Abiotic nonthermal methods include chemical processes such as reaction with molten sodium, sodium naphthalide, sodium salt in amine, catalytic dechlorination,

FIGURE 8: ENVIRONMENTAL FATE OF PCBs



wet air oxidation, ozonation, and physical methods including adsorption, microwave plasma, and photolysis. Photolysis is another possible route of environmental breakdown of PCBs. The process appears to occur by C-Cl bond cleavage to produce biphenyl free radical species which then abstract hydrogens Photolytic degradation depends on the degree of chlorination, position of chlorine substitution in the ring, and the solvent used for the PCB dissolution. For example, while the half-life of monochlorobiphenyl range from 0.62-1.4 days that of pentachlorobiphenyl is over 67 days. The photolysis of the o-chlorine has been shown to be probably due to steric hindrance to the preferred excited state geometry. Hence the more highly chlorinated commercial PCBs often photolyze preferentially in environmental samples. Bunce et al., (1978) reported that in shallow waters, at least one chlorine atom from highly chlorinated PCBs is photolyzed annually.

Biodegradation

The only form of biodegradation process is microbial degradation and includes different bacteria methods, activated sludge and trickling filters. Microbial degradation has been shown to depend on the degree and position of chlorination (Moolenaar, 1983). For example, the half lives of monochloro biphenyls has been shown to be about 2-3 days and over 3000 days for the pentachloro biphenyls. The fewer the number of chlorine atoms the higher the efficiency of degradation (Moolenaar, 1983). The substitution of chlorine also affects extent of dechlorination; it has been reported that ortho substitution markedly decreases the rate of degradation. Typical end products found were hydroxychlorinated biphenyls and chlorobenzoic acid (Messier et al., 1983).

Bioaccumulation, Bioconcentration and Biomagnification

Bioaccumulation. The hydrophobic and lipophilic nature of PCBs is a strong indication of their tendency to partition into the fatty tissues of animals. Their stability or persistence is an additional factor required for their accumulation since they cannot be readily degraded by enzymes. It has also been shown that species which have high lipid contents also tend to accumulate relatively large concentrations of PCBs. PCBs exhibit bioaccumulation tendency very similar to DDT and some chlorinated pesticides and the higher the degree of chlorination, the more readily it will be accumulated (Hansen et al., 1983). Other factors that affect PCBs bioaccumulation are:

1) Duration of exposure
2) Temperature
3) Solubility
4) Species age
5) PCBs concentration
6) Adsorption
7) Lipid content

Bioconcentration. Uptake of PCBs from surrounding water and sediments has been demonstrated for many aquatic animals such as young oysters, clams, worms etc.

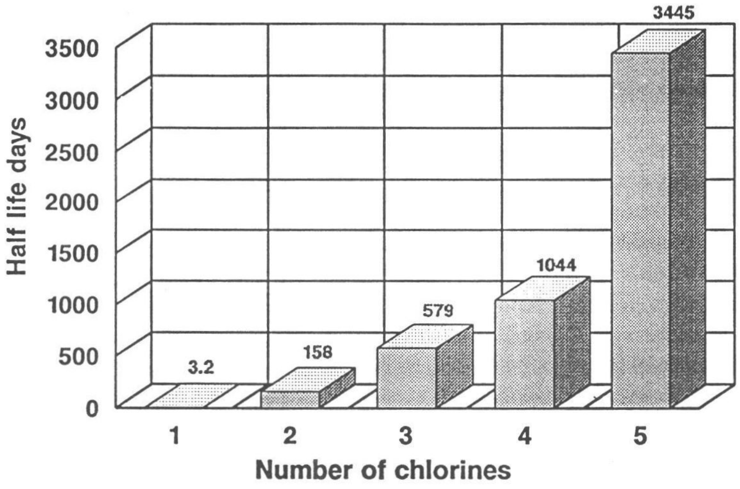


FIGURE 9: ENVIRONMENTAL PERSISTENCE OF PCBs

Biomagnification. Several authors have reported that PCBs concentration in the food web components show a stepwise increase at each trophic level. PCBs are accumulated by lipid-water partitioning via the food chain.It is possible that different PCBs uptake mechanisms exist at different trophic levels.

Previous Spill Experience and Lessons to be Learned

In this section the two worst case histories of a PCBs spill and a fire are presented that will exemplify some aspects of PCBs behaviour and environmental fate as described above.

Polychlorinated Biphenyl Spill at the Federal Pioneer Limited, Regina, Saskatchewan, 1976.

In the summer of 1976, a large spill estimated between 6,800 and 21,000 liters of a transformer oil formulation (Inerteen 70-30) containing PCBs (Aroclor 1254), trichloro and tetrachlorobenzenes were spilled when an underground pipe broke at the Federal Pioneer Limited's manufacturing plant in Regina, Saskatchewan (Haug and Atwater, 1992; NRCC, 1980). The exact time was not known. The spill generated considerable interest because the spill site is located on a major aquifer that supplies drinking water to the city (there is also a potential for contamination of future water supply wells and aquifer not distant from the site). After the discovery, methods were sought to determine the extent, the surface and subsurface distribution of the spill. Six major hydrostratigraphic units were identified from detailed test drilling and sampling as shown below. These are from the top down: a thin surface fill, the Regina clay, the Condie silt, the till zone, the interglacial silt, and the Regina aquifer system.

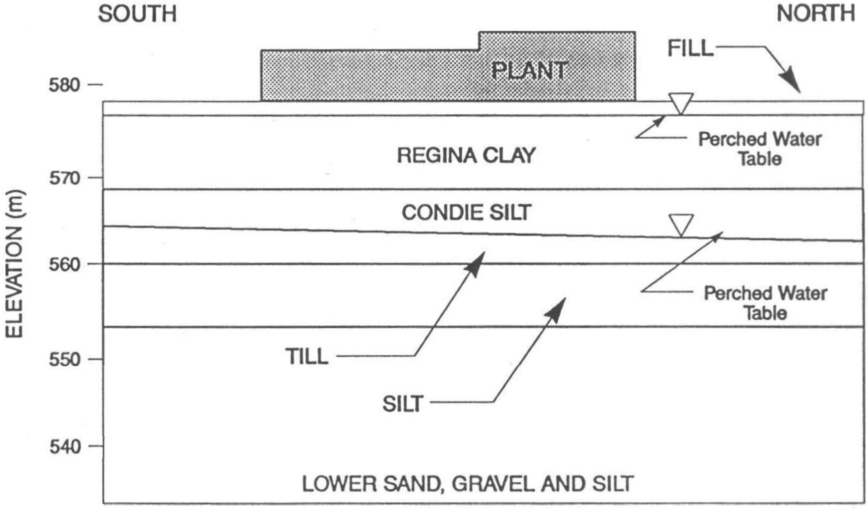
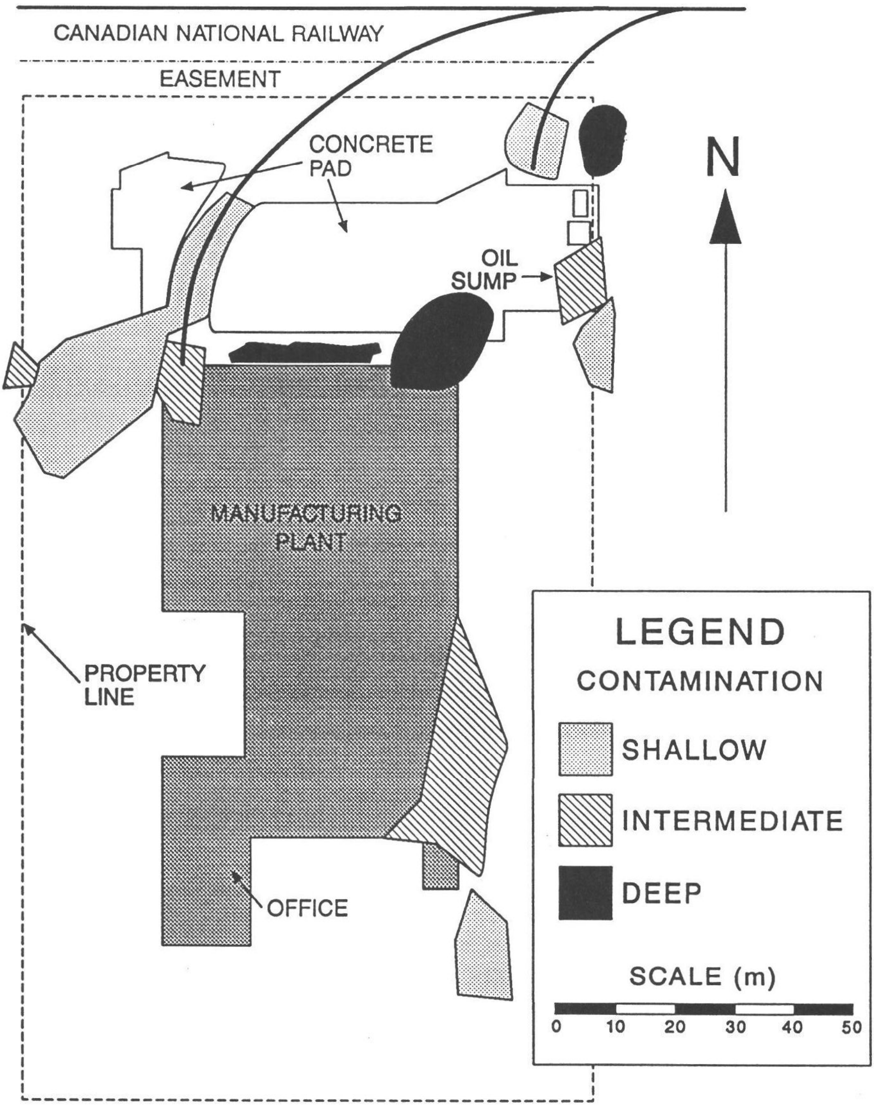


FIGURE 10: STRATIGRAPHIC CROSS SECTION OF SPILL SITE

FIGURE 11: LOCATION OF MAJOR CONTAMINATION AREAS



The permanent water table is situated below the Condie silt and the sandy glacial till. It was reported that an active perched ground water had developed within the thin fill layer beneath the the floor of the plant. The spread and extensive contamination of the PCBs have been the result of the lateral flow of the ground water. It was also found that PCBs have also moved downwards through fractures in the Regina clay and in the upper part of the Condie silt. It has been suggested that the potential for transport as a dissolved phase in the groundwater may be the mechanism for the PCBs migration downward to the aquifer or laterally to the surrounding sites.

Shallow sumps and deep wells were dug to dewater the site. The effectiveness was measured by a net work of piezometers. The extent of ground water contamination was also determined. PCBs concentration in the water collected from sumps on the site ranged from 1 to 500 ppm. High concentrations in the neighbourhood of 5,000 ppm were also detected in some cases. Excavation of soil containing over 50 ppm was done and transported to a storage facility nearby.

The remedial measures to contain and mitigate the effects of the spill consist of: the construction of a cutoff wall extending down through the clay to the silt on the spill site, the objective being to contain the spill; installation of a thick surface seal over the entire surface and active dewatering, this, it is hoped will prevent further downward migration of PCBs since one of the driving forces is the downward movement of moisture through the clay.

It has been suggested that the PCBs dissolved in mineral oil was the feasible mechanism for the contamination of the deeper wells. The PCBs have moved downward through fractures in the Regina clay and in the upper part of the Condie silt. It was also mentioned that the possible existence of fracture connections to the Regina aquifer and the possibility of transport in the dissolved phase may allow not only downward migration but also lateral off-site flow. A large amount of the PCBs found at great depths could have moved as discrete fluid.

The PCB Storage Depot Fire at Saint-Basile-le Grand, Quebec.

At about 2040 hours on August 23, 1988, a warehouse containing about 3,800 barrels of PCBs and PCBs contaminated oils (22,400 gallons of askarels in 45-gallon drums) was on fire. The warehouse, located on Road 116, at St.-Basile-le-Grand on the south shore of St. Lawrence River, is approximately 50 km east of Montreal, population, 12,000 (Journault et al., 1989; Phaneuf et al., 1995; Emergency Preparedness Canada, 1988). It took seven hours to put out the fire and four fire departments including the Canadian Forces Bay, St. Hubert and two police forces. Over 3,800 people were evacuated in the incident. At one time, the heat generated by the fire was so great that the roof and walls started to collapse and the PCBs drums were exploding.

When the fire subsided, a team of scientists from the River Road Environmental Technology Centre arrived on the scene during the night to determine the extent of contamination. The Quebec Environmental Department, the TAGA 3,000 team of the Ontario Ministry of the Environment, the TAGA 6,000 research group of the New York State Department Environmental Conservation were also involved. Contaminant levels in air, water, soil, vegetation, and livestock were measured. These

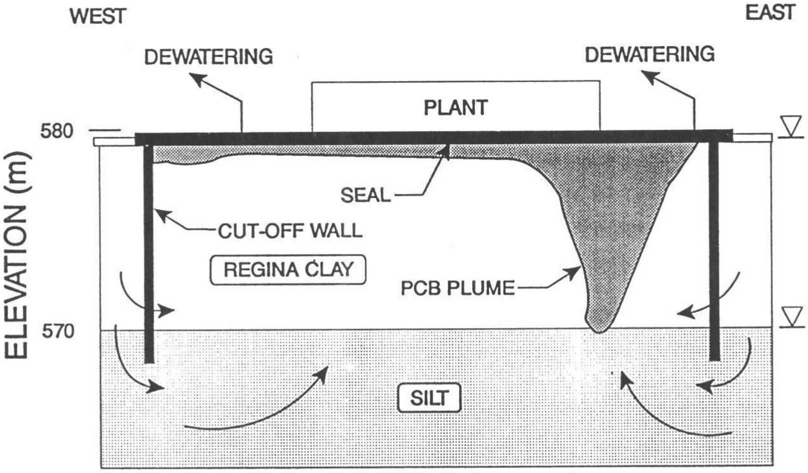
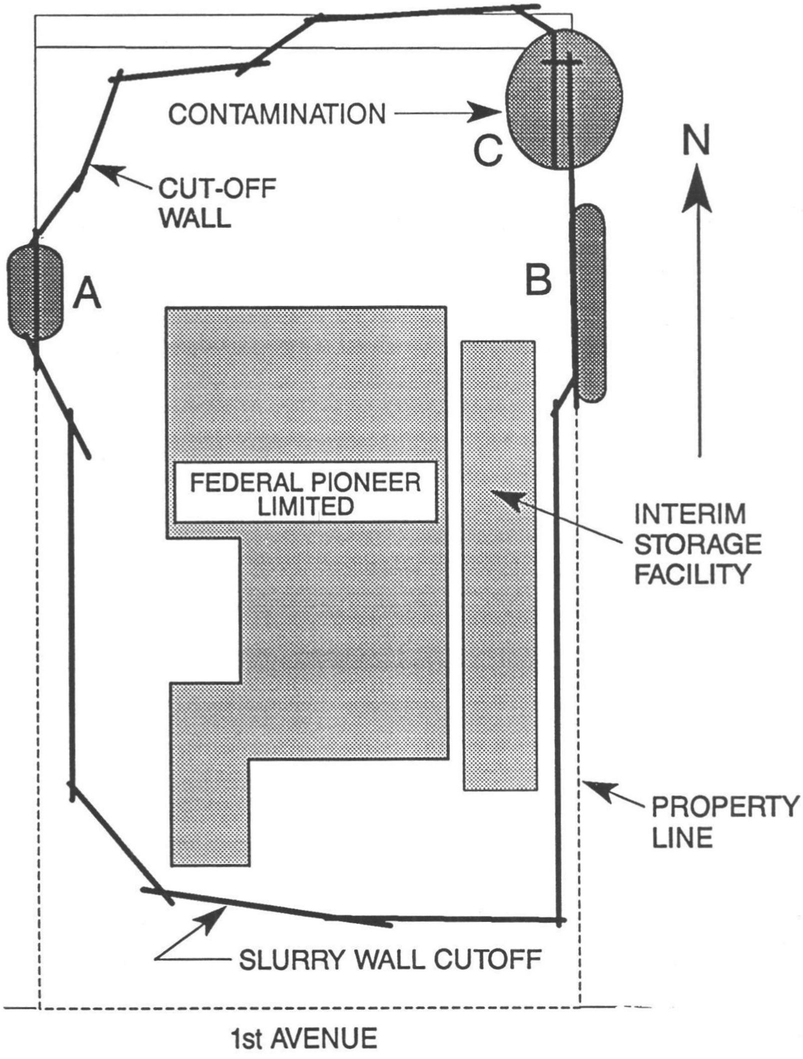


FIGURE 12: CROSS SECTION OF CUT-OFF WALL

FIGURE 13: CUT-OFF WALL AROUND PERIMETER



are some of their findings:

1.) All the air samples from the schools and residences were below the detection limits (100 ng/m^3).
2.) The maximum concentration of PCBs detected in the air samples was 11,512 ng/m^3).
3.) Mostly T_4CDF, P_5CDF and H_6CDF were found and small quantities of dioxins. The dioxins were generally H_6CDD, H_7CDD and O_8CDD.
4.) Most of the determinations were below the detection limits. One or two samples of PCBs were found in the soil and surface waters that exceed the guidelines toxicity equivalents (15 pg/L for surface water; 1 μg/kg for soil).
5.) None of the positive values for the PCBs and dioxins detected off site presented any health hazards since they are well below the guidelines (0.25 ng/100 cm^2) and cannot be of concern.
6.) Near the site, the levels of both dibenzodioxins and dibenzofurans were as high as several hundreds of ppm.
7.) Plenty of oil droplets that vapourized in the fire and particulates were found to contain PCBs and furans two times below the exposure limit.

Complete combustion of PCBs will produce hydrogen chloride gas and carbon dioxide, while incomplete combustion will yield in addition, plenty of soot and smoke, and far more toxic products such as polychlorinated dibenzo furans (mostly) and polychlorinated dibenzo dioxins as shown above.This is why incineration of PCBs is strictly regulated. The guideline is 99.9999% combustion.

Lessons to be learned.

1.) The two hazmat incidents amply illustrate the severe consequences of PCB spills and fires that will impact the environment for many decades to come.
2.) They demonstrate several aspects of spill science and technology. The cause, mechanisms, remedial measures, and how to minimize the impact and prepare for similar occurrences in the future.
3.) Fortunately no lives were lost, hazardous material disasters could be very expensive, St. Basile-le-Grand fire cost over $6.6 million, while that of Regina spill is over $5 million. In both cases, regular maintenance and vigilance is all that is needed.
4.) As far as the fire goes, a sprinkler system could have helped put out the fire at the initial stages or at least cool down the warehouse structures. A chemical foam and fire alarm system that can be activated on temperature or smoke basis could also have been installed in such storage places; materials for clean up, self contained breathing apparatus, protective clothing and portable fire extinguishers should also be available.
5.) The broken pipe at the Federal Pioneer in Regina also could have been prevented with accurate leak detection system. It was reported that the pipe had been leaking for some time in which case it could have been detected much earlier.
6.) Steps should also be taken to incenerate or get rid of all the PCBs and PCBs contaminated oils that are in storage to avoid fire accidents such as this.

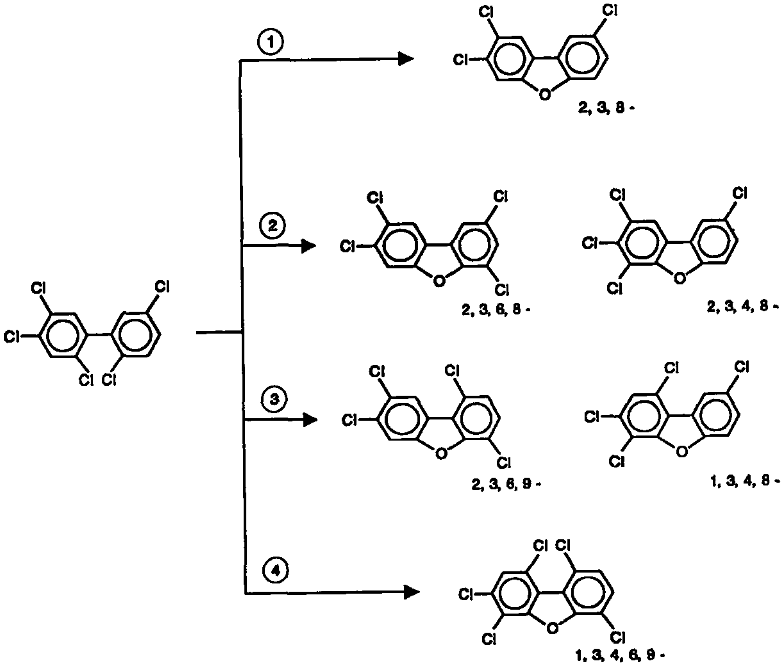


FIGURE 14: DIBENZOFURANS FROM A PCB THERMAL DEGRADATION

TOXICOLOGICAL PROFILE

PCBs do not appear to be toxic for short-term exposure. There are no reported deaths of humans as a result of a single ingestion. However, experiments in animals suggest that an ingestion of 6-10 fluid ounces would cause death to a healthy 150 lb adult. Much lower dose levels for chronic exposures have been found to show various toxic effects which are very similar to those of polychlorinated dibenzo furans and other halogenated aryl hydrocarbons and include such symtoms as shown below. The Yusho and Yucheng incidents have provided much of the information on PCBs effects on humans (W.H.O., 1976; NIOSH, 1977; Gaffey, 1983a and 1983b).

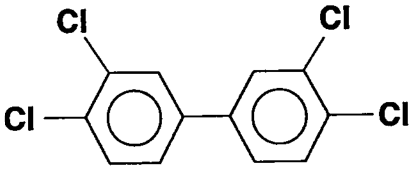
1.) Chloracne, black beads, skin lesions in many laboratory animals and humans.
2.) Immunotoxic effects.
3.) A wasting syndrome.
4.) Reproductive and fetal toxicity.
5.) Carcinogenesis and fetal toxicity.
6.) Porphyria and hepatotoxicity.
7.) The induction of various drug-metabolizing enzymes.

Other effects include unusual eye discharge by all routes, liver damage and digestive disturbance, burning feeling in the eyes, nose and face, dry throat, lung and throat irritation, nausea, and dizziness (Kimbrough, 1980c). PCBs toxicity is not only dependent on the degree of chlorination but also on the types of isomer. For example, PCBs which are devoid of ortho-substitution but are heavily substituted at the meta and para positions can assume a planar conformation that can interact with the same receptor as TCDD. Examples of these isomers area: 3,3',4,4'-tetrachlorobiphenyl; 3,3',4,4',5-pentachlorobiphenyl; and 3,3',4,4',5,5'-hexachlorobiphenyl.

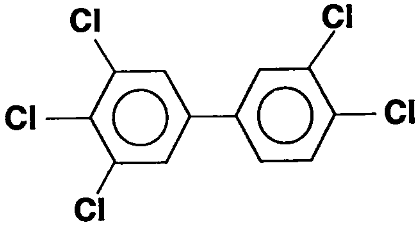
TABLE 3: HEALTH EFFECTS ON WORKERS EXPOSED TO PCBs.

Duration (years)	Enviro. level (mg/m^3)	Blood level (ppb)	Effects
Not known	10	-	Unbearable irritation
0.33-0.66	5-7	-	Chloracne
1-20	0.2-1.6	370	Chloracne, hyperpigmentation, liver injury
2.5	-	820	Chloracne
2.5-18	0.013-0.27	36-286	Irritation, liver injury
1.17	0.1	-	Chloracne, liver injury
2-23	0.32-1.44	>200	Chloracne, liver injury
Up to 15	-	7-300	Chloracne, elevated triglycerides.

FIGURE 15: NON-ORTHO COPLANAR PCB MOLECULES



(I)



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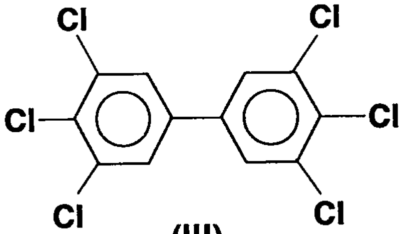


(III)

PCBs are included in the list of extremely hazardous substances compiled by the U.S. EPA. Some PCBs have been classified as suspected carcinogens while others have been confirmed by IARC. Even though the data below (Table 4) show that small quantities are not lethal overall, great care should be excercised when spills occur. Table 4 shows the large range in LD_{50} values for rats. This could result from the nature of formulation, nature of impurities, and structure of the molecules themselves.

Table 4: PCBs LD_{50}-(RAT-ORAL).

PCBs type	**LD_{50} (g/Kg)**
Aroclor 1016	2.3
1221	3.98
1232	4.47
1242	4.25
1248	11
1254	1.01
1260	1.315
1262	11.3
1268	10.9
2565	6.31
4464	16
Kanechlor 300	1.1
400	1.1

Chronic Toxic Effects on Animals

All animals respond differently to the same chemical in a variety of ways. Toxicity studies on PCBs are very difficult for many reasons: 1) PCBs are extremely

TABLE 5: CHRONIC TOXIC EFFECTS ON ANIMALS

Test (chronic feeding)	Effects
Aquatic species	Threshold effects in egg hatchibility of vertebrates and invertebrates at levels of 2-5 μg/L. Embryo toxicity evident at 50 μg/L
Terrestrial species	**Mouse** -some liver change with exposure to high chlorine- containing products, 300-500 μg/g. **Rat** - some liver changes, minimal reproductive effects, 100-500 μg/g. **Monkey** - Yusho symtoms, altered reproductive cycles, hyperplastic gastritis and alceration, 2.5-5 μg/g. **Chicken** - some morphologic deformity, reproduction decline, subcutaneous edema, 20-50 μg/g. **Mink** - dose response relationship in growth and reproduction 10 μg/g. **Pelican** - some hepatocellular changes, 100 μg. **Dogs** - reduced growth, some liver changes, 100 μg. **Wildfowl** - some reproduction changes, varies with species, 50-200 μg/g.
Teratogenicity	Effects seen in avian species, 50-200 μg/g.
Mutagenicity	Chromosomal abnormalities - negative Dominant lethal mutations - negative Ames test - 1221, tetrachloro biphenyl significantly mutagenic.
Oncogenicity	Highly chlorinated compounds produced tumors in rats and mice, relationship with PCBs not always clear.

heterogeneous, each formulation consisting of several isomers 2) no two formulations are identical 3) samples of the same formulation may be different 4) composition of the same sample when exposed to the environment often changes (NRC, United States, 1979).

STANDARDS

The Table below shows a summary of standards, recommendations, guidelines, and criteria for PCBs in the environment. A large margin of safety has been built into these values.

The threshold limit value (TWA) as determined by American Conference of Governmental Industrial Hygieneists (ACGIH) for 42% chlorine is 1 mg/m^3 for skin; for 54% chlorine it is 0.5 mg/m^3. Health Canada has suggested a tolerable exposure level (tolerable daily intake) for PCBs of 1 μg/kg body weight per day. The figure was arrived at from studies on rhesus monkeys with dietary exposure of 100 μg/kg body weight per day causing reproductive defects. A 100-fold safety margin was used.

TABLE 6: PCBs ENVIRONMENTAL STANDARDS AND CRITERIA

Environmental Medium	Region	Concentration	Notes/comments
Air-ambient	Ontario	35 ng/m^3 (1Y ave.)	Air quality criteria
Water-ambient	Great Lakes-IJC	1 ng/L	Aquatic life
Water-ambient	U.S. EPA	0.79 -0.79 x10^{-3} ng/L	Human health
Water-recreation	Quebec	0.1 μg/L	Standard recomm.
Water-drinking	Nova Scotia	3 μg/L	Max. concentration
Sediments	Canada	1 mg/kg	Disposal (marine)
Soil	Saskatchewan	<5 mg/kg	Clean-up
Solid waste	Canada	≥50 mg/kg	PCB wastes
Fish	Canada	2 mg/kg	Health Canada
Food (TDI)*	Canada	1 μg/kg/d	Estimated tolerance

*TDI - Tolerable daily intake.

Estimated Dietry Intake of PCBs in Canada

Most meat and dairy products contain some amounts of PCBs. Major exposure routes are contaminated water, vegetation, feed, and atmosphere.

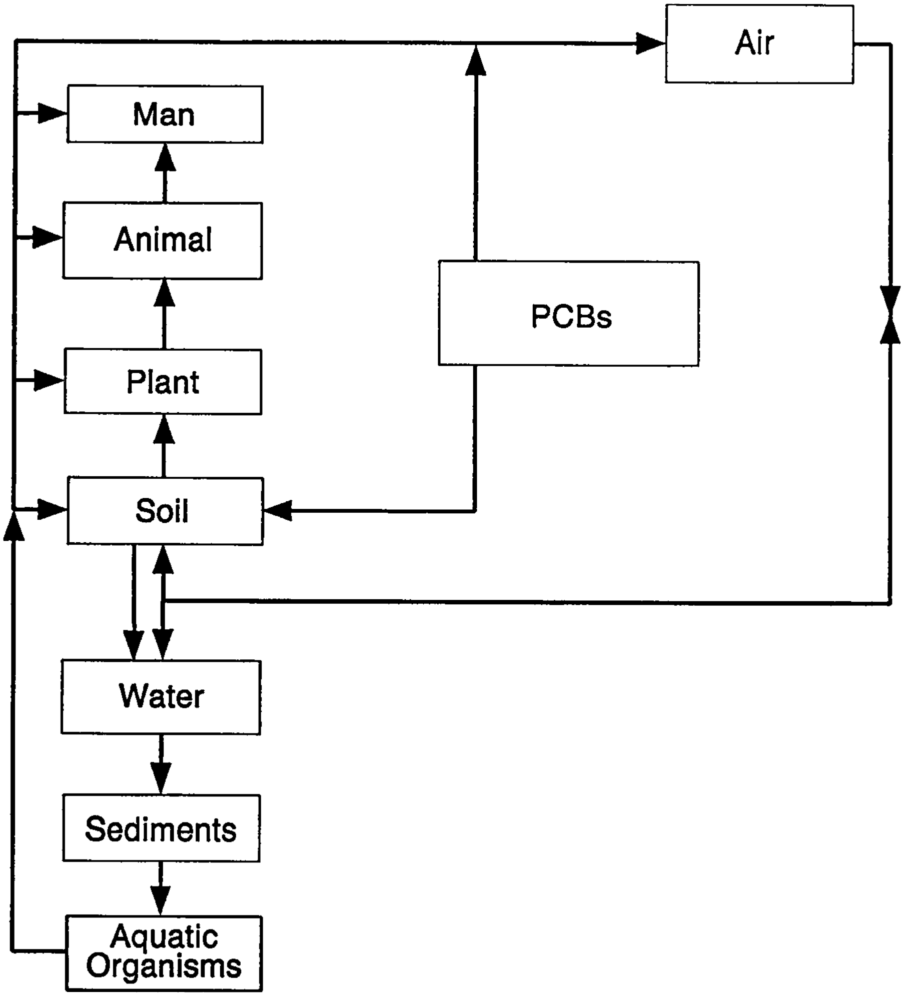
TABLE 7: PCBs DIETARY INTAKE

Food-Source	Food intake (g/person/day)	PCBs intake (μg/person/day)
Dairy	32.8	6.6
Meat	48	9.6
Poultry	3.6	1.8
Eggs	34	3.4
Fish	20	40
TOTAL		61.4

CONCLUSION

The human health risks from environmental exposure through dermal and inhalation have been assessed with occupationally exposed workers as shown in table 3 above. It has been found that these chronically exposed workers exhibit few adverse effects. One can only conclude that the potential adverse human health effects that can result from accidental exposure and low level environmental impact are very low. The chronic low-level long-term impact on the environment and human health is still unclear. On the other hand, the persistence of PCBs in our environment threatens the existence of wildlife and aquatic organisms.

FIGURE 16: PCBs SPILL IMPACT SUMMARY



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Chemical Spills : Prevention and Preparedness Activities of Public Health Agencies in Quebec.

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Abstract

Technological accidents involving hazardous substances, in particular chemical spills, have attracted much attention in Quebec. This paper deals with prevention and preparedness activities related to chemical spills that have to be undertaken by Quebec Public Health Agencies (DRSPs). The Quebec ministry of Public Safety (MSPQ) has recently presented a new reference framework for planning and improving emergency prevention, preparedness, response and recovery in Quebec : in this framework, Regional Health and Social Services Boards (RRSSS) have to plan and co-ordinate action with respect to three main activities in their respective regions : "physical health", "public health" and "psychosocial health". Since a recent reform, DRSPs are now branches of these boards. In terms of prevention activities, DRSPs must identify the major hazards on their respective territories, estimate the risks for 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. Examples from the Quebec City region are given. The paper then describes recent preparedness activities regarding chemical spills in Quebec : the training program set up by the ministry of Health and Social Services (MSSS) and a full scale simulation exercise involving a chlorine truck organized by the City of Quebec and the Quebec Health and Social Services Board.

Introduction

Technological accidents involving hazardous substances, in particular chemical spills, are a frequent problem in North America (Ouzilleau & Sérodes, 1990) and have attracted much attention in Quebec as elsewhere on the continent (Godon, Guerrier et al., 1990). Indeed, Quebec has its share of accidents involving hazardous substances. A few examples during this present decade in Quebec are the PVC fire in Saint-Thérèse (June 1993) which required the evacuation of 250 persons (Carrier, 1993), the explosion of a propane tank in Warwick (June 1993) which resulted in the death of four volunteer firefighters (CSST, 1995), and a major sulfuric acid spill in Little Masketsi Lake following a train derailment in Hervey Junction (January 1995) which killed aquatic life and temporarily prevented residents along a downstream river to drink the water (Provost, 1995).

The awareness of the Quebec public health agencies (Directions régionales de santé publique - DRSP) concerning accidents involving hazardous substances increased dramatically at the end of the last decade after serious accidents like the fire in a PCB storage site in Saint-Basile-le-Grand (August 1988) (Godon, Guerrier et al., 1990) and the fire at a tire depot in Saint-Amable (May 1990) (Jacques, Carrier et al., 1994) where public health officials were much involved.

Since the PCB fire in Saint-Basile-le-Grand, a lot of attention has been given to the response activities carried out by DRSPs and other agencies during this event which received plenty of media coverage (Leroux, 1989) (Denis, 1990). This paper, rather, concentrates on prevention and preparedness activities related to chemical spills, that have to be undertaken by the DRSPs.

1. The Quebec Government reference framework for emergency management and the mandates of public health agencies (DRSPs).

In Quebec, the ministère de la Sécurité publique (MSPQ) is responsible for implementation of the Act respecting the Protection of Persons and Property in the Event of Disaster (RSQ, c.P-38.1) and the Fire Prevention Act (RSQ, c. P-23). The Direction générale de la sécurité civile (DGSC) of the MSPQ exercises its leadership in emergency management. This branch of the MSPQ recently presented a new reference framework for improving emergency prevention, preparedness, response and recovery in Quebec. A manual introduces a number of concepts, definitions and administrative structures required to facilitate these activities in Quebec and to improve, in particular, administrative coordination. Its goal is to assist the relevant authorities to prepare their agency (municipality, business, institution or government department) to deal with disasters (MSPQ, 1994).

All Quebec government departments or agencies that are members of the Quebec Emergency Management Committee (Comité de sécurité civile - CSC) are to :

- plan civil security in their agency
- provide liaison between the provincial, regional and municipal levels
- co-operate with the DGSC in civil security planning at the provincial level
- train their staff
- recognize and support, where necessary, the volunteer associations working in their areas of response
- negotiate service agreements with private or volunteer resources working in their areas of response
- cooperate with the Quebec Communication office in any communications activity.

At the ministère de la Santé et des Services sociaux (MSSS) level, emergency planning in its 16 administrative regions is the responsibility of the Regional Health and Social Services Boards (RRSSS). These boards have to plan and co-ordinate action with respect to three main activities in their respective regions : "physical health", "public health" and "psychosocial health" (Table 1). Since a recent reform, the DRSPs are now branches of the RRSSSs.

2. Prevention of chemical spills

2.1 Background

As stated previously, public health agencies in Quebec (DRSPs) must, in risk assessment terms, identify the major hazards on their respective territories, 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.

These risk assessment activities naturally lead to consideration of possible risk control measures and their effect in reducing the identified risks (Holmes & Zaharko, 1992). They require the collaboration at the local level of other organizations such as municipalities and industries and at the provincial level of other governmental agencies.

In Quebec, the municipality plays a major role in making the community a safe place to live. Each municipal council is responsible for emergency planning on its territory (MSPQ, 1994). As in other provinces, in relation to hazardous substances, the municipality must be prepared to reduce the likelihood of an incident as well as to respond to those incidents that may occur (Holmes & Zaharko, 1992).

Therefore, the DRSPs frequently work with municipalities and also industries to prevent accidents involving hazardous substances : these activities may be linked to existing industries where hazards have been identified or to industrial regulated projects such as the recent cogeneration power plant projects. In the case of projects where public hearings take place, the health risk communication to the public is greatly facilitated.

At the provincial level, the DRSPs work closely with various agencies such as the ministère de l'Environnement et de la Faune (MEF). The MEF's mandate is to :

- enforce legal requirements or regulations aimed at minimizing the frequency and severity of technological and natural disasters
- cooperate with various partners working in prevention, notably with regard to spills.

The DRSPs also benefit from their close relationship with the Quebec Occupational Health and Safety Commission, the CSST (Commission pour la santé et la sécurité du travail). The CSST is in charge of applying laws setting out the rights and obligations of workers and employers, and establishing terms and conditions for their enforcement. The Act respecting Health and Safety deals with prevention while the Act respecting Industrial Accidents and Occupational Diseases provides for worker compensation and rehabilitation. These laws make both workers and employers responsible for health and safety in the workplace. The CSST's duties with regard to prevention are to :

- promote occupational health and safety
- assist workers and employers in their efforts to achieve a healthier, risk-free work environment
- inspect work premises.

According to the Act respecting Occupational Health and Safety, the DRSPs and local community service centres (CLSCs) have the mandate to offer preventive health services (CSST, 1994).

2.2 Prevention activities in the Quebec City region.

Since 1990, several prevention activities have been set out by the DRSP- Quebec City Region, mainly in the Quebec City metropolitan area where a number of companies handle large quantities of chemicals and petroleum products. The major risks located and identified in a previous study were potential accidents involving chemicals using manufacturing sites in the Port of Quebec (Guerrier & Patry, 1987).

The first activities were undertaken through a project called P.I.G.E.S. based on the APELL program philosophy (UNEP, 1988). This project involved various stakeholders, among them the City of Quebec, the Port of Quebec and several industries, in particular a major pulp and paper company and a liquid storage company. The successful collaboration produced detailed inventories of the industries hazardous materials with information on their storage conditions, health risks, etc. Such efforts allowed all the stakeholders to have a better knowledge of their partners in terms of roles, resources and concerns as well as a better awareness of the major hazardous installations and spill hazards. It has also contributed to reduce major risks like the transportation of chlorine by rail through urban areas in the region.

One of the major challenges was the vulnerability analysis. Thanks to financing by Emergency Preparedness Canada, the MSSS, MEF and MSPQ, a Decision Support System (DSS) integrating a Geographic Information System (GIS) and a Relational Database Management System (RDBMS) application was created (Guerrier, 1992). The RDBMS application allows the viewing of data such as vulnerable populations on windows designed specifically for emergency management purposes while the GIS allows the user to obtain map views, row and column views, graph or chart views (Guerrier & Godon, 1993). This system, named SOS IGLOU™, is currently used by several organizations, among them the Quebec City Emergency Operations Centre (Guerrier, 1994). All intellectual property rights associated with SOS IGLOU™ technology are held by Synergie Information Systems.

Figure 1 : Identifying vulnerable populations with the GIS (MapInfo™).

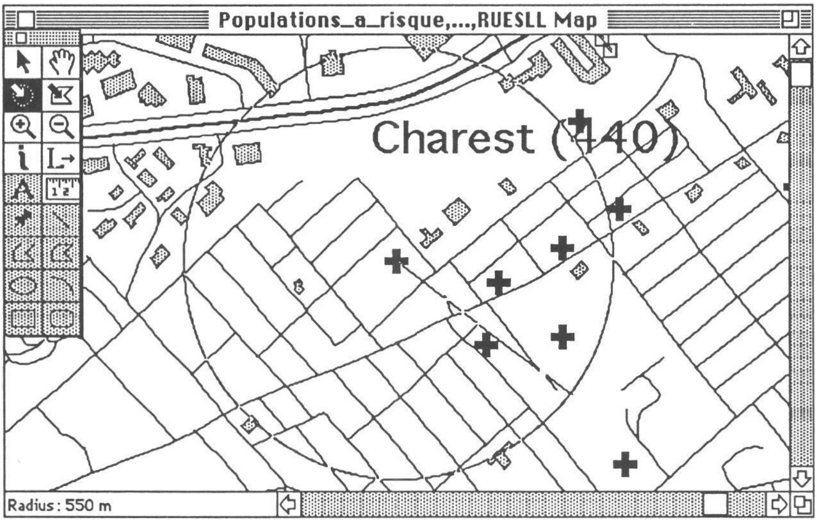

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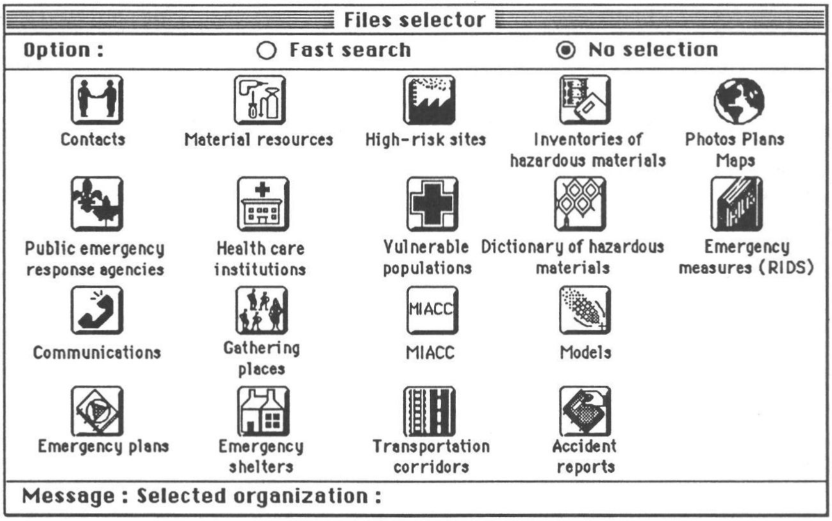
Figure 2 : The SOS IGLOU™ navigation window (developed with OMNIS 7™).



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3. Preparedness for chemical spills.

3.1 Background

Emergency preparedness is mainly an educational activity which aims at reducing unknowns during an emergency and facilitating the taking of appropriate decisions and actions on the scene. Preparedness measures recognize an emergency will happen and the focus shifts to reducing the impact on the public and the environment as a result of an accident (Holmes & Zaharko, 1992). There are three main characteristics in emergency preparedness : resistance to emergency preparedness is a given, modest planning is a reasonable goal and training response personnel is an important measure (Krebs, 1991) (Godschalk, 1991). The purpose of training emergency response personnel is to give the employees the knowledge and skill to perform an emergency response activity with minimal risk to themselves and others (Turpin, 1993).

When a chemical spill strikes, the response 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. The Ministère de la Santé et des Services sociaux (MSSS) recently developed a training program on emergency management (including "physical health", "public health" and "psychosocial services").

This program ("L'intervention sociosanitaire dans le cadre des mesures d'urgence") has one overriding goal: to adequately train Quebec Health and Social Services responders regarding their own roles and the roles of others so that they will respond effectively to the population needs when a disaster strikes (MSSS, 1994). The public health part of the training program was given in 1994 in three locations in Quebec : Longueil (Montérégie Region), Montreal and Quebec City.

The MSSS public health training program includes sixteen (16) modules :
module 1 : disasters and emergencies : a reality
module 2 : emergency operations : a specific response activity
module 3 : the Quebec Health and Social Services network emergency plan
module 4 : the emergency management phases
module 5 : information services and available resources
module 6 : identification of industries at risk
module 7 : response : the first steps
module 8 : hazardous materials
module 9 : medical diagnostic
module 10 : first aid
module 11 : protection measures
module 12 : health risks analysis
module 13 : public health monitoring
module 14 : hot-line services for the public
module 15 : behaviors of victims
module 16 : stress management for responders

According to the participants, these training sessions have been a success. One of the suggestions received highlighted the importance of preparing more practical hands-on sessions which would concentrate on specific high risk chemicals.

3.2 Preparedness activities in the Quebec City region.

One of the most important recent preparedness activities has been a full scale simulation exercise called "Yellow Alert" (Turgeon, 1994). This joint project led by the Regional Health and Social Services Board and the City of Quebec was designed mainly to test and improve the emergency response in Quebec City. The committee began its work in August 1992. The project lead to a training program for first responders, an evaluation of protective clothing for hazardous material accidents for fire fighters, ambulance and hospital personnel, the simulation exercise as such in May 1994, the publication of an evaluation report concerning the public health response in September 1994 (Rhainds, Auger & al., 1994) and an in-depth study on the life-cycle of chlorine in the region in May 1995 (Guerrier, 1995).

Chlorine (UN 1017) was chosen for the scenario after the study of the Spill Priority List for all hazardous chemicals developed by Emergency Sciences Division (ESD) at Environment Canada (Lawuyi & Fingas, 1993). Chlorine places second on this list, just after Ammonia (UN 1005). As a result of its use mainly by municipal drinking water treatment plants and pulp and paper companies, chlorine is stored in large quantities (up to 22 tons) in the Quebec City region. This toxic gas is therefore commonly transported as a liquid through the Quebec City region (up to 19 tons) (Guerrier, 1995). Most accidents have been minor and handled quickly with no risk to the public. Unfortunately, some accidents have required a more important response effort, in particular from Quebec City firefighters. Other documents such as the MIACC Chlorine Life-Cycle Management Accident Prevention Workshop Report and experts from CANUTEC and chlorine manufacturers were also consulted to design a realistic scenario that finally evolved into a transportation accident. The scenario involved the collision of a truck carrying 21 cylinders with a school bus. The simulated 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. The accident created several "injured" and "fatalities" to actually test the firefighters, police, ambulance and hospital response systems (Rhainds, Auger & al., 1994).

The exercise identified several opportunities for improvement in public health response. The most important were :

- telecommunications problems: public health responder call-in was too long and use of phones was a problem (including overload)
- identification problems : lack of an identified vehicle and no proper personal identification for the public health responder made access to the site more difficult. The roles of the public health responder was sometimes unknown by other responders (police)
- data gathering: problems with data concerning environmental contamination on site, data from the decision support system at the Emergency Operations Centre was hard to get, therefore risk analysis and implementation of protection measures (confinement, evacuation) were difficult to undertake
- media control required attention
- little or no communications with other responders, even when present in the emergency mobile command vehicle.

There were also many good points such as the fair knowledge about the hazardous material involved, the expertise to identify populations at risk and the ability to request other health responders on site (psychosocial services).

The "Yellow Alert" simulation was a great learning experience for all participants. Cooperation between the various agencies during the development of this simulation was successful while the simulation itself was able to pinpoint the good and bad points of the numerous responders. This simulation presented many of the problems that a responder would encounter in a real major chemical spill in this region and confirmed, as in other Canadian chemical spills simulations, that communications systems are the "life blood" of any emergency response process and therefore must be designed to enable the appropriate agencies to talk to each other under all circumstances (Hatfield, 1993).

Concluding remarks

In Quebec, the public health agencies'awareness concerning hazardous materials has increased dramatically over the recent years. This has resulted in the generation of joint municipal-governmental-industrial prevention and preparedness activities in response to the complex issues related to the life-cycle management of these materials.

In only a few years, the approaches, methods and training programs have evolved rapidly in Quebec. On-scene municipal first responders, government officials, private companies, whether standing on the site or in the boardroom, should now have a much more similar perception of the situation from which decisions and actions must be based.

Today, it is inevitable for Quebec public health agencies to deal with chemical spills. During the last decade, public health responders have been asked to perform activities for which they were not always properly trained. In their role of responding to potential or actual hazardous material spills, public health personnel have now received the basic training to ensure their own safety and protect the health of the people involved in such accidents. In a near future, it will certainly be important to train such public health staff even more practically about the most commonly spilled materials identified in the Environment Canada priority list. Some activities have already been done in that field on a regional basis. At the Research and Development level, now that Decision Support Systems have been created and are beginning to be more frequently used, the idea of computer-assisted instruction (CAI) for hazardous materials training may be envisaged. CAI provides an easily accessible, cost-effective means of individualized high-quality instruction (Lancaster & Willis, 1994). This perspective is important as health and social services administrators seek more and more to achieve optimal resource utilization.

Table 1: **Regional Health and Social Services Boards mandates related to disasters (Summary) (Adapted from MSPQ, 1994).**

	Physical Health	Public Health (DRSPs)	Psychosocial Services (CLSCs)
Prevention & Preparedness Activities	• develop and maintain the response plan provided by local authorities with respect to physical health	• list risks and their effects on public health and ensure active monitoring • inform the public about health risks	• list resources • negotiate service agreements • prepare and update an emergency plan
Response Activities	• provide pre-hospital care • provide hospital care • provide primary care	• analyze health risks for the public and responders • develop protection measures and public health notices	• define the target population • evaluate psychosocial needs of victims and responders • provide services
Recovery Activities		• provide epidemiological follow-up and evaluate short, medium and long term health effects • evaluate response	• organize discussions on the event for victims and stakeholders • supervise a recovery program • provide services

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A.S.A.P. - The Air Safety Applications Package for Front-Line Emergency Response - Part 1: User Interface

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Abstract

During the response to a hazardous materials incident, knowledge of the spatial concentration of the pollutant is needed for operational and safety decisions. Several hazardous gas models have been developed for this purpose; however they often require inputs which are not available to the front-line response teams or they are confusing and complicated to run, making their predictive capabilities ineffective. This paper discusses this problem and presents the *A*ir *S*afety *A*pplications *P*ackage, an emergency response system designed with special attention to the needs of first-responders (e.g. police, firefighters, industrial personnel). *A.S.A.P.* runs in Windows™ and takes full advantage of the icon driven *point-and-click* technology used in that operating system. The conditions of an emergency release of hazardous material are defined by clicking five icons to describe the **Weather**, the **Chemical**, the **Tank**, the **Terrain** roughness and the **Map** location of the accident. Once all five icons are checked off (✓), the user clicks **GO** to rapidly compute and map the hazard zones. *A.S.A.P.* automatically determines: the atmospheric stability, the amount of hazardous material released into the air, and the transport and dispersion model to run (heavy gas puff or plume or neutral gas puff or plume).

INTRODUCTION

During the response to a hazardous materials incident, knowledge of the spatial concentration of the pollutant is needed for operational and safety decisions. Several hazardous gas models have been developed for this purpose; however, many of these require inputs which are not available to the front-line response teams, or they take too long to run, or they are confusing and complicated, making them ineffective for first-response applications. The purpose of this paper is to describe the *A*ir *S*afety *A*pplications *P*ackage (*A.S.A.P.*), an emergency response system which has been designed specifically to meet the needs of first-responders (e.g. police, firefighters, industrial personnel).

Unlike many other hazardous gas modelling systems, *A.S.A.P.* does not ask the user to define the atmospheric stability or the horizontal and vertical dispersion coefficients, nor does it require the user to specify the amount of hazardous gas escaping from a tank. Instead, the system relies on information which is readily available to the first-responder.

SYSTEM DESIGN

A.S.A.P. has been developed with three modes of operation: **Respond Mode**, for use by first-responders; **Analyse Mode**, for use by air-quality experts; and **Prepare Mode**, for use by experts responsible for preparing the CHEMICAL, TANK and MAP DATABASES for emergency operations and risk assessments. This paper focuses on **Respond Mode.**

A.S.A.P. has been designed to run in Windows™ and to take full advantage of the icon driven *point-and-click* technology used in that operating system. The system uses colours, images, icons, and maps and, in **Respond Mode**, it is fully operable using only the mouse. An effort has been made to make the system *clear* and *intuitive* by providing explicit instructions and on-line help. A user, with only a basic familiarity of the Windows™ operating system, is able to operate ***A.S.A.P.***'s **Respond Mode** with confidence and without instructions.

A.S.A.P. employs the chemical data set and six models developed by Daggupaty (1988; 1994) for the Air Quality Emergency Response PACkage (AQPAC). The stability class model uses a modelling routine based on the well established Pasquill-Gifford-Turner method (Turner, 1964). It computes atmospheric stability based on observations which are readily available to first-responders; the model requires: the date, time, wind speed, cloud cover and location of the accident.

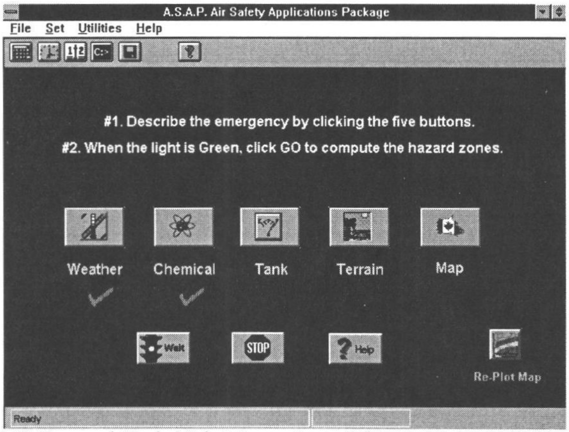
The size and shape of the hazard zones predicted by ***A.S.A.P.****'s* dispersion models is critically dependent on the amount of hazardous material released into the air. This information is very often not known in the early stages of an accident. The source strength model provides a first estimate of the quantity of hazardous material spilled into the air and it determines the appropriate dispersion model needed to predict the hazard zones (Daggupaty, 1990). This model uses readily available information on the weather conditions at the accident site, the chemical involved (supplied by the CHEMICAL DATABASE), the size of the tank involved (supplied by the TANK DATABASE) and the location and size of the rupture in the tank. It should be noted that the source strength model used in ***A.S.A.P.****'s* **Respond Mode** has been set to provide *worst case* (conservatively high) estimates of the amount of hazardous material released into the air (particularly from pressurized tanks containing liquefied gases).

The four dispersion models currently used in ***A.S.A.P.*** are: a heavier-than-air gas puff dispersion model based on the work of Matthias (1990; 1992); a heavier-than-air gas plume dispersion model based on the works of Colenbrander (1980), Havens and Spicer (1985) and Alp and Matthias (1991); a neutral density gas (Gaussian) puff dispersion model (Daggupaty, 1988); and a neutral density gas (Gaussian) plume dispersion model (Daggupaty, 1988). *Puff* models are used to compute the hazard zones resulting from an instantaneous (or sudden) release of hazardous material which travels like a "dense cloud" from the accident site. *Plume* models are used to compute the hazard zones resulting from a continuous (on-going) release of hazardous material which travels like a "plume" from a chimney. These dispersion models were selected for use in ***A.S.A.P.*** because they run quickly (run times for the computationally most demanding dispersion models are less than 30 seconds on a 486/66 PC), they require inputs which are readily available, and their accuracy has been reported to be well suited for hazard assessments in real-time air quality emergencies (Daggupaty, 1994). The accuracy and limitations of the ***A.S.A.P.*** models are discussed in more detail in McGillivray *et al.* (1995).

OPERATION

As shown on Figure 1, the Main Menu for ***A.S.A.P.'s*** **Respond Mode** presents the user with two direct instructions (for running the system), five large icons (for describing the accident), a WAIT icon (indicating that the models are not yet ready to run, which changes to a GO icon when the models are ready to run), a STOP icon to exit the system, a HELP icon to access an on-line user's guide and a RE-PLOT MAP icon which functions only after the models have been run. The conditions of an emergency release of hazardous material are defined by clicking five icons to describe the **Weather**, the **Chemical**, the **Tank**, the **Terrain** roughness and the **Map** location of the accident. Note that the system can also be operated like any Windows™ program from the Menu Bar at the top of the screen. Several utilities are also available including access to the Windows™ calculator, clock, calendar, and DOS prompt, as well as a file save utility, to save a scenario for analysis later in **Analyse Mode**.

Once all five icons are checked off (✓), the user clicks **GO** to rapidly compute the hazard zones. ***A.S.A.P.*** automatically determines the atmospheric stability (and the associated horizontal and vertical dispersion coefficients) and the amount (or rate) of hazardous material released into the air. It computes the hazard zones, maps the results in colour and scales the map to ensure that the entire hazard zone is shown. Model default parameters (e.g. sigma types, mixing heights, effective emission heights) and intermediate model results (e.g. atmospheric stability and source strength) may not be adjusted in this mode of operation. Such adjustments are of course possible for expert users in **Analyse Mode**.



A.S.A.P. Air Safety Applications Package

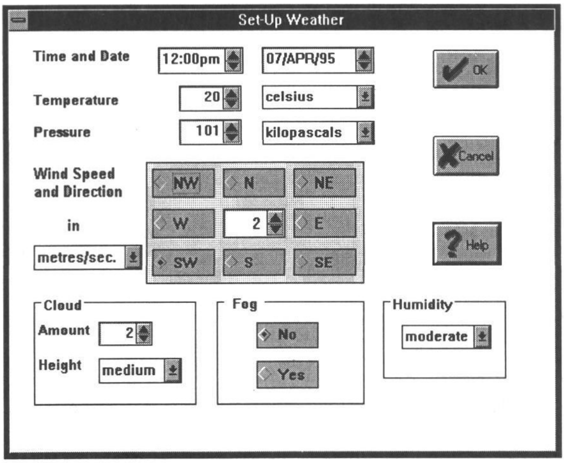
#1. Describe the emergency by clicking the five buttons.

#2. When the light is Green, click GO to compute the hazard zones.

Figure 1: **A.S.A.P.** Respond Mode Main Menu. As each icon is clicked and the conditions of an emergency release of hazardous material are described, the icons are checked off (✓).

Weather Input

Clicking on the **WEATHER** icon presents a data entry screen (Figure 2) which allows the user to define the key meteorological conditions at the accident site: the time and date of the accident, air temperature, air pressure, wind speed and direction, the cloud cover and its height (high, medium or low), whether fog is present and whether the humidity is dry, moderate or humid. To simplify the entry time and date, the system assumes that the time of the accident is "now"; the default time and date are read from the computer's clock. To simplify the entry of air temperature, air pressure and wind speed, different units are provided; these are automatically converted to the units needed by the models.

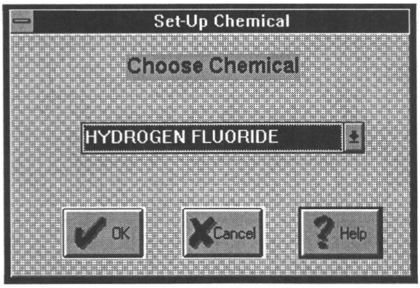


Time and Date: 12:00pm 07/APR/95
Temperature: 20 celsius
Pressure: 101 kilopascals
Wind Speed and Direction: 2 in metres/sec.
○ NW ○ N ○ NE
○ W ○ E
● SW ○ S ○ SE
Cloud: Amount 2, Height medium
Fog: ● No ○ Yes
Humidity: moderate

*Figure 2: **A.S.A.P.** Input Screen for Weather Conditions.*

Chemical Input

When the **CHEMICAL** icon is clicked, a chemical selection menu is presented (Figure 3) listing the names of chemicals in alphabetical order. Presently the ***A.S.A.P.*** CHEMICAL DATABASE contains 68 high priority chemicals and more can be added. The user may click on the arrows to move up and down the list or skip to the required section by typing the first letter of the chemical name.

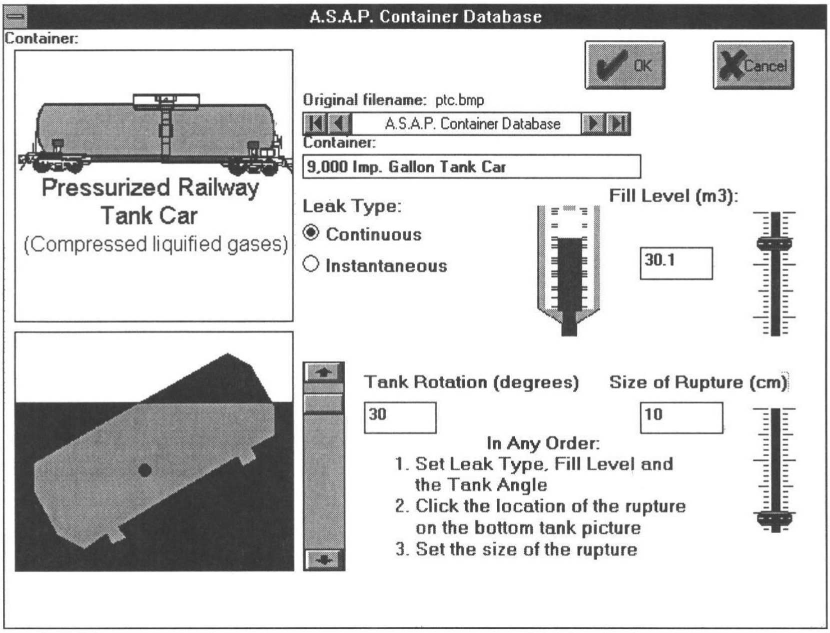


Choose Chemical: HYDROGEN FLUORIDE

Figure 3: Chemical Selection Screen.

Tank and Rupture Input

Clicking the TANK icon presents the screen shown in Figure 4. This screen is designed to allow the user to transfer what they see at the accident site into the system. The tank involved in the accident is selected *visually*. The type of leak being observed is defined as continuous or instantaneous. The fill level of the tank is defined by clicking and dragging the scale icon (the default is full). The angle of the damaged tank may be simulated by rotating the tank shown in the lower left portion of the screen. The location and size of the rupture are described by clicking on the tilted tank and clicking and dragging the scale icon to set the rupture size. The system automatically computes the position of the puncture relative to the liquid level in the tank and determines whether liquid or gas (or both liquid and gas) is escaping from the tank.



Container:

Pressurized Railway Tank Car
(Compressed liquified gases)

Original filename: ptc.bmp

Container: 9,000 Imp. Gallon Tank Car

Leak Type:
● Continuous
○ Instantaneous

Fill Level (m3): 30.1

Tank Rotation (degrees): 30

Size of Rupture (cm): 10

In Any Order:
1. Set Leak Type, Fill Level and the Tank Angle
2. Click the location of the rupture on the bottom tank picture
3. Set the size of the rupture

*Figure 4: **A.S.A.P.** TANKS DATABASE: This screen allows the user to select the tank, establish the type of leak (continuous or instantaneous), set the fill level of the tank (default is full), set the angle of the tank and click on the location of the rupture and set the size of the rupture.*

Terrain Input

Clicking the TERRAIN icon presents a screen (Figure 5) which requires the user to specify the type of terrain surrounding the accident site. Land use terms which are visible to the first-responder are used to define the surface roughness lengths (Z_0) required by the dispersion models.

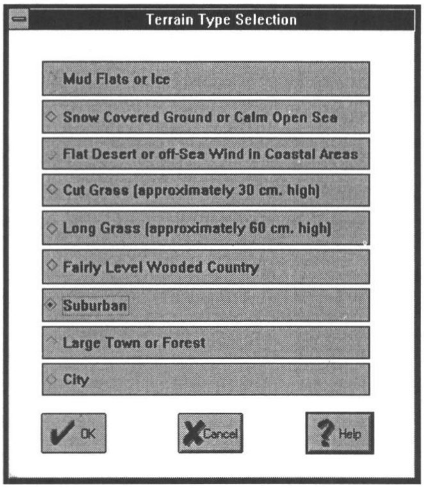
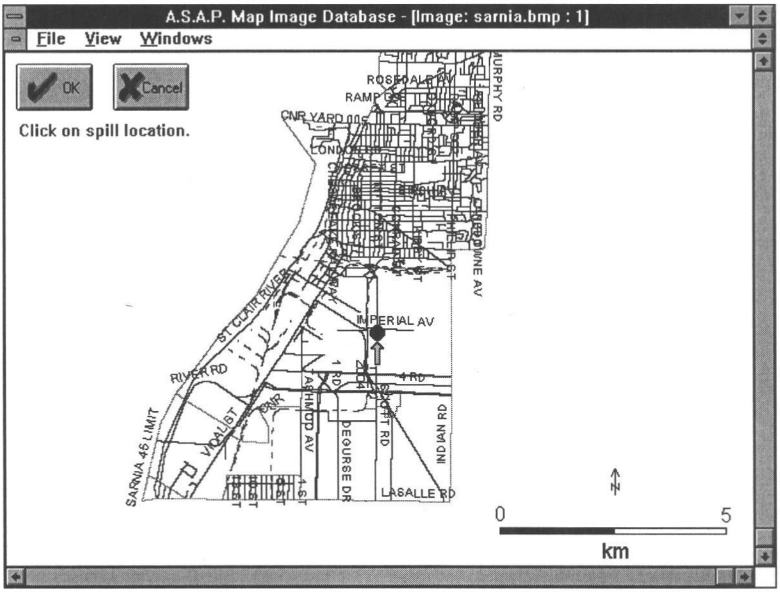


Figure 5: Terrain Type Menu

Map Input

Clicking the **MAP** icon allows the user to specify the location of the accident. The system will show a series of small "thumbnail" maps of different cities (or different parts of the same city). Clicking on the thumbnail selects and expands the map. As shown in Figure 6, the spill location is specified on the map by moving the cursor (⇧) and clicking on the site.


A.S.A.P. Map Image Database - [Image: sarnia.bmp : 1]

Click on spill location.

Figure 6: Spill Location Screen: The accident site is specified on the map by moving the cursor and clicking. Note the map cursor (⇧) and dot (●) mark the hypothetical accident site near the centre of the map.

Once all five icons are checked off (✓) and the conditions of the spill have been defined, the traffic light on the Main Menu will turn green and indicate GO. Clicking the **GO** icon will cause the system to compute the atmospheric stability and the source strength, to select the appropriate dispersion model, and to run the model and map the hazard zones.

A sample output screen is shown in Figure 7. This screen allows the user to see the hazard zones, to review the chemical information, to review the response information, and to print the results. The printed output is presented on a single 8½" by 11" sheet of paper so that it can be easily faxed; it includes a map of the hazard zones and a summary of the response information (e.g. Figure 8). The printed output may faxed directly from any computer running Windows™-based facsimile software and connected to a modem.

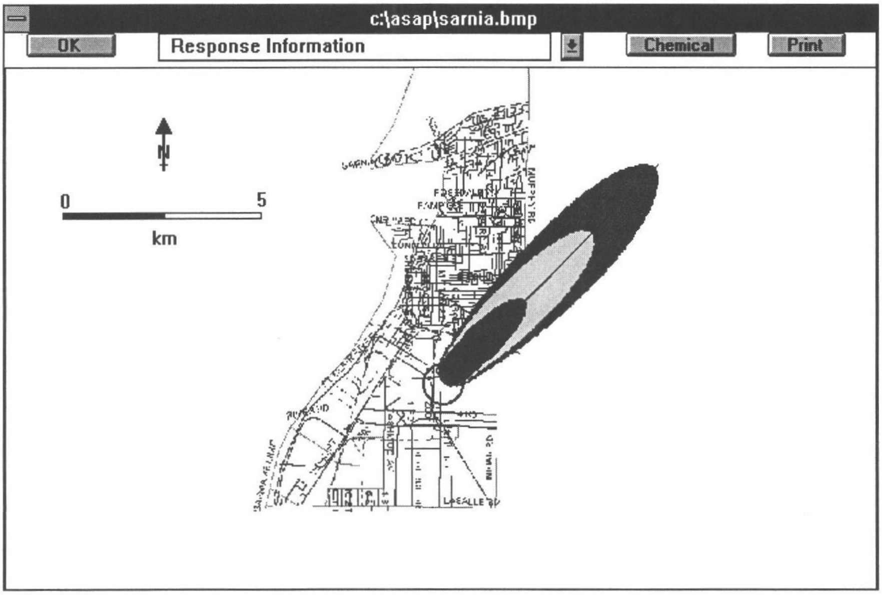


Figure 7: A.S.A.P. Output Screen: Hazard zones are mapped in colour; the circle marks a 1 km radius around the accident site. A pull down menu of the response information is available to see key inputs, the source strength computations and the length of the hazard zones. The chemical text file may be viewed and the results may be printed.

USING THE *A.S.A.P.* OUTPUT

Each substance in ***A.S.A.P.***'s CHEMICAL DATABASE, has been identified with one or more of four threshold hazard limit values (LFL or LEL, IDLH, STEL, TLV). These thresholds are defined from the recently published literature on industrial safety. They identify whether the material is *toxic* to humans (as defined by IDLH, STEL and/or TLV), *flammable* (as defined by LFL) or *explosive* (as defined by LEL) or both *toxic and flammable (explosive)* (as defined by LFL (LEL) as well as at least one of the toxic limit thresholds).

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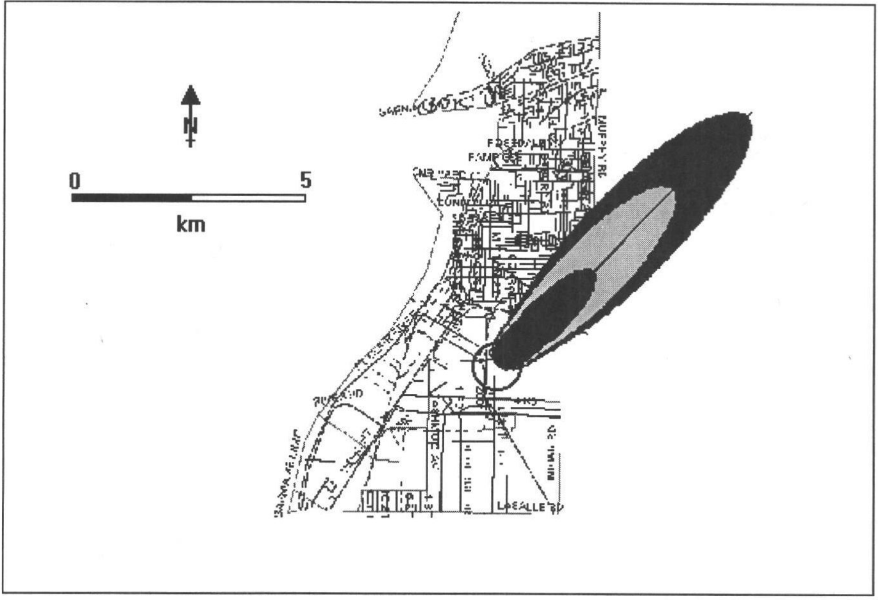

Hypothetical Hydrogen Fluoride Spill - Sarnia - April 7, 1995 - 12:00 pm
A.S.A.P. Heavy Plume Model Output - Valid for 60 minutes.

Weather: Wind speed and direction (m/s, deg) - 2.00, 225
Temperature and Pressure (C, kPa) - 20.0, 101.0
Stability Class: B
Chemical: Hydrogen Fluoride
Tank: 9,000 Imp. Gallon Tank Car
Leak Type: continuous
Rupture (cm): 10
Terrain: suburban

Source Strength:
Respond Mode (worst case) Estimate:
Heavy Plume has been run automatically with a Source Strength = 42 kg/s
Analyse Mode Estimates:
Gas + Flash (Q1) is 0.3 kg/s for time less than or equal to 11.8 minutes
Evaporation (Q2) is 42.2 kg/s for time less than or equal to 11.8 minutes
Estimated time for total liquid to leak from tank 11.8 minutes
Estimated time for liquid pool to evaporate completely 11.8 minutes
Run the Heavy Plume Model with Q1 + Q2 = Source Strength of 42.4 kg/s

Hazard Zones:
TLV 3 ppm Length (m) = 7500
STEL 6 ppm Length (m) = 5300
IDLH 20 ppm Length (m) = 2900

*Figure 8: Sample of **A.S.A.P.**'s printed output page.*

LFL (*Lower Flammability Limit*) is the minimum concentration of material in air which will support combustion on contact with a source of ignition. The risk of fire is high. In the context of emergency response, this defines a first priority hazard zone. Note the *Lower Explosive Limit* (**LEL**) may substituted for LFL in **Prepare Mode** if the gases are explosive.

IDLH (*Immediately Dangerous to Life or Health*) is the maximum concentration level from which one could escape within thirty minutes without any impairing symptoms or any irreversible health effects. In the context of emergency response this also defines a first priority hazard zone.

STEL (*Short Term Exposure Limit*) is the concentration level to which humans can be exposed continuously for a period of up to fifteen minutes without suffering from irritation, chronic or irreversible tissue change, or narcosis of sufficient degree to increase the likelihood of accidental injury, to impair self rescue, or to materially reduce work efficiency, provided that the daily TLV (Threshold Limit Value) is not exceeded. In the context of emergency response this defines a second priority hazard zone.

TLV (*Threshold Limit Value*) is the time weighted average concentration for a normal 8-hour workday and 40-hour workweek, to which nearly all humans may be repeatedly exposed, day after day, without adverse effect. In the context of emergency response, this defines a third priority hazard zone.

The hazard zones are defined in ***A.S.A.P.*** as the areas with concentrations which exceed the threshold limit values; the zones are defined on the output maps in colour:

- BLUE defines the zone where concentrations equal or exceed LFL;
  a 1st priority hazard zone;
- RED defines the zone where concentrations equal or exceed IDLH;
  also a 1st priority hazard zone;
- YELLOW defines the zone where concentrations equal or exceed STEL;
  a 2nd priority hazard zone;
- GREEN defines the zone where concentrations equal or exceed TLV;
  a 3rd priority hazard zone.

It should also be noted that a 1 km radius around any hazardous chemical spill site is assumed to be a first priority hazard zone. This area is marked on the output maps by an open red circle.

A.S.A.P. is designed for short range applications (less than 50 km), it may therefore be reasonably assumed that the modelled concentrations and hazard zones are valid for one hour or less; this time is indicated in the response information. It is based on the assumption that the weather inputs are valid for that time period or that the puff of hazardous material has moved out of the hazard zones and dissipated to lower concentrations. For accidents involving gas releases over prolonged periods, it is advised that the plume models be re-run in **Analyses Mode** using updated meteorological data.

CONCLUSIONS

This paper shows that a user interface for an air quality emergency response system may be designed to ask only questions which can be answered by first-responders. The *A*ir *S*afety *A*pplications *P*ackage (*A.S.A.P.*), focuses on input information which is readily available to the front-line response teams. It automatically computes the atmospheric stability and source strength, and it selects and runs the dispersion model needed to predict the hazard zones. ***A.S.A.P.*** provides a modelling capability, traditionally used by experts, to the front-line responders where it can be used in the critically important first few minutes of an emergency response to a hazardous chemical spill.

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A.S.A.P. - The Air Safety Applications Package for Front-Line Emergency Response - Part 2: Model Accuracy

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Abstract:

The *A*ir *S*afety *A*pplications *P*ackage, employs the six AQPAC models developed by the Atmospheric Environment Service, Environment Canada: Stability Class Model; Source Strength Model; Neutral Gas Puff Model; Neutral Gas Plume Model; Heavy Gas Puff Model and Heavy Gas Plume Model. This paper examines the operational performance of these emergency response models in two ways: (i) comparisons are made between model predictions and published field observations to demonstrate the skill of the models under ideal conditions where all inputs are known; and (ii) a series of sensitivity tests are reported which reflect operational performance of the models in the context of input data uncertainties. It is concluded that the *A.S.A.P.* models are very well suited for hazard assessments in real-time air quality emergencies. The models use inputs which are readily available to first-responders, they are fast and they show a slight bias towards over-estimating pollutant concentrations under ideal conditions, providing confidence in their operational performance under real-time emergency conditions.

INTRODUCTION

The purpose of this paper is to explore the accuracy of the models used in the Air Safety Applications Package (*A.S.A.P.*) and to outline their limiting assumptions. It is important to keep in mind that models are abstractions and simplifications of the real world. Their accuracy is therefore strongly related to the quality of the input data, the limiting assumptions made in modelling complex processes and the user's ability to interpret the output information.

This paper examines the skill and operational performance of the *A.S.A.P.* emergency response models in two ways: (i) comparisons are made between published field observations and model predictions to demonstrate the *skill* of the models under ideal conditions; and (ii) a series of sensitivity tests are reported which reflect model operational performance in the context of input data uncertainties.

MODEL SKILL AND LIMITATIONS

A.S.A.P. employs the chemical database and six models developed by Daggupaty (1988; 1994) for the Air Quality Emergency Response PACkage (AQPAC). The models are: a stability class model based on the well accepted Pasquill-Gifford-

Turner scheme (Turner, 1964), the Source Strength Model developed by Daggupaty (1990) and four dispersion models - Neutral Gas Puff Model (Daggupaty, 1988); Neutral Gas Plume Model (Daggupaty, 1988); Heavy Gas Puff Model based on the work of Matthias (1990; 1992) and Heavy Gas Plume Model based on the works of Colenbrander (1980), Havens and Spicer (1985) and Alp and Matthias (1991).

The accuracy and limitations of the models used in ***A.S.A.P.*** have been reported in the scientific literature; this information is summarized below along with some preliminary results from a series of experiments currently being conducted by Atmospheric Environment Service (AES) to statistically compare the dispersion models against the same field observations used by Hanna *et al.* (1993) to test 15 other hazardous gas models.

Like most first-response models, the main limitations of the ***A.S.A.P.*** models are: they assume that the meteorological conditions and the source strength are constant during the travel time of the puff or plume; they assume that the puff or plume travels in the direction of the mean wind and that wind speed and direction are constant and uniform over a distance range of less than 50 km. They do not account for changes in terrain roughness or topography and they do not simulate the effects of fires or chemical reactions. Each of these assumptions cause errors in the model predictions of gas concentration when compared with field observations even when the input information is known. It is generally agreed that the best that can be expected form models under real world conditions it that the predictions are within a *factor of 2* of the field observations (e.g. AMS, 1977). Thus predictions of pollutant concentrations which are within the range which is 2 times higher or 2 times lower than the observed concentration is considered a *good estimate*.

Most "accuracy tests" of emergency response models are conducted under *ideal conditions* when all the inputs are known (e.g. Hanna *et al.*, 1991; 1993). Such *hindcast* experiments reflect the "best the models can do". Under emergency conditions the input data available to first-responders (e.g. police, firefighters, or industrial personnel) are much less than ideal. They consist of real-time weather conditions and *forecasts* and direct observations of the damaged tank and chemical involved. For these reasons it is imperative that first-response models be *conservative* in their estimates. That is, they should provide predictions which are as accurate as possible but given the uncertainties, the models should tend to *over-estimate* the gas concentrations and the size of the hazard zones.

Neutral Gas Models

Predictions from the modules used in the Neutral Gas Puff and Plume Models have been shown to be within 20% of the observed concentrations under "ideal conditions" (homogeneous turbulence and weather conditions and uniform terrain). Under "real world conditions" (varying terrain height and nonuniform weather) the predictions were reported to be *the best that can be expected*, within a *factor of 2* of the observed concentrations (AMS, 1977). Validation tests of the modelling procedures used in the Neutral Gas Models, under all stability conditions, showed that between 50 and 80% of the predicted values of concentration fell within a factor of 2 of the measured values (Irwin, 1983).

Preliminary results of tests conducted by AES using the so called "Hanna data" (see Hanna *et al.*, 1993) indicate that the Neutral Plume model is performing well within the *factor of 2* limits and has a tendency on average to slightly *over-predict* the observed concentrations. This result is considered to be very good for first-response applications.

Heavy Gas Models

Tests of the Heavy Gas Puff Model have demonstrated that the location of the leading edge of the cloud was within 5% of the observed value and predicted surface concentrations were within 30% of the measured concentrations for stationary clouds and 60% for a drifting cloud (Matthias, 1990; 1992). Alp and Matthias (1991) have reported that tests of the dispersion modules used in the Heavy Gas Plume Model show that the predicted values of the length of the hazard zone are within a factor of 2 of the observed values.

Preliminary results of tests conducted by AES using the "Hanna data" indicate that the Heavy Puff Model is performing well within the *factor of 2* limits and has a tendency on average to slightly over-predict the observed concentrations. The preliminary results for the Heavy Gas Plume Model are not as encouraging. While some results look good showing predictions within a *factor of 2* of the observations others suggest a tendency for the model to under-predict the observed concentrations. If the Heavy Plume Model proves to under-predict consistently, it will be revised or replaced, possibly with the heavy plume model recently developed by Matthias (1994) which compares favourably with the best of the 14 models reviewed by Hanna *et al.* (1991).

Source Strength Model

The size of the hazard zones predicted by ***A.S.A.P.****'s* dispersion models is critically dependent on the amount of hazardous material released into the air from a damaged container. Very often this information is not known in the early stages following an accident. ***A.S.A.P.***'s **(Response Mode)** Source Strength Model was designed to provide the first-responder with *worst case* estimates of the amount of hazardous material released into the air.

The Source Strength Model is capable of responding to five different types of accidents:

In case of only gas contents -

1. Instantaneous gas release.
2. Continuous gas release.

In case of liquid contents with rupture above the liquid level -

3. Continuous gas release due to flashing and/or evaporation.

In case of liquid contents with rupture below liquid level -

4. Instantaneous liquid release and subsequent evaporation.
5. Continuous liquid release and subsequent evaporation.

The chemical involved may be gaseous or liquid, the release may be continuous or instantaneous, and the rupture in the tank may be above or below the liquid level. Furthermore the tank may be pressurized, refrigerated or at ambient (surrounding) conditions. The Source Strength Model is also designed to deal with the case of super boiling liquid releases. In this case, the physical processes of flash vapourization and evaporation to the atmosphere, from either the surface of the container or from a liquid pool near the container are simulated.

Test results from field experiments for each of the five conditions simulated by the Source Strength Model are not readily available in the literature. Nevertheless, comparisons have been made between field observations of evaporation rates reported by Kawamura and Mackay (1980) and predicted evaporation rates from the Source Strength Model (Table 1). The chemicals tested were all volatile liquids which have their boiling points above the ambient temperature and are non-flashing substances. All are in ***A.S.A.P.***'s high priority chemical list except Pentane.

Table 1: Comparisons between field observations and predicted evaporation rates of volatile liquids.

Experiment No.	Chemical	Air Temperature °C	Source Strength Model Evaporation Rate kg/(m^{2}h)	Field Observation Evaporation Rate kg/(m^{2}h)	Percentage Difference
1	Toluene	21.3	3.3	4.5	-26.7
2	Toluene	29	4	3.4	17.7
3	Cyclohexane	24	5.9	5.9	0
4	Cyclohexane	25.3	7.4	5.9	25.4
5	N-Hexane	-5	6.4	5.6	14.3
6	Methylene Chloride	-6.3	20.7	9.5	117.9
7	Methylene Chloride	1.2	13.8	7.5	84
8	Pentane	1	17.4	10.5	65.7
9	Pentane	5	16.2	6.8	138.3
10	Pentane	7.3	18.9	8.1	133.3
11	Pentane	9	25.2	10.4	142.3

Wind speeds for Experiments No. 1 to 4 were derived from the closest weather station; for Experiments No. 5 to 11 winds measured at 0.35 m above the ground were converted to the 10 m level for the model. Despite the uncertainty of the wind data, and the limited number of experiments, it appears that the Source Strength Model tends to over-estimate the evaporation rates from liquid pools. This is considered reasonable for first-response applications.

Atmospheric Stability Class Model

As noted above, the Stability Class Model used in ***A.S.A.P.*** employs a modelling routine based on the Pasquill-Gifford-Turner method (Turner, 1964). It computes atmospheric stability based on observations readily made by first-responders; the model requires: the date, time, wind speed, cloud cover and location of the accident. The atmospheric stability is reported as a series of classes denoted by one of the first six letters of the alphabet, each representing a different condition of atmospheric turbulence. This turbulence is dominated by convective mixing under Classes A, B or C or by mechanical mixing under Classes D, E and F. Class A refers to extremely unstable conditions, class D is neutral and class F depicts relatively stable conditions.

The Pasquill-Gifford-Turner method is popular in air quality modelling because it is simple and fast in its application. However it is well known to "bias" towards "D" stability and does not account for fog conditions. ***A.S.A.P.***'s **Respond Mode** requires first-responders to report the presence of fog and if present, the system assumes that the atmospheric conditions are stable and automatically sets the stability class to "F".

SENSITIVITY TESTS

Table 2 lists the input requirements for the ***A.S.A.P.*** models and indicates whether the required information is supplied by the user (**X**) or computed internally by the system (**O**); additional details are provided in McGillivray et al. (1995). Note that the inputs which are set as defaults or are computed internally may not be changed in ***A.S.A.P.***'s **Respond Mode** (designed for use by first-responders); however they may be changed in **Analyse Mode** (designed for use by air-quality experts).

The purpose of the following tests is to illustrate the sensitivity of the ***A.S.A.P.*** models to different input parameters and to identify the possible effects of input data uncertainties on the computed hazard zones. The sensitivity tests focus on the effect of inputs supplied by the user (wind speed, air temperature, relative humidity, terrain roughness) as well as inputs which are computed internally by the system (atmospheric stability and the diameter of the liquid pool which may form near a leaking tank). In each of the sensitivity tests reported below, only one input parameter was changed while the others were held constant.

Table 2: *A.S.A.P.* Inputs

Note the difference between user inputs (**X**) and automatic inputs (**O**) which are used directly in **Respond Mode** and may be changed by the user in **Analyse Mode**.

MODEL INPUTS	**Stability Class Model**	**Source Strength Model**	**Neutral Puff Model**	**Neutral Plume Model**	**Heavy Puff Model**	**Heavy Plume Model**
Weather: Time:	X					
Date:	X					
Wind Speed:	X	X	X	X	X	X
Wind Direction:			X	X	X	X
Temperature:		X	X	X	X	X
Pressure:		X				
Relative Humidity:						O**
Cloud Amount:	X					
Cloud Height:	X					
Fog:	X					
Latitude/Longitude:	O*					
Chemical:		X	X	X	X	X
Liquid or Gas:		O				
Rupture Location:		X				
Spill type instant/continuous		X				
Tank type:		X				
Tank Temperature:		O				
Tank Pressure:		O				
Container Volume:		O				
Liquid Volume:		X				
Rupture Diameter:		X				
Height of liquid above rupture:		X				
Pool Diameter:		O***				
Surface Roughness:			X	X	X	X
Source Type - point, area or volume:			O	O	O	O
Sigma Type Briggs/Doury:			O	O		
Mixing Height:			O	O	O	O
Eff. Emission Height:			O	O		
Source Height:			O	O		
(Briggs) Source Diameter:			O	O		
(Briggs) SourceGas Temp:			O	O		
(Briggs) Exit Gas Vel.:			O	O		
Receptors:			O	O	O	O
Height above ground:			O	O	O	O
Crosswind distance:			O	O	O	O

* Latitude and longitude are "entered" automatically when the map is selected.

** Relative humidity may be eliminated as an input in **Respond Mode**. See text.

*** Pool diameter may be required as an user input in the case of instantaneous releases of non-flashing liquids. See text.

Wind Speed

Wind speed is used by all of the ***A.S.A.P.*** models; it is used in the assessment of atmospheric stability, in determining the rate of evaporation from a liquid chemical pool in the source strength model and in each of the dispersion models. Wind speed is a difficult parameter to estimate and predict with precision at a given location (usually some distance from a weather station). The effect of wind speed on the size and shape of the hazard zones is examined below and found to be an important input parameter.

As shown in Figure 1, the hazard zones predicted by the Neutral Puff Model are unaffected by wind speed. These hazard zones are defined by the envelop of the growing puff (i.e. the peak concentration contours) as it travel downwind. This is not affected by wind speed but the speed at which the puff travels is directly affected by wind speed. Future versions of ***A.S.A.P.*** could show this by including time on the downwind axis.

The hazard zones predicted by the other dispersion models are directly affected by wind speed. The Heavy Puff Model predicts smaller hazard zones under higher wind speeds because of the dilution of the dense cloud by air entrainment (Figure 2). Tests using the Neutral Plume Model (Figure 3) and the Heavy Plume Model (Figure 4) show that even a small change in wind speed (on the order of 10%) results in a comparable (and inverse) change in the hazard zones predicted. As the wind speed increases, the size of the hazard zones are reduced because the pollutant is dissipated and diluted, reducing the concentrations.

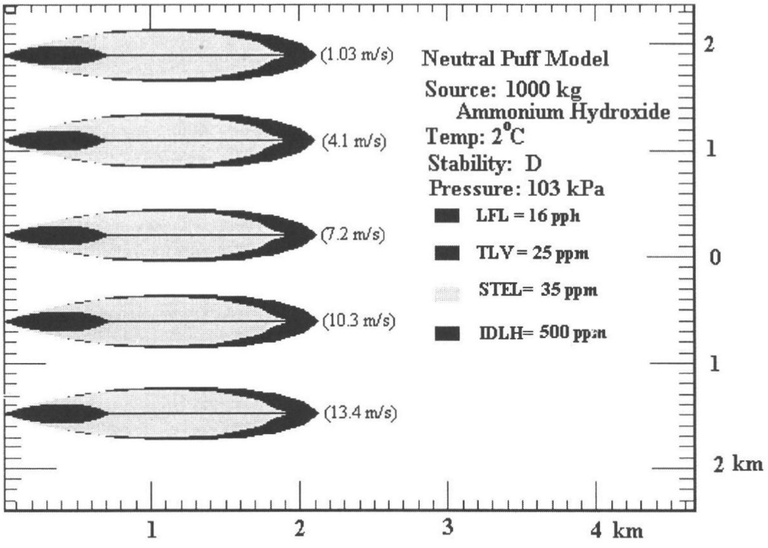

Figure 1: The effect of wind speed on the hazard zones predicted by the Neutral Puff Model. The inputs shown were held constant, a suburban terrain was used; only the wind speed was changed.

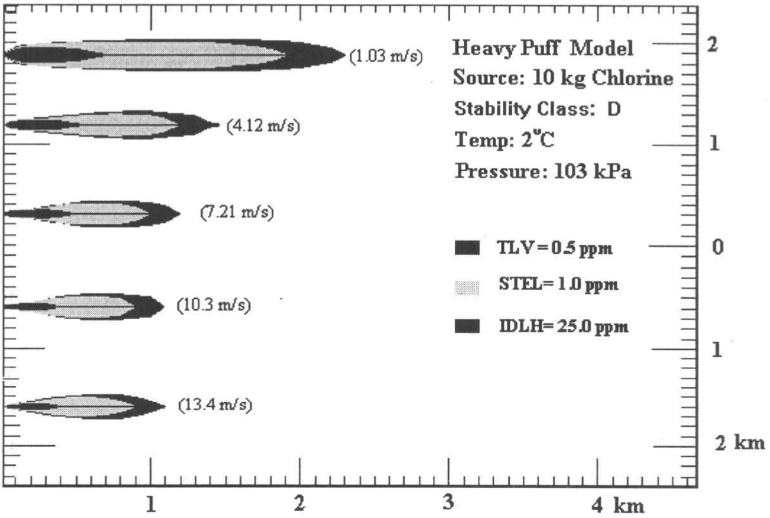

Figure 2: The effect of wind speed on the hazard zones predicted by the Heavy Puff Model. The inputs shown were held constant, a suburban terrain was used; only the wind speed was changed.

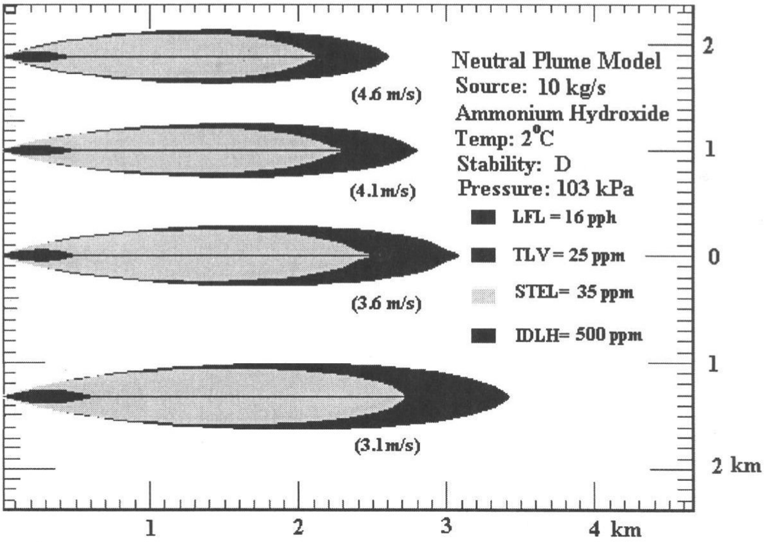

Figure 3: The effect of wind speed on the hazard zones predicted by the Neutral Plume Model. The inputs shown were held constant, a suburban terrain was used; only the wind speed was changed.

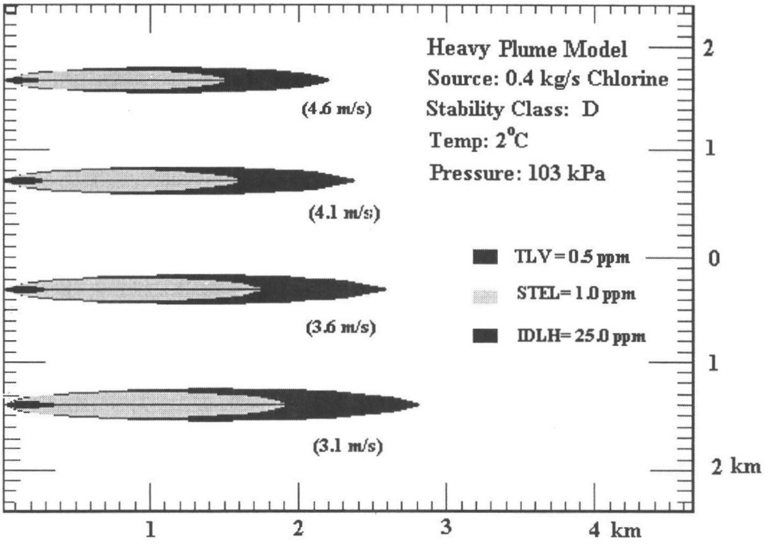

Figure 4: The effect of wind speed on the hazard zones predicted by the Heavy Plume Model. The inputs shown were held constant, a suburban terrain was used; only the wind speed was changed.

Air Temperature

Air temperature is employed by all of the dispersion models and by the source strength model. The horizontal area of the hazard zones predicted by the four dispersion models is relatively unaffected by temperature. Air temperature is not an important factor in the dispersion of heavy gases and controls only the effective height of the puff or plume in the Neutral Models.

Nevertheless, the Source Strength Model is potentially very sensitive to changes in air temperature, particularly when modelling the flashing process involved when liquefied gases (pressurized liquids at stored at temperatures above its boiling point) are released into the air (e.g. Figure 5). Since the source strength directly affects the size of the hazard zones, air temperature is considered to be an important input parameter.

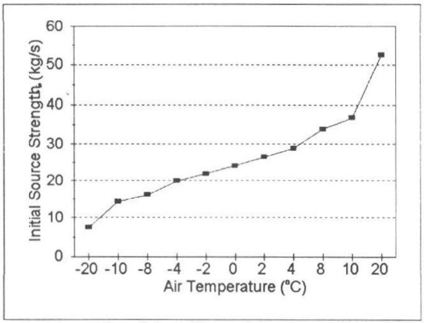

Figure 5: Example of the effect of air temperature on the initial source strength predicted from a continuous Chlorine spill.

Relative Humidity

Only the Heavy Gas Plume model requires the input of relative humidity. This is used to account for the exchange of heat between the relatively cold dense gas cloud and the surrounding air. The humidity of the surrounding air affects the rate of this heat transfer. Sensitivity tests conducted in this study reveal that this input parameter has little or no effect on the size or shape of the hazard zones predicted. If additional tests verify this observation, this input will no longer be required in ***A.S.A.P.***'s **Respond Mode**.

Terrain Roughness

A.S.A.P. requires the input of the type of terrain at the accident site. This information is used to define the surface roughness lengths (Z_O) in each of the dispersion models. As shown in Figure 6, the Neutral Plume Model is very sensitive to this input parameter. Tests conducted in this study on the other dispersion models showed the same trends demonstrating the critical importance of this input parameter.

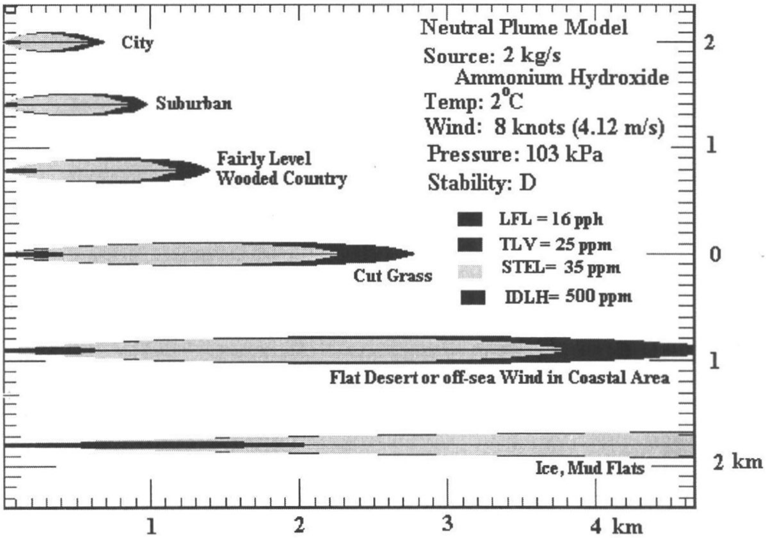

Figure 6: The effect of terrain type (surface roughness) on the hazard zones predicted by the Neutral Plume Model. The inputs shown were held constant; only the terrain was changed. Note: over Ice surfaces or mud flats the TLV hazard zones extend out to 20 km.

Atmospheric Stability

The effect of atmospheric stability on the dispersion of air pollutants has been well established in the literature (e.g. Turner 1970); however this work does not focus on the size and shape of hazard zones predicted. As shown in Figure 7 changes in the atmospheric stability class results in large changes in the size of the hazard zones predicted using the Heavy Gas Puff Model. The hazard zones tend to be much longer and not as wide under relatively stable conditions (E and F). Tests conducted on the other dispersion models showed essentially the same results.

The dispersion of pollutants in the layer of air adjacent to the ground (the boundary layer) is largely controlled by the prevailing conditions of atmospheric stability. In simple terms, the dispersion of a pollutant is *wide-spread* under conditions of strong instability and a deep mixed layer (e.g. a sunny day in summer); this would result in relatively smaller hazard zones from a chemical spill. Conversely, the dispersion of a pollutant is *less* when there is a temperature inversion and the boundary layer is stable. Turbulence is then suppressed and upward motion is effectively eliminated. This would result in relatively larger hazard zones from a chemical spill. There are of course exceptions; however it should be clear that the effects of atmospheric stability are critically important in predicting the dispersion of hazardous gases.

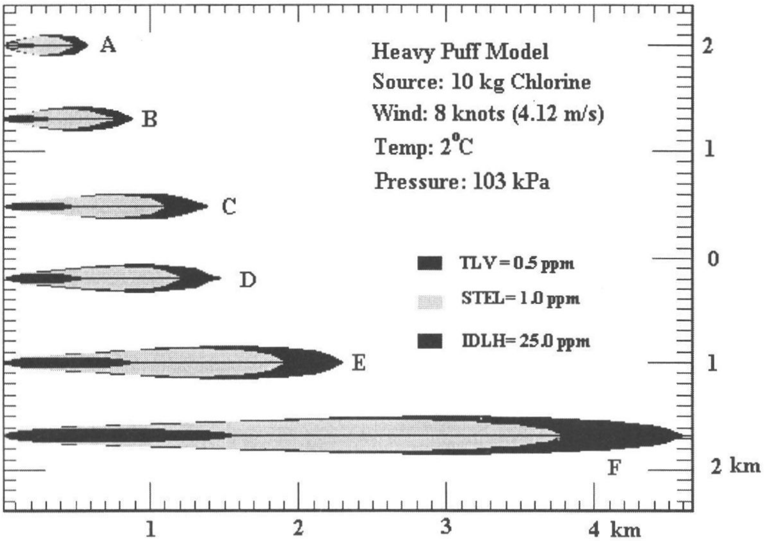

Figure 7: The effect of atmospheric stability on the hazard zones predicted by the Heavy Puff Model. The inputs shown were held constant; a suburban terrain was used. Only the atmospheric stability class (labelled A to F) has been changed.

Pool Diameter

The diameter of the liquid pool that forms near a damaged tank is extremely difficult to observe at an accident site. For this reason the current version of ***A.S.A.P.*** does not require the first-responder to enter this parameter. Instead a large default pool diameter is used (300 m).

This is considered a reasonable approximation for continuous liquid spills because the pool diameter is re-estimated internally by the Source Strength Model to be the largest possible assuming conservation of the mass balance between the liquid release rate and the evaporation rate. This results is a conservatively high estimate of the rate of gas released to the air by evaporation (e.g. Figure 7).

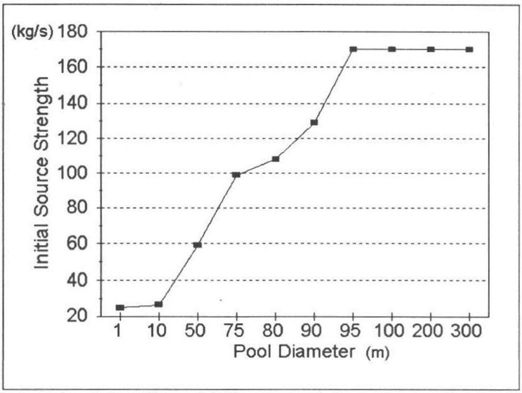

Figure 7: Example of the effect of different pool diameters on the predicted initial source strength from a continuous Chlorine spill.

Setting a default value for pool size has proved to be more difficult in cases where the tank is damaged extensively causing an instantaneous liquid release. Under these conditions, if flashing liquids are involved, we can reasonably assume a *worst case* situation where the entire amount the liquid is vapourized into the air. However, if non-flashing liquids are involved, the total surface area of the liquid pool (or pools) becomes a critically important input to determine the evaporative release of the chemical into the air. For this latter situation, it may be necessary to modify ***A.S.A.P.***'s **Respond Mode** to allow the input of pool size for instantaneous non-flashing liquid releases. Further study is required to find the best way to deal with this problem.

CONCLUSION

The models selected for use in ***A.S.A.P.*** appear to produce results which compare favourably with experimental field observations. The predictions from the dispersion models are shown to be within a *factor of 2* of the field observations and on average show a slight bias towards over-prediction of pollutant concentrations measured at specified downwind points. Only the Heavy Gas Plume Model showed a potential tendency to under-estimate the pollutant concentrations and these results are still under review. One concern with the tests of model accuracy is that they focus on model skill under *ideal conditions*, where the inputs are known with certainty, and on a spatial range which is within about 2 km of the source. These tests do not examine the models operational performance under real-time emergency conditions, where the inputs are less certain and the spatial range may be much broader.

The sensitivity tests show that the inputs used by ***A.S.A.P.*** (with the possible exception of relative humidity) all directly or indirectly affect the size and shape of the hazard zones predicted. Clearly, under real-time emergency conditions when input data are less certain, the accuracy of the models will likely be reduced. Nevertheless, ***A.S.A.P.***'s Source Strength Model has been designed to compute *worst case* estimates of the pollutant released into the air and the dispersion models show a slight bias to over-predict. These features should provide confidence in the hazard zones predicted.

A.S.A.P. is designed to predict the area of the hazard zones, rather than point concentrations, but field data to test this feature of the system are lacking. There is a need for field experiments which focus on measurements of areas of gas concentration (or the lateral spread of the plume). There is also a need to develop actual emergency data sets which identify the problems encountered with data uncertainties when determining the hazard zones.

It is concluded that the ***A.S.A.P.*** models are very well suited for hazard assessments and operational safety decisions in real-time air quality emergencies. The models use inputs which are readily available to first-responders, they are fast and they show a slight bias towards over-estimating pollutant concentrations under ideal conditions; these qualities give confidence to their operational performance under real-time emergency conditions.

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THE U. S. ENVIRONMENTAL PROTECTION AGENCY/ENVIRONMENTAL RESPONSE TEAM'S (EPA/ERT) ROLE IN AUDITING ON SITE AIR-MONITORING SYSTEMS

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INTRODUCTION

Many hazardous waste sites require a perimeter air monitoring system (AMS) in order to assure that fugitive emissions from the site are within site specified limits. Increasing demands on the AMS are straining the resources of even the most sophisticated and up to date equipment. The need to provide instantaneous, or near instantaneous results, at detection levels in the parts per billion (ppb), and even in the parts per trillion (ppt) range, is pushing the technological envelope. More exotic and unusual analytes present greater challenges to the sampling and analytical systems. All too often, appropriate standards and quality control protocols may not be available.

In order to assure the quality of the data obtained by AMS at various hazardous waste sites, the USEPA/ERT conducted audits of the AMS systems. Coupled with the increasing demands on the AMS, the auditing protocols and equipment have also required increasing sophistication and flexibility.

Generally, an ERT audit will consist of a review of the site monitoring equipment, site quality assurance/quality control (QA/QC) plans and documents. The site stations are challenged with known certified standards at several concentration levels. Preferably, the challenges are conducted through the station sampling port in order to mimic, as closely as possible, actual site sampling conditions. In order to easily adjust challenge concentrations, a dilution apparatus setup was built which allows easy and accurate changes in the challenge gases. The purpose of this paper is to demonstrate the need of a site audit program based on ERT case studies.

SITE A

This hazardous waste site is a former refinery. Primary operations included the recovery of petrochemicals from styrene tars, the regeneration of copper catalysts, and the production and recovery of many other chemicals such as cresylic acid, sodium sulfide and vinyl chloride. Storage lagoons were excavated to support the styrene tar processing operations. The lagoons were ultimately closed by removing any free liquids, mixing soil and calcined clay with the residues and covering with clean soil. Plans for remediation included excavation of the buried lagoons and on-site incineration of the waste, though these plans have since been reevaluated.

While the one hour action limits for the volatile organic compounds were set to equal the 24 hour fence line ambient air quality standards (FLAAQS), the site analytical requirements include updates every 15 minutes. The AMS includes collection of fenceline real-time air data using: gas chromatographs (GCs) for volatile organic hydrocarbons (known as the AQMS); methane and non-methane hydrocarbon (NMHC) analyzers (known as the BAMS); and real-time air data collection using handheld instruments and mobile gas chromatographs downwind of excavation activities. Data from the fenceline monitoring systems are instantaneously routed to a control room by telemetry. Volatile organic data are recorded and updated at least every 15 minutes; methane and non-methane hydrocarbon data are recorded and updated every three minutes.

The Air Quality Monitoring System (AQMS) is composed of seven volatile organic compound monitoring stations at fixed and mobile locations, and monitors for the eight targeted volatile organics (operational range .005 - 5.ppm) Each of the AQMS stations includes a MINICAM™ GC equipped with a FID detector connected to an ambient air sampling system and is manifolded to a span gas for a daily Quality Control (QC) check. Each system is calibrated from a standard gas blend containing the eight gases of interest: vinyl chloride, methylene chloride, ethylene dichloride, benzene, 1,1,2-trichloroethane, toluene, styrene and bis(2-chloroethyl)ether. Each GC is equipped with a three-bed sorption tube for concentration of ambient air analytes prior to thermal injection onto the GC column.

The AQMS audit consists of challenging each of the GCs with a standard gas at two concentrations. For the mid-range concentration challenge, referred to as the audit gas, a standard gas blend with analyte concentrations in the 20 ppm range, is diluted with ultrazero air to provide a concentration of 20 to 400 ppb (as specified by the OSC/RPM) in the final mixture. Figure 1 illustrates the audit setup. The dilution apparatus uses electronic mass flow controllers (MFC) to monitor and control the gas flows. Blank runs are conducted with the flow from the ultrazero air cylinder maintained and flow from the standard gas blend shut off. The MFC flows are checked prior to the audit using a Gilibrator™ soap bubble flow meter. A flow rate of four L/min, similar to actual sample flow, is used for the audit gas. All lines are heat traced to minimize condensation effects. All audit challenges are conducted by connecting the challenge gas at the inlet to the AQMS sample manifold.

A low-range concentration challenge, referred to as the span gas, is conducted by using a gas blend prepared and certified by the gas vendor at the practical quantitation limit (PQL) level for each analyte (Table 1). The flow from the cylinder is monitored using a single-tube flow meter at a nominal rate of four L/min.

Total methane and NMHC are measured (operational range 0.5 - 20 ppm) at separate BAMS stations at five locations at the fenceline. Particulate data and meteorological data are also obtained and are monitored real time at the central control room. Each of the BAMS stations consists of a Byron™ Model 301 Analyzer, a gas chromatograph equipped with a flame ionization detector and valving to provide both methane and NMHC analysis within a three-minute cycling time. Sampling ports are provided at both the five foot and fifteen foot levels which are connected to a sampling pump connected to the GC inlet.

The BAMS audit consists of challenging the BAMS stations with standard gases at known concentrations. A cylinder of standard gas is connected to the five-foot sampling port through a flow meter and regulated with a needle valve to assure a flow of 60 to 120 mL/min into the port. To test the response of the analyzer, methane, propane and vinyl chloride at nominal concentrations of 10 ppm are used.

During the course of the EPA audits the on-site contractor modified and improved the AMS. GC run times were increased from 8.1 to 13.5 minutes in order to improve the chromatography and expand and upgrade the retention time windows used in quantitation of the target analytes. The sampling manifold was improved by increasing sample flow rates to five L/min and heat tracing the lines to avoid condensation of the less volatile analytes.

Problems observed during the audits included:

- Improper retention time windows caused loss of and/or clipping of target analytes.
- Carryover of less volatile compounds between sample runs.
- Failure of the telemetry system with loss of data. While the AQMS had hard copy backup, the BAMS had no backup.
- Major loss of the styrene and bis(2-chloroethyl)ether in the challenge gases.
- Low recoveries for styrene and bis(2-chloroethyl)ether observed during one audit were traced to the decomposition of the analytes in the standards cylinder and were attributed to blending of the standard in air. However, gas blends in nitrogen have shown good stability for several months.

Tables 2, 3 and 4 detail the recoveries obtained during a recent audit. Almost all results are within the required Data Quality Objectives. Note that the response observed for vinyl chloride in Table 2 reflect the relative response of vinyl chloride to the flame ionization detector used in the Byron™ analyzer. The instrument is calibrated versus propane and therefore will give a lower response to the vinyl chloride.

TABLE 1

AQMS SPAN GAS

ANALYTE	CONCENTRATION
BENZENE	5 ppb
BIS-(2-CHLOROETHYL)ETHER	50
ETHYLENE DICHLORIDE	10
METHYLENE CHLORIDE	10
STYRENE	20
TOLUENE	20
1,1,2-TRICHLOROETHANE	20
VINYL CHLORIDE	30
NITROGEN	BALANCE

TABLE 2

AIR MONITORING SYSTEM

AVERAGE RESPONSE PER STATION, MAY 1994

ANALYTE	EXPECTED VALUE	BAMS-1	BAMS-2	BAMS-3	BAMS-4	BAMS-5
	ppmv	ppmv	ppmv	ppmv	ppmv	ppmv
METHANE	10.00	12.05	10.16	7.55	10.38	10.40
PROPANE	9.89	10.91	10.80	9.68	9.47	9.89
VINYL CHLORIDE	10.30	6.14	5.93	5.36	6.08	6.38

TABLE 3

SPAN GAS AVERAGE RECOVERIES (%)

STATION NUMBER	VINYL CHLORIDE	METHYLENE CHLORIDE	ETHYLENE DICHLORIDE	BENZENE	TRICHLORO-ETHANE	TOLUENE	STYRENE	BIS(DCE)
1	110.5	98.1	91.7	92.9	120.3	91.3	106.7	78.7
2	96.4	99.3	100.9	92.9	76.5	97.7	107.9	103.9
3	86.1	95.0	91.7	111.5	118.4	*57.4*	100.5	114.8
4	104.1	105.5	103.5	100.9	95.5	101.0	108.9	**126.0**
5	98.7	93.5	91.7	92.9	93.5	92.1	101.4	116.7
6	92.1	87.9	84.4	92.9	89.7	85.6	91.3	90.6
7	88.1	86.0	91.7	92.9	93.5	93.0	100.5	**130.5**

Values > ±25% in bold
Values > ±40% in italics

TABLE 4

AUDIT GAS AVERAGE RECOVERIES (%)

STATION NUMBER	VINYL CHLORIDE	METHYLENE CHLORIDE	ETHYLENE DICHLORIDE	BENZENE	TRICHLORO-ETHANE	TOLUENE	STYRENE	BIS(DCE)
1	109.6	95.3	90.1	91.2	94.4	**126.1**	78.0	81.4
2	89.9	89.9	87.0	103.7	106.6	91.8	79.8	89.1
3	87.2	89.2	86.1	85.2	92.7	**132.2**	81.2	107.5
4	93.4	89.2	84.2	79.4	106.6	88.8	76.1	97.1
5	93.1	82.0	79.1	79.9	81.5	77.2	79.0	91.6
6	93.1	87.3	85.6	84.9	90.8	86.0	74.6	78.6
7	85.4	88.1	84.4	*55.8*	*67.7*	90.2	89.3	114.0

Values > ±25% in bold
Values > ±40% in italics

SITE B

This site is an old creosote wood-treating site located within a 100 year flood plain of a bayou. Numerous releases of creosote onto the site with spillage into the bayou have occurred. Initial investigations by the United States Coast Guard revealed that creosote was discharging overland via runoff into the bayou. In 1970, the plant burned down and a large amount of creosote was released from storage tanks into the bayou. In 1982, the site was incorporated into the National Priorities List. Remediation efforts include dredging of the bayou adjacent and downstream of the site and on-site incineration of the contaminated soils.

There are six AQMS stations at the site. Two are land based; the rest of the stations are based on barges on the bayou. Each of the AMS stations includes a Mine Safety Appliance Baseline Industries™ Model 8550 GC equipped with a photoionization (PID) detector connected to an ambient air sampling system; ambient air is sampled through a 1/4" stainless steel line. A sample pump pulls the air through a 1/4"stainless steel line through a loop in the GC sampling valve. Two permeation tubes for benzene and ethylbenzene are manifolded to the sampling line via automatic valves. For calibration, a standard gas from the permeation tube system is injected into the GC. Benzene and ethylbenzene response factors are obtained directly from the response to the permeation tube gases. The calibration for the other analytes, toluene, 1,2,4-trimethylbenzene and naphthalene, are determined by using relative response factors. Data from the AQMS are telemetered to a central computer and reported using software, provided by the GC vendor, designated as the Data Acquisition Network System™. Output may be reported in time weighted averages of several minutes to hours.

The site audit consisted of challenging each of the GCs with a standard gas prepared and certified by the gas vendor at the Practical Quantitation Limit (PQL) level for each analyte (Table 6). The flow from the cylinder was monitored using a single-tube flow meter at a rate of one to 1.5 L/min. All audit challenges were conducted by connecting the challenge gas at a tee in the sampling line immediately downstream of the sampling port. The gas flow at the inlet of the sampling port was monitored to assure that excess flow was introduced into the line.

The results of the challenges to the AQMS include:

- Recoveries during the initial audits ranged from 40 to 380% (Table 5).
- Major discrepancies were observed between the GC reported results and the results reported by the central computer Data Acquisition Network System. Most of these problems were addressed in followup audits.
- Benzene and ethylbenzene are calibrated directly via a permeation tube setup. Problems with recoveries on these key analytes, as well as, with the other target analytes, indicated that careful attention needs to be addressed to the

calibration conditions, including permeation tube parameters and response factors.

- Several stations showed erratic and/or high response to benzene, which may be due to calibration problems or baseline designations.
- None of the stations were able to identify naphthalene at the PQL during the initial audits.
- Samples of the audit gas and site QC gas were exchanged and sent to both ERT/TAT's Edison lab and to the site vendor corporate lab for analysis. Results of these crosschecks show that the site QC standard was approximately 50% of certification (Table 6). Since these standards were used in calibration of the monitoring stations, recoveries would then be expected to be 200% or more.
- Instrument conditions for each station varies widely. Among the stations, GC temperatures range from 50 to 70°C and flow rates are also varied to obtain equivalent retention times for each analyte between the stations. Backflush times also vary from station to station. Since the configuration of each station GC is equivalent, i.e., same columns, detectors and equipment, temperatures and flow rates should be similar, as well.
- The peak shape of the naphthalene peak at one station was unusual, having a trailing shoulder with an abrupt return to baseline. Relative response factors (RRF) on this GC were also drastically different from the RRF of the other GCs.

Several of these issues still need to be resolved and will be the focus of future audits.

CONCLUSIONS

Site audits by ERT provide a mechanism to assure the quality of the data provided by site monitoring systems. As a result, they have proven critical in assuring public health and safety at hazardous waste sites. A draft AQMS audit standard operating procedure is available by contacting the U.S. EPA Environmental Response Team, Environmental Response Center, 2890 Woodbridge Avenue, Edison, New Jersey 08837.

TABLE 5

AVERAGE RECOVERIES (%)

STATION NUMBER	BENZENE	TOLUENE	ETHYL BENZENE	TRIMETHYL BENZENE	NAPHTHALENE
CERTIFIED (PPM)	0.102	10.1	10.1	2.52	1.01
4	40.8	87.4	133.5	112.0	2.4
6	153.3	159.4	201.8	217.2	103.0
8	57.6	395.8	361.2	272.9	258.6
9	66.0	230.7	278.8	364.1	195.2
10	43.7	267.5	375.9	380.7	269.1
11	68.5	187.8	251.4	192.3	76.7

TABLE 6

POST AUDIT COMPARISON OF CHALLENGE AND SITE CALIBRATION GAS STANDARDS

DATA IN PPM

ANALYTE	AUDIT GAS			SITE CALIBRATION GAS		
	EXPECTED[1]	ERT/TAT[2]	PRP[3]	EXPECTED	ERT/TAT	PRP
BENZENE	0.1	.14	0.1	1.3	1.0	0.8
TOLUENE	10.1	10.5	10	3.4	2.0	1.8
ETHYLBENZENE	10.1	11.4	10	3.4	2.2	1.7
1,2,4-TRIMETHYLBENZENE	2.5	N/A[4]	1.8	2.5	N/A	1.3
NAPHTHALENE	1.0	N/A	(0.16)[5]	-	-	-

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[1] As specified by manufacturer.

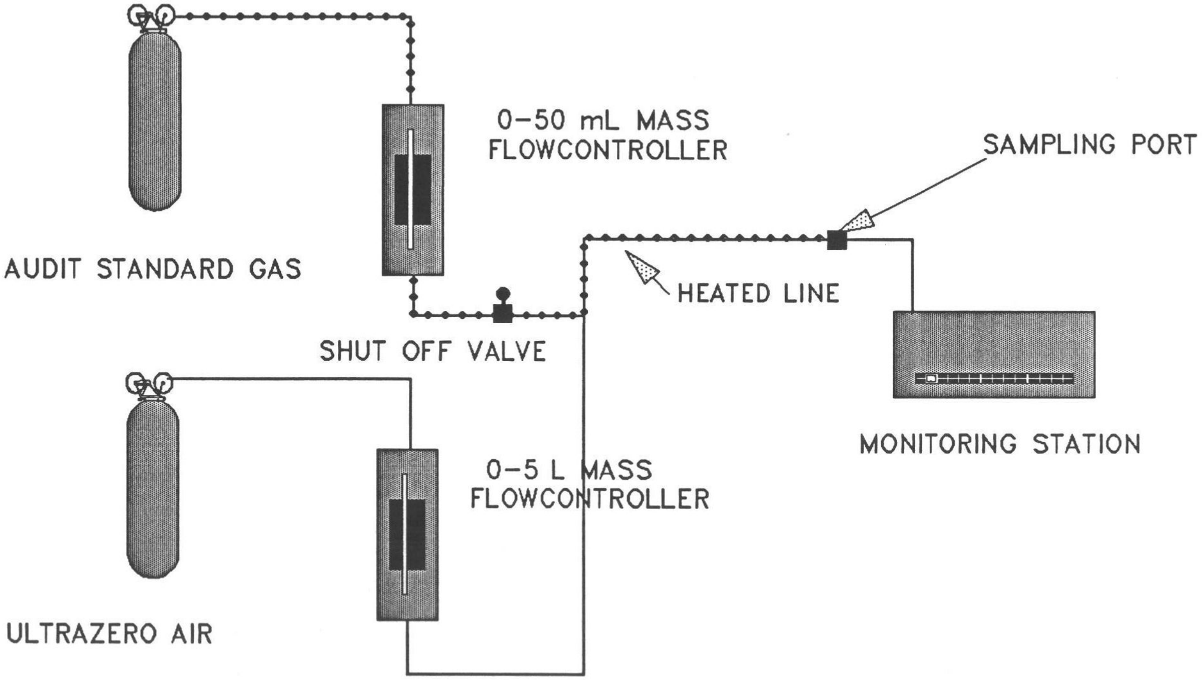
[2] Analyzed by ERT/TAT GC/MS lab in Edison NJ.

[3] Analyzed by principle responsible party's corporate lab.

[4] Not analyzed.

[5] Value low due to low pressure in cylinder.

FIGURE 1: AQMS AUDIT CONFIGURATION



PUBLIC HEALTH EVALUATION OF EMISSIONS FROM IN-SITU BIODEGRADATION TREATMENT CONDUCTED AT UNCONTROLLED HAZARDOUS WASTE SITES ;

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ABSTRACT

In-situ biodegradation, biological treatment performed in place, employs natural biological activity to decompose organic constituents into carbon dioxide and water. The capital costs for this type of treatment, used at uncontrolled hazardous waste sites, are substancially lower than those associated with other remediation options, such as incineration, excavation and removal, soil vapor extraction and soil washing/solvent extraction. This cost factor presents in-situ biodegradation as an attractive method in treating organic wastes on Superfund projects.

Field studies have shown that volatilization may account for the loss of many volatile organic chemicals (VOC) being treated via in-situ biodegradation. Air emission data on full scale process effectiveness and contaminant fate have been limited. The land tracts being treated are generally expansive resulting in a surface area where air emissions can be elevated.

Based upon available data, emissions should be modeled prior to full scale site implementation using the SEAMS Landtreatment, RTI Landtreatment, LAND7 or CHEMDAT7 Models. These models provide time dependent algorithms for the estimation of volatile emissions from land treatment operations. These models have specific algorithms to describe the conditions at the site including contamination, the phase in which the contaminant is present, soil moisture, and efficiency of biodegradation. The results from these models may be incorporated into dispersion models to evaluate impact off-site.

INTRODUCTION

In-situ methods of hazardous waste treatment became used at increasing frequency following the land disposal prohibitions, or "land bans", issued by the U.S. Environmental Protection Agency (EPA) in the 1984 amendments to the Resource Conservation and Recovery Act (RCRA). With these amendments, EPA prohibited the land disposal of specific hazardous wastes in order to protect human health and the environment for as long as the waste remains hazardous. One exception to this prohibition are wastes treated so as to substancially reduce their toxicity or the migration potential of the hazardous constituents. Biological processes are used to treat and remediate contaminated soils, and have proven to be a cost effective means of achieving contaminant reduction.

Bioremediation is a managed, active treatment process that uses microorganisms to degrade and transform the chemicals in contaminated soils and sludges.[1] The microbial activity can be heightened by the introduction of nutrients(nitrogen, phosphorous and trace metals) and oxygen to the contamination area by injection wells or infiltration systems. Under aerobic conditions the microbes will then degrade a wide range of contaminants into carbon dioxide and water.

The more stringent requirements on hazardous waste remediation and the limitation of historical technologies have brought forward the development of in-situ methods to treat contaminants in place. In-situ biodegradation involves stimulation of the biological breakdown of contaminants at a site without excavation of the material, and relies entirely upon the contact between contaminants and the microorganisms.[2] The microorganisms which are capable of breaking down hydrocarbons and other materials are generally indigenous in soil and groundwater. The native microorganisms are thought to have advantages over adapted organisms because they also have been acclimated to the subsurface conditions such as temperature, light, soil salinity and the predator mix.

Systems that try to enhance natural biological activity typically use injection wells to provide an oxygen source (i.e.,air, pure oxygen,or hydrogen peroxide) to stimulate aerobic degradation or to support growth of contaminant metabolizing organisms.[1] Hydrogen peroxide is the most frequently used oxygen source for enhanced biodegradation. Peroxide is capable of releasing enough oxygen to saturate injected groundwater to its oxygen solubility limit of approximately 40 mg/L.[3] Enhanced biodegradation processes add artificial sources of nutrients and non-native organisms capable of degrading specific contaminants.[1,4]

In-situ biodegradation generally has one or more of the following features:

- The active agents are microorganisms that biodegrade the contaminants;
- The microorganisms are present in the aquifer or soils and perform their reactions in place;
- Naturally occurring or added bacteria are stimulated to bring about rapid biodegradation rates;
- Stimulation means that the number of microorganisms active in the bioremediation is increased by many orders of magnitude. Controlled addition of materials normally missing from the environment allow growth and activity of desired microorganisms.[5]

All microorganisms require adequate levels of inorganic and organic nutrients, growth factors (vitamins, magnesium, cooper, manganese, sulfur, potassium, etc.) water, oxygen, carbon dioxide and sufficient biological space for survival and growth. Other factors which can influence microbial biodegradation rates include inhibition by chemicals in the waste stream being treated, the number and physiological state of the organisms as a function of available nutrients, the seasonal state of microbial development, predators, pH and temperature.[6]

CONTAMINANT AIR EMISSIONS

There has been a growing scientific and regulatory interest in assessing emissions of volatile constituents into the atmosphere during and after waste applications at bioremediation locations. Preliminary studies have shown significant fractions of the total hydrocarbons applied at a refinery landfarm could be emitted into the air.[7] Typical emission losses from in-situ treatment processes are evaporation of volatile and semi-volatile compounds. Air emission from in-situ biological treatment processes, along with leaching and runoff, are important alternate routes of contaminant loss from land treatment processes.

Effective land treatment is in general limited to the upper 6 to 24 inches of soil. At depths greater than 12 inches, the oxygen supply is often inadequate to support bioremediation processes. Tilling is used to mix the soil and increase oxygen levels. Generally, when soil treatment to a depth of greater than 12 inches is desired the upper layer of soil is treated first, then tilled so that the lower layers are moved to the surface for treatment.[8] The volatile materials in the soil have the potential for partitioning into four different phases: 1) a vapor phase; 2) an oil phase where volatile material is dissolved in the oil; 3) a water phase where volatile material is adsorbed in the soil moisture; and 4) a soil phase where volatile material is absorbed by organic carbon within the soil.[9] Only the vapor phase is available for diffusion out of the soil/waste mixture.

When a sludge containing volatile chemicals is tilled into the soil at a land treatment site, the maximum rate of air emissions will occur immediately after tilling. Volatile organic compounds will leave the surface and enter the ambient air via wind currents. Within a few hours following tilling, the rate of air emissions from volatile compounds will be substantially less than the maximin rate because the volatiles at the surface have been removed by the wind and the remaining volatiles must diffuse up through layers of porous solids.

Emissions from the surface of the soil/waste mixture are limited by the diffusion of vapors through the pore spaces in the mixture. In a land treatment operation, diffusion of vapors out of the soil must take place within the confines of the air-filled spaces within the soil. This characteristic of the soil is referred to as the air porosity. Soil air porosity undergoes substantial changes over time as soil dries out and when moisture is added by rainfall or by watering. As a result, accurately accounting for soil porosity when determining emissions is difficult.

Studies of emission rates of volatile organic compounds over time have not revealed specific relations between rainfall or moisture and volatilization. Sorption curves, the relationship between evaporation rates in soil, of water and some volatile organics are very similar. This means that the presence of one may inhibit the volatilization of the other. The addition of liquids into the system (i.e.,rain) will, initially, fill the pore spaces in the soil and drive the vapors out (the wet dog effect). The liquid then forms a barrier repressing the release of other gasses. A study of surface emissions over time[10] revealed the variability of flux emissions before, during, and after a significant rain event (wind speed minimal before and following the rain event). The concentration of 1,1,2-trichloroethane in each of samples collected at thirteen locations over a six day period are reported in Figure 1. Day One was hot and humid; day two it rained; then conditions returned to hot and humid for the remainder of the period. The results did not reveal an increase in the emissions during the rain or a reduction in the emissions following the rain (at all of the sampling locations). The concentrations of other compounds measured during this study also varied and their variability was inconsistent with that of the 1,1,2-dichloroethane.

Field studies have shown that volatilization may account for the disappearance of the majority of volatile organic compounds being treated at a land treatment facility.[11] Bioremediation of a 24,330 kg gasoline discharge from a service station to the subsurface was conducted in a residential area. The authors estimate removal of 17,640 kg (72%) can be attributed to bioremediation, with 6,240 kg of gasoline removal accounted for by soil venting and air stripping.[12] A former solid waste dump, used in part to dispose of semi-liquid wastes from refinery operations was addressed using forced aeration in-situ bioremediation. Polycyclic aromatic hydrocarbon (PAH) removal from the soil was attributed 20% to microbial transformation with volatilization being the major factor attributed to the disappearance of PAHs.[13] The authors concluded the forced aeration stripped and volatilized most of the PAHs in the soil. The inherent design of a forced aeration, or bioventing, system is to vaporize and transport volatile organic chemicals upward from the suburface to media more amenable for biodegradation.[14,15] This design results in a varying degree of air stripping of contaminants depending on their nature and site specific conditions.

The primary environmental factors, in addition to the biodegradability and volatility of the soil contaminants, which influence air emissions are wind speed and temperature. At higher wind speeds the driving force for mass transfer into the gas phase increases, so evaporative emissions tend to be higher. The microorganisms tend to perform best within a narrow temperature range (50-60 degrees C).

Deviations from these optimal temperatures will tend to diminish microbial activity and result in slower biodegradation. As a result, competing mechanisms such as volatilization may predominate. Air emissions from land treatment facilities are initially high and decrease as the concentration of volatiles in the soils falls off; tilling of the soils tends to increase the emissions by at least a factor of three.[11] Another field test demonstrated that approximately 25% of raw oily refinery waste applied to a land treatment facility were lost to the atmosphere.[16] Compounds with boiling points less than 400 degrees F tended to be volatilized while compounds with boiling points greater than 400 degrees F tended to remain in the soil and be degraded.

In land treatment sites, the area over which air emissions are generated is often quite large. Therefore, it is impossible to apply traditional volatile organic compound control technologies, such as emission-controlling foams and impermeable covers. These approaches are not applicable since the controls are designed to inhibit the transfer of gases between the soil and the atmosphere. While this reduces volatile organic emissions, it will also limit the replenishment of oxygen to the soil and may cause anaerobic conditions to develop. Other control approaches such as wind barriers tend to be inapplicable due to the large treatment areas. One VOC reduction/control approaches that is specific for land treatment is subsurface injection of waste. It is applicable for liquid waste, but not for contaminated soil. In this practice, a tank truck containing the liquid waste is driven across the treatment area and the waste is introduced into the soil at a depth of 6-12 inches below groundlevel via a series of hollow tines on a tilling device pulled behind the truck. Some researchers have claimed that subsurface injection can reduce emissions 80% or more over a 24-hour period.[7] However, other data suggests that over a longer period, subsurface injection provides only a minor reduction in emissions, especially where the soil is frequently tilled for aeration.[9]

To evaluate the potential public health impact of these emissions, data from landtreatment operations were evaluated and modeled. The models used provide time dependent algorithms for estimation of volatile emissions from land treatment operations. They have specific algorithms to describe conditions at the site including contamination, the phase in which the contaminant is present, soil moisture, and efficiency of biodegradation.

EMISSIONS MODELING

The Superfund Environmental Assessment Manual System (SEAMS) land treatment model describes the time-averaged emissions from soil initially contaminated with a uniform concentration from the surface to a fixed depth. The model assumes that all of the liquid waste is incorporated into the surface soils (in pore spaces) and is not present as discrete film. The model does not consider adsorption to the soil particles or biodegradation. The model assumes that a "dry"zone develops near the surface as the contaminant volatilizes. The liquid vaporization occurs at the boundary between the "dry"and "wet"zone. As vaporization occurs, the "dry"zone increases in depth as the "wet"zone shrinks. The concentration in the "wet"zone remains the same as the initial concentration. Equations are presented for calculating the depth of the two zones and the time required for total evaporation of the contaminant. This model is used for screening purposes. When more data is available about the soil, refined models may be used.

The Research Triangle Institute (RTI) land treatment model, a more refined model, describes the time dependent emissions from land treatment operations in which liquid or slurry wastes are applied and then tilled into the soil. The model assumes that the soil is initially contaminated uniformly to a fixed depth. The basis for the model is the premise that emissions are limited by the vapor phase diffusion of contaminants through the soil cover. The model also accounts for the removal of contaminants from the applied waste by biodegradation. However, biodegradation is usually significant for the less volatile compounds (e.g., polyaromatic hydrocarbons with 4 rings or more).

The RTI land treatment Model has both a short-term and long-term version. The short-term model describes emissions from an oil-layer on the surface that is present shortly after waste application and tilling. Emissions for short time periods result from direct evaporation of the compound into the atmosphere and are driven by temperature, wind speed, and the volatility of the compound. The long-term model assumes that the contaminants have seeped into the surface soils. Long-term emissions are limited by the diffusion of the vapors through the soil and are strongly dependent on the soil properties (total and air-filled porosity). Both short-term and long-term models have provisions for biodegradation losses, although it is usually a competitive removal pathway only for semi-volatile compounds.

The RTI land treatment model may also be applied to estimate emissions from a number of different applications that are physically similar. The short-term RTI model can be used to predict emissions from fresh spills or excavation of soils where the soil surface exhibits liquid pools/layers exposed to the atmosphere. The long-term RTI model is applicable to old spills where the liquid has seeped into the soil matrix. For these cases, biodegradation is neglected. The RTI model is included in both the CHEMDAT7 and the LAND7 programs.

CHEMDAT7 is a menu driven computer program that uses a collection of analytical models to estimate volatile organic compound (VOC) emissions from treatment, storage, and disposal facility (TSDF) processes. CHEMDAT7 is used in conjunction with CHEM7, a chemical compound property processor program, which provides data organized in file structures compatible with the requirements of CHEMDAT7. These specific compounds can be selected in CHEMDAT7 to evaluate site specific concerns. CHEMDAT7 uses Lotus 123 to provide a spreadsheet format in order to calculate an estimation of VOC fugitive emissions. The landtreatment model portion is used to evaluate emissions from the bioremediation process performed at woodtreatment facilities. The Land 7 model is a menu driven database program that allows the user to set up and run a model simulating a landtreatment case study. It is easier to run than CHEMDAT7 and allows for more specifically regarding the biomass in the waste but it only will calculate the emissions of 18 compounds at a time and limits the use to calculation only those emissions due to tend treatment (CHEMDAT7 includes several other models). Required inputs for the CHEMDAT7 landtreatment and the LAND7 models include:

- the portion of the soil contaminated with the oil or aqueous solution
- the concentration of contaminant in the oil
- the depth of tilling
- total porosity
- air porosity
- molecular weight of the oil
- time
- biodegradation factor
- temperature
- wind speed
- landtreatment area

The model outputs include the fraction of each selected compounds lost to the air through volatilization and to biological factors due to microbial activity. The models also calculate landtreatment emission rates at various time scales for each of the compounds selected.

DISPERSION MODELING

Gaussian-based dispersion models are typically used to model the air-pathway transport of emissions. Two EPA accepted models, the Point, Area, and Line (PAL) model and the Fugitive Dust Model (FDM), are preferred by the EPA/ERT and REAC for numerous reasons—most importantly because they use an integrated line-source algorithm recommended[17] to predict emissions from area sources with close proximity to receptors ensuring the safety of the residents who live closest to the source. Modelers would typically select PAL to model emissions for periods of a week or less and the FDM for longer periods—with their preference based on the ease in which the models are set up.

These models offer the ability to simulate rectangular area sources of varying length and width dimensions unlike others which limit the modeler to square shaped area sources only. These models also allow the user to calculate dispersion from irregularly oriented line sources to aid with the evaluation of road emissions from your site operations. Additionally these models allow for calculations of ambient air concentrations for receptors located directly above the source. This aids in the support of health and safety of personnel working on the source.

Case Study: Beta Woodtreating Site

Information collected at the Beta Woodtreating Site is used as an illustrative example of how to evaluate emissions from landtreatment facilities. CHEMDAT7 and LAND7 were both used to evaluate the emissions that were produced from the landtreatment process at the site. The pilot scale landfarm experiment was set up and initiated by EPA/ERT and REAC. The experiment was located in a garage and consisted of a wooden box fabricated from 3 inch X 3 inch lumber. The approximate dimensions of the wood framework were 2 feet in height X 8 feet in width X 22 feet in length. The structure was divided into two compartments (approximately 8 feet X 8 feet; and approximately 8 feet X 14 feet) by means of a wall made from 3 inch X 3 inch lumber. Plastic 40 mil sheeting was then used to line the interior of each of the two compartments. After lining the compartments, styrofoam insulation sheets approximately 1 inch thick were placed in the floors of both compartments to reduce heat loss from the landfarm soil during cold weather. Sheets of 1/2 inch plywood were then placed on top of the styrofoam to provide a barrier able to resist mechanical damage that might occur during subsequent soil handling operations (i.e., rototilling and soil sampling).

Soil used in the treatability study was collected from the site and transferred into an untreated (method 1) and a treated (method 2) landfarm plot. Both landfarm plots were initially rototilled to obtain a homogeneous soil matrix prior to sampling. The treated and untreated plots were adjusted to approximately 15 percent moisture content and 20 percent moisture content, respectively. Soil samples were collected from the treated and untreated plots following rototilling and moisture addition. The soil analysis data was then used to evaluate the emissions. Figure 1 displays the input and output information for compounds in oil at the Beta Woodtreating Site for a period of 7 days. Note the large fractional loss of Pentachlorophenol (PCP) due to biodegradation corresponding with low air emission rates (relative to the other compounds listed). LAND7 produces the results for each compound on a separate page. the results for Devzone we provided in Figure 2; these values corresponded well with those calculated by CHEMDATA7. The LAND7 results for PCP, reported in Figure 3, differ slightly from those calculated by CHEMDATA7. This is due to the a slight variance in the physical characteristics calculated by each of the models.

The CHEMDAT7 model (more conservative than LAND7) was run at 7 day increments for the 110 day duration of the project. The predicted fraction of PCP remaining in the soil during the biotreatment process in both the oil and aqueous phases is plotted along with the measured values for the two processes in Figure 4. The fraction of PCP removed by bioremediation in method 2 is similar to the curve produced by the predicted oil phase; however, the rate of removal is over predicted. The slope of the curve of the predicted fraction remaining in the aqueous phase is similar to the fraction measured in method 1. However, the rate of removal is well under predicted. These results imply that a large percentage of PCP in method 1 is available in the aqueous phase and a large percentage of PCP in method 2 is available in the oil phase.

The emissions calculated by the model is input into the FDM dispersion model to evaluate long-term exposure. The FDM was set up for the illustrative example provided above. The area source was 8 feet X 8 feet and emitted at a level 20 inches above the ground. The meteorological conditions included surface data collected at local National Weather Service stations. Receptors were placed in a grid with nodes placed at 33 feet (10 m) intervals surrounding the site and its adjacent neighborhoods.

The results of the dispersion model were statistically contoured and then superimposed over a map of the site. The results are displayed in Figure 5. These values were scaled up to evaluate impact of a full scale operation and the results are displayed in Figure 6. The concentration contours are displayed in micrograms per cubic meter ($\mu g/m^3$). These units are preferable for evaluating dose and inevitably health risk. The results for PCP, the most prevalent contaminant associated with this site, do not indicate airborne concentrations which would produce inhalation health risks of concern for either the pilot or full scale operations. While the contaminants with boiling points below 400 degrees F do volatilize out of the soil, the concentrations at this site are not of significance due to the small relative volume of these contaminants. Additionally, the microorganisms are a sink for much of the PCP, removing quantities which would otherwise be available for volatilization.

CONCLUSIONS

Considerable research has been conducted over the past ten years and has concluded that microorganisms are able to break down many of the organic chemicals considered to pose health and environmental hazards at uncontrolled hazardous waste sites. In-situ biodegradation methods require minimal equipment and therefore relatively low capital costs for startup and operation, making them an attractive cost effective method for use at Superfund sites

Air emissions from in-situ biological treatment processes are an important route of contaminant loss from land treatment processes. Available data indicates that prior to full scale implementation of a bioremediation process, emissions should be modeled using the SEAMS Landtreatment, RTI Landtreatment, LAND7 or CHEMDAT7 Models. These models have specific algorithms to describe the conditions at the site including contamination, the phase in which the contaminant is present, soil moisture, and efficiency of biodegradation. The results of these models may be incorporated into dispersion models to evaluate impact off-site.

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LAND TREATMENT MODEL DATA
(land treatment)

L, Loading (g oil/cc soil)	0.1
Concentration in oil (ppmw)	460
l, Depth of tilling (cm)	20
Total porosity	0.61
Air Porosity (0 if unknown)	0
MW oil	266.4
For aqueous waste, enter 1	0
Time of calc. (days)	7
For biodegradation, enter 1	1
Temperature (Deg. C)	5
Wind Speed (m/s)	4.47
Area (m2)	5.946

COMPOUND NAME	LANDTREATMENT FRACTION LOST		INTERMEDIATE TIME 7 DAYS	
	AIR	BIOL.	AIR	BIOL.
Benzene	0.866	0.134	0.488	0.061
Chloroform	0.989	0.011	0.779	0.007
Cresol (-m)	0.023	0.977	0.002	0.116
Cresol (-o)	0.036	0.964	0.004	0.117
Cresol (-p)	0.022	0.978	0.002	0.116
Methyl Ethyl Ketone	9.81	0.019	0.483	0.007
Methylene Chloride	0.970	0.030	0.935	0.028
Naphthalene	0.027	0.973	0.005	0.199
Pentachlorophenol	0.001	0.999	0.000	0.340
Toluene	0.385	0.615	0.232	0.260
Trichloroethylene	0.951	0.049	0.404	0.014
Xylene (-o)	0.229	0.771	0.047	0.234

	LANDTREATMENT EMISSION RATES (g/cm2-s) TIME (Hours)				
COMPOUND NAME	0.25	1	4	12	48
Benzene	8.92E-09	4.70E-09	2.41E-09	1.40E-09	6.91E-10
Chloroform	1.52E.08	7.87E-09	4.00E-09	2.32E-09	1.16E-09
Cresol (-m)	1.10E-11	1.03E-11	9.18E-12	7.89E-12	5.82E-12
Cresol (-o)	2.28E-11	2.10E-11	1.82E-11	1.51E-11	1.06E-11
Cresol (-p)	7.46E-12	7.17E-12	6.57E-12	5.86E-12	4.59E-12
Methyl Ethyl Ketone	8.54-09	4.51E-09	2.32E-09	1.35E-09	6.81E-10
Methylene Chloride	2.36E-08	1.20E-08	6.07E-09	3.50E-09	1.71E-09
Naphthalene	3.55E-11	3.15E-11	2.56E-11	2.00E-11	1.28E-11
Pentachlorophenol	1.14E-13	1.12E-13	1.08E-13	1.02E-13	8.52E-14
Toluene	4.19E-09	2.32E-09	1.22E-09	7.08E-10	3.32E-10
Trichloroethylene	6.98E-09	3.73E-09	1.93E-09	1.13E-09	5.68E-10
Xylene (-o)	1.40E-09	8.71E-10	4.94E-10	3.00E-10	1.50E-10

Figure 1. LAND7 Input and Output Information for Compounds in Oil at the Beta Woodtreating Site for 7 day Period

```
Equilibrium Keg                                  3.26507E-03
biological time const days-1                     72.32917
maximum fraction biodegraded                     .1345276
fraction biodegraded during time period          6.202272E-02
fraction emitted during time period              .4875692
residual concentration in oil (ppmw)             207.1877
diffusion coef cm2/s                             4.038319E-02
emission rate during time period (g/s)           4.409987E-05
                 (Mg/year)                       1.390733E-03
emission factor (g/cm2-s)                        7.416728E-10

Short term emissions, first day (g/s)            1.200111E-04
Peak Emissions, fifteen minutes (g/s)            5.763925E-04
```

Figure 2. LAND7 Benzene Results Over 7 Day Period at Beta Woodtreating Site

```
Equilibrium Keg                              8.590418E-08
biological time const days-1                 10.57119
maximum fraction biodegraded                 .9977548
fraction biodegraded during time period      .4842487
fraction emitted during time period          1.087283E-03
residual concentration  in oil (ppmw)        236.7455
diffusion coef cm2/s                         .0256984
emission rate during time period (g/s)       9.834307E-08
                   (Mg/year)                 3.101347E-06
emission factor (g/cm2-s)                    1.653937E-12

Short term emissions, first day (g/s)        1.283068E-07
Peak Emissions, fifteen minutes (g/s)        3.908185E-07
```

Figure 3. LAND7 Pentachlorophenol Results Over 7 Day Period at Beta Woodtreating Site

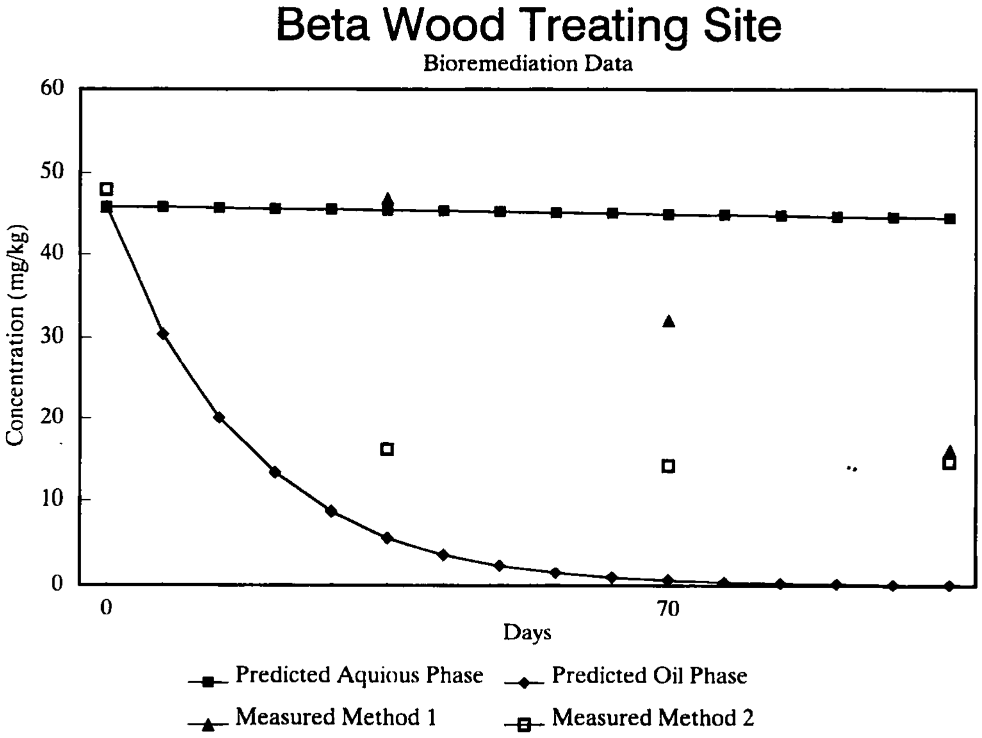

Figure 4. CHEMDAT7 Predicted PCP Soil Concentrations Vs. Measured Values

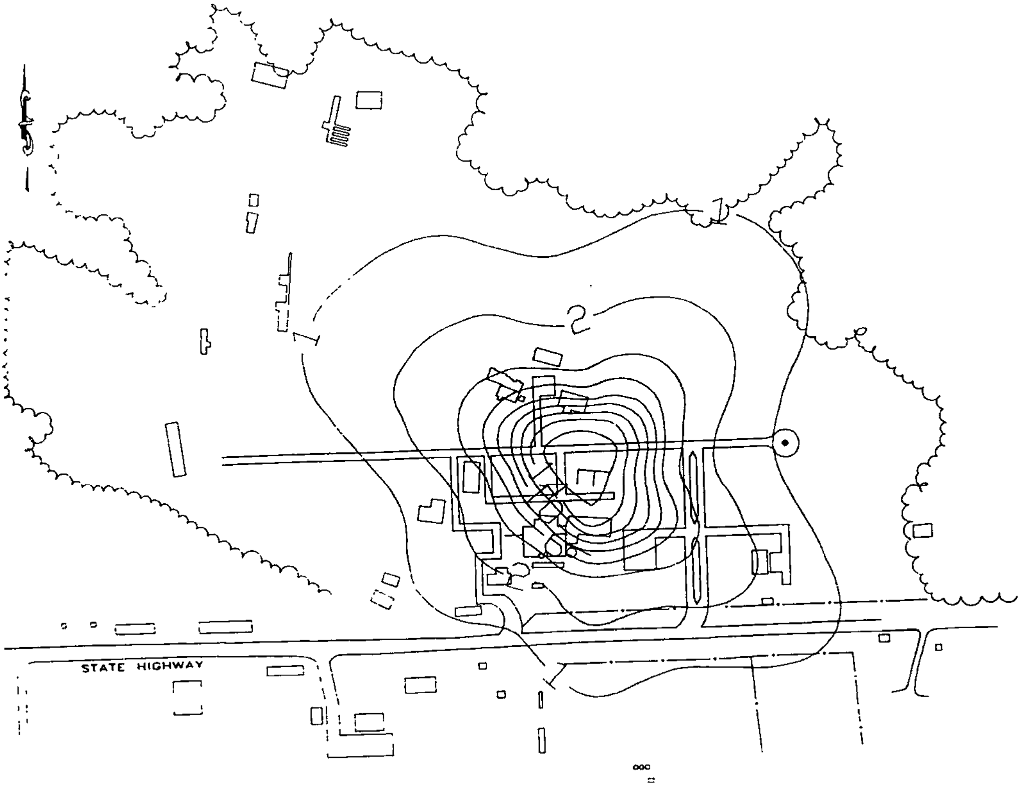

Figure 5. Long-Term Air Pathway PCP Exposure Concentrations - Pilot Scale
(Isopleths Presented in Micrograms Per Cubic Meter [ug/m^3])

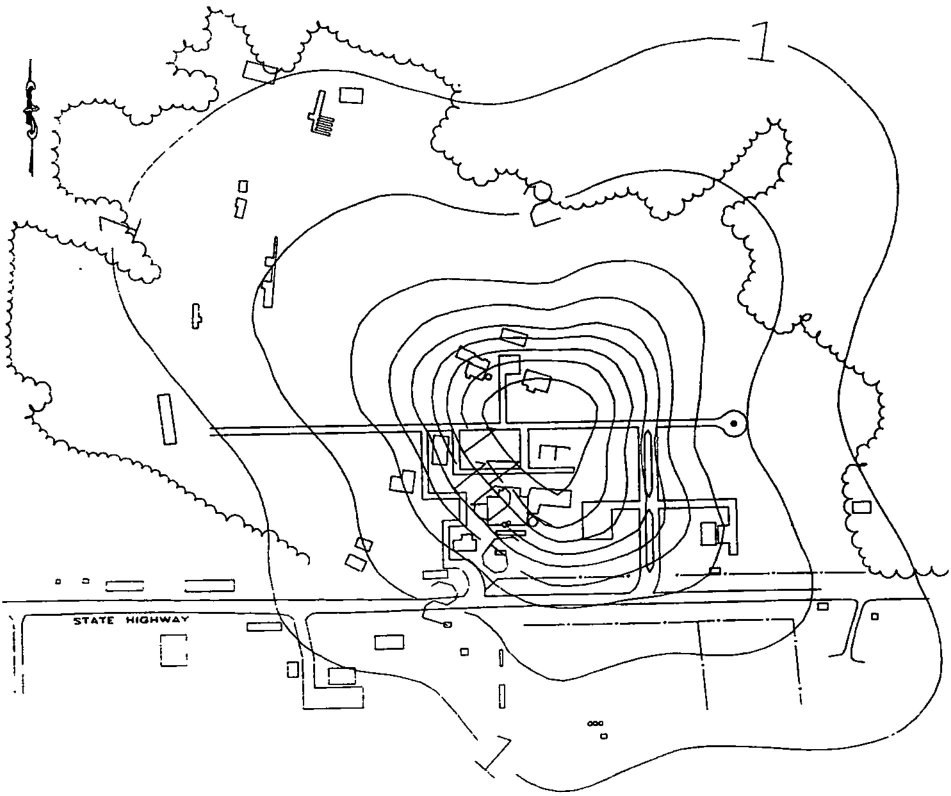

Figure 6. Long Term Air Pathway PCP Exposure Concentrations - Full Scale (Isopleths Presented in Micrograms Per Cubic Meter [ug/m^3])

APPLICATIONS OF THE MICROWAVE-ASSISTED PROCESS (MAP^{TM}) TO POLYURETHANE FOAMS (PUFS) AND FILTERS FOR MONITORING OF POLYCYCLIC AROMATIC HYDROCARBONS

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ABSTRACT

The Microwave-Assisted Process (MAP^{TM})* has been investigated in the use of cleaning polyurethane foams (PUFs) and their subsequent extraction of polyaromatic hydrocarbons (PAHs). These PUFs are used to monitor and assess air quality, and are part of the National Air Pollution Surveillance Network in Canada. A large number of PUFs are used every year. The cost involved are significant as a result of the current Soxhlet extractions being used; they consume large volumes of solvent and large amounts of energy in addition to occupying valuable work space in the fumehood. The Microwave-Assisted Process was used for the extraction of PUFs. Comparison of PAH results showed similar or higher yields than conventional Soxhlet extractions, with a dramatic reduction in sample preparation times and in energy consumption. Furthermore, the smaller volumes of solvent used make for reduced costs associated with solvent purchase and waste disposal. Finally, the space required to perform simultaneous multiple-extractions represent a small fraction of that associated with Soxhlet work.

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* MAP is a trademark of Her Majesty The Queen in Right of Canada as represented by the Minister of the Environment.

INTRODUCTION

The Microwave-Assisted Process (MAP^{TM}) is an extraction technology developed and patented by Environment Canada (1-3). Some of the features of MAP are its ability to extract quickly a variety of target compounds, while using less solvent and energy than conventional techniques (4). Various compounds present in materials such as PUFs (used to collect ambient air sample), urban dusts filters, sediments, soils, plants, animal and human tissues can be extracted using MAP (5-8). The material is then exposed to microwaves and the substrate is subsequently filtered off. Following this step, the filtrate is processed as per conventional methods.

As demonstrated by examples provided thereafter, MAP offers considerable advantages when compared to conventional analytical sample preparation technologies such as Soxhlet, ultrasound or others. This technique provides for a method that is both selective and rapid, which consumes less solvent and energy and that supports sustainable development.

This paper reports on results obtained when MAP was used as an extraction method for the recoveries of PAH. These PAHs were extracted from PUFs as well as urban dust glass fiber filters. This technology has proven efficient and very time effective which improve time factors to take into account when field work is required in emergency spill situations. In this paper, MAP was compared to the conventional Soxhlet extraction methods as usually used by the Environmental Technology Centre of Environment Canada(9).

EXPERIMENTAL

MICROWAVE OVEN. A CEM MES-1000 microwave oven designed for solvent extraction operating at a frequency of 2450 MHz was used for all the experiments described here.

STANDARDS. Analytical standard solutions of 15 native PAHs was obtained from Supelco Inc. (Catalog No. 4-8743) with ten-fold dilutions. The 7 deuterated PAHs were purchased from Cambridge Isotope Laboratory and the surrogate solution was prepared at 10 μg/mL level for each compound.

MAP EXTRACTION PROCEDURES. A PUF or filter derived from an ambient air sample was placed in a 100 mL CEM microwave oven Teflon extraction vessel to which was added 80 mL of acetone/hexane (1:1). One hundred microliter of surrogate solution was spiked prior to the extraction. Three vessels were closed and placed on a rotor inside the microwave oven and all connection hooked up. The temperature was allowed to raise up to 100 °C, at which the extractions were performed for a period of 10 minutes at power of 500 Watts. The microwave-heating program was as follows: (a) to reach the set point temperature, (b) to be maintained at the set temperature for 10 minutes, and (c) upon removal of the vessels from the microwave oven, to allow them to cool to ambient room temperature. The extracts were filtered through precleaned glass wool and anhydrous sodium sulphate and then combined with 15 - 20 mL hexane/acetone rinse originating from the Teflon extraction vessels containing the matrix. The extracts were rotor evaporated to about 2 mL and subjected to silica column cleanup(9). The PAH-containing eluent from the silica column was blowndown under nitrogen to 800 µL and spiked with 100 µL of recovery standard d_{10}-Fluoranthene and/or d_{12}-Perylene. The extract was finally made up to 1000 µL for GC/MS analysis.

SOXHLET EXTRACTION. Soxhlet extractions were performed in cyclohexane as described in the "Summary of the Analytical Method for the Determination of PAH in Ambient Air Samples" (9).

GC/MS ANALYSIS. One microliter of the extract was directly injected into a Hewlett Packard 5890 series II GC which was equipped with a DB-5 capillary column (30m x 0.25mm, 0.25µm coating 5%-phenyl / 95%-methyl silicon) and a 10m x 0.5mm deactivated fused silica precolumn. The GC oven started at 90 °C with a one-minute hold, 90 °C to 200 °C at 20 °C/min, 200 °C to 210 °C at 3 °C/min, 210 °C to 290 °C at 5 °C/min with 10 minute hold. A Hewlett Packard 5970 MSD was operated at 70 eV electron energy with a source temperature set at 250 °C to monitor the 26 PAHs of interest. Spectral data were acquired at a rate of 1.2 s/scan (scanning range was 40-500 amu). The instrument was tuned daily with PFTBA introduced via the calibration gas valve. Data was collected using a HP G1034C MS ChemStation

Software. A calibration standard was used to determine ion ratios and response. The detection limit for each PAH ranged from 0.05 to 0.1 ug/mL.

RESULTS AND DISCUSSION

Table 1 presents the result of PAH recoveries using MAP as the primary technique of extraction followed by soxhlet extraction for the same PUF. The recoveries of PAH extracted from the second extraction mode, Soxhlet were below 5% with only two exceptions, these being high molecular weight compounds B(ghi)P and its deuterated counterpart. The light PAHs such as acenaphthalene, acenaphthene and fluorene gave relative wide ranges of variation due probably to their volatility. It is to be noted that all medium to high molecular weight PAHs gave high recoveries. The recovery of surrogates spiked before the extraction showed similar pattern as those of natives.

Table 2 illustrates MAP as the primary and Soxhlet as the secondary one on various type of ambient air samples. Examples of individual PUF, Filter, and PUF/Filter were chosen to demonstrate the efficiency of the extractions by the MAP. The real ambient air PUF sample showed the same results as the spiked PUFs listed in Table 1. The extraction of the filter alone using MAP showed very good efficiency for all these filter samples that have been done in this laboratory(10). The PAH level in the filters ranged from 2 to several hundred µg/sample gave nondetected PAH during secondary Soxhlet extraction.

The higher the contamination level of PAH, the higher the recovery of surrogates was also observed in most cases probably due to the interference of sample matrices.

CONCLUSION

The Microwave-Assisted Process has demonstrated potential to replace time and solvent consuming conventional extraction techniques. This is one of the new technology of accelerated sample preparation method for emergency response where analysis are required to support decision making in a short period of time.

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Table 1. PAH recoveries from PUFs extracted by MAP and re-extraction of the same PUF by Soxhlet.

	% recovery Primary-MAP			% recovery Secondary-SX		
	1	2	3	1	2	3
AL	70	46	49	2	3	2
AE	73	94	80	3	2	2
FL	59	50	62	2	2	2
PHE	99	100	100	5	4	2
AN	94	84	84	3	2	2
FLT	89	85	84	4	4	3
PY	88	85	84	3	3	2
B(a)A	90	89	90	3	2	1
C&T	89	92	88	4	2	2
B(b+k)F	89	91	90	5	2	2
B(a)P	88	92	88	4	1	1
IP	94	96	95	5	2	2
D(ah)A	92	93	91	5	2	2
B(ghi)P	86	87	85	8	3	4
Surrogates						
*AE	96	81	102	2	4	_
*AN	89	90	98	2	2	_
*PY	83	80	85	3	3	2
*B(a)A	85	88	97	3	_	3
*B(a)P	78	83	90	3	_	_
*D(ah)A	80	81	86	5	1	2
*B(ghi)P	75	76	82	7	2	3

MAP: Microwave-Assisted Process SX: Soxhlet Extraction
_: not detected
Method blanks were performed to ensure that no contamination was present.

Legend: PAH abbreviation

AL: acenaphthalene;
AE: acenaphthene;
FL: flourene;
MFL: 2-methyl-flourene;
PHE: phenanthrene;
AN: anthracene;
FLT: Flouranthene;
PY: pyrene;
B(a)F: benzo(a)fluorene;
B(b)F: benzo(b)fluorene;
MPY: 1-methyl-pyrene
B(ghi)F: benzo(ghi)fluorene;
B(a)A: benzo(a)anthracene;
C&T: chrysene/triphenylene
MB(a)A: 7-methyl-benzo(a)anthracene;
B(b)F: benzo(b)flouranthene;
B(k)F: benzo(k)flouranthene;
B(e)P: benzo(e)pyrene;
B(a)P: benzo(a)pyrene;
PER: perylene;
MCH: 2-methyl-benzo(j)aceanthrylene;
IP: indo(1,2,3-cd)pyrene;
D(ah)A: dibenzo(ah)anthracene;
B(b)C: benzo(b)chrysene;
B(ghi)P: benzo(ghi)perylene
ANT: anthanthrene.

Table 2. PAH found in ambient air samples extracted by MAP and re-extraction of the same sample by Soxhlet.

Sample Type	PUF		Filter		PUF + Filter	
	1st-MAP	2nd-SX	1st-MAP	2nd-SX	1st-MAP	2nd-SX
	µg/sample					
AL	0.314	_	_	_	2.087	0.087
AE	5.376	0.112	_	_	1.587	0.112
FL	5.374	0.095	0.041	_	5.680	0.411
MFL	4.568	0.128	0.141	_	3.184	_
PHE	7.622	0.333	0.395	_	16.600	1.096
AN	_	_	_	_	_	0.037
FLT	2.203	0.079	0.566	_	4.076	0.221
PY	1.443	0.052	0.422	_	3.355	0.186
B(a)F	0.208	_	0.145	_	0.542	_
B(b)F	0.073	_	0.049	_	0.228	_
MPY	0.067	_	_	_	0.259	_
B(ghi)F	0.095	_	0.094	_	0.477	0.017
B(a)A	0.023	_	0.225	_	0.312	_
C&T	0.011	_	0.470	_	0.542	0.017
MB(a)A	_	_	_	_	_	_
B(b+k)F	_	_	0.727	_	0.855	_
B(e)P	_	_	0.288	_	0.339	_
B(a)P	_	_	0.260	_	0.334	_
PER	_	_	0.045	_	0.061	_
MCH	_	_	_	_	_	_
IP	_	_	0.265	_	0.385	0.013
D(ah)A	_	_	0.060	_	0.053	_
B(b)C	_	_	_	_	_	_
B(ghi)P	_	_	0.391	_	0.744	0.043
ANT	_	_	_	_	0.050	_
Surrogates % Recovery						
*AE	29	3	69	_	117	4
*AN	72	4	62	_	99	4
*PY	84	5	73	_	90	4
*B(a)A	94	4	75	_	99	3
*B(a)P	79	5	84	_	102	3
*D(ah)A	79	7	84	_	90	5
*B(ghi)P	73	9	100	_	84	9

MAP: Microwave-Assisted Process SX: Soxhlet Extraction

_: not detected

Method blanks were performed to ensure that no contamination was present.

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Evaluation of the Hewlett Packard HP7680T Automated Supercritical Fluid Extraction System

Abstract

The Hewlett Packard (HP) 7680T automated Supercritical Fluid Extraction (SFE) system has been evaluated with respect to suitability for emergency response analytical work. The system used in this study is a laboratory extractor physically linked to a gas chromatography/mass spectrometer/flame ionisation (GC/MSD/FID) analytical system using the HP Bridge. The entire system is operated by the Bench Supervisor, a software that controls the sequence of extraction and analysis of the prepared sample. The operation and instrumental parameters of the system have been optimised. Studies conducted include parameters such as extraction temperature, flow rate, trapping material for the analytes and rinsing conditions and use of modifiers. Extraction efficiency of a few model compounds spiked on a variety of matrices have also been investigated. SFE extractions are intrinsically fast compared with traditional extraction methods: the described system, by virtue of its sophisticated degree of automation offers turnaround time from extraction to analysis in the order of 1.5 hrs per sample .

Introduction

The main task of sample preparation, in the case of a solid sample is the initial extraction which separates the analytes from the bulk of the matrix. The traditional methods are by soxhlet, ultrasonic and mechanical agitation. While all these methods are well established and generally do not entail any major capital cost, they are often labour intensive, requiring many manual manipulations of different pieces of glassware which subsequently need to be vigorously cleaned afterwards. As such, the traditional approach consumes large amount of high purity solvents: the acquisition and disposal costs are increasingly expensive.

In addition, because of the demand on manual participation, such methods are often dependent on the techniques of the person and the progress of extraction cannot be controlled precisely.

By comparison, SFE extracts samples by non-toxic, relatively low cost supercritical (SC) grade carbon dioxide (CO_2). The innate properties of CO_2 are ideally suited for sample extraction. They exhibit solvation power comparable to common solvents while having lower viscosities and thus higher diffusitivities, thus offering faster extraction process. Another benefit of SC CO_2 is that being a gas at ambient temperature and pressure, the extract can simply be allowed to expand, leaving the analytes in a trapping liquid or a solid accumulator, thus avoiding the lengthy concentration step by vacuum evaporation in a traditional extraction process.

The HP 7680A is an automated SFE system that can handle up to 8 samples. Setup of extraction parameters and control of the instrumentation is carried out by a ChemStation based on a 486-personal computer. The SFE system alone is capable of producing injection-ready sample extracts. On the system under evaluation, the sample analysis proceeds further by having the robotic arm of the HP 7680 automatic liquid sampler (ALS) pass the extracts on to an adjoining analytical instrument. This is carried out by the Bridge, which is a collection of dedicated hardware and software that controls the operation and sequence of analysis on the SFE and GC/MSD. The obvious advantage is true walk-away automation of sample preparation and chemical analysis.

This work describes our experience with a SFE-GC/MSD system operated under the bridge system. The performance of the entire system will be presented. Various parameters such as extraction temperature, flow rate of extraction, choice of sorbent in the solid trap and the subsequent elution by rinsing solvent have been optimised. As the solvating power of SC CO_2 is directly related to its density, SFE offers the potential of selective extraction. This 'tunable' power of extraction was used to separate different types of petroleum products spiked onto soils.

The emphasis of emergency response lies with fast sample turn-around, rather than exhaustive extraction of samples. The SFE extraction time was limited to half an hour or less, using an universal set of parameters to have a wide range of applicability. Ability to handle a variety of sample matrices, such as soot/filter from fires, sludge and soil/vegetation matter were investigated by spiking with representative spilled chemicals or environmentally important compounds. Precision, recovery and limits of detection for these chemicals are presented.

Experimental Section

Extractions

The HP 7680T was linked to an adjoining HP 5890 Series 2 GC-FID/5972 MSD equipped with an ALS by a positioning pad as part of the Bridge. This physically aligns the transfer of sample vials from the ALS tray back and forth to the output turret of the SFE. Supervision of the entire operation of the system, from initial setup of extraction methods of the SFE to the analysis of the sample extract on the GC/MSD was controlled by the Bench Supervisor software. Individual operation of either SFE or GC/MSD could still be carried out for a single sample, but not sampling sequence. The Bridge was particularly invaluable in situations in which a lengthy sequence of multiple sample/multiple extractions were to be carried out, followed by subsequent analyses of the SFE output vials by multiple analytical methods. For example, assuming 8 soil samples were to be extracted by a SFE method at two different densities, this generated 16 vials at the end of the extraction sequence. These could then be injected into the GC/MSD by multiple GC/MSD methods such as Linear Scanning or Selected Ion Monitoring (SIM) method. For the above example, running two injection for each vial would generate a total of 32 chromatograms at the end of the entire operation. The bench supervisor would allocate the resource, allowing both instruments to be run simultaneouly and supervise the proper sequence of events so samples were extracted and analysed 'on the fly'. The advantages of total automation and high sample throughput are evident.

In a typical SFE, the weighed sample was spiked with a mixture of surrogate compounds, wrapped loosely in glassfibre (GF) filter and loaded into a 20-mL extraction thimble. Glass inserts ranging from 2-to 10-mL volume could be used to reduce the thimble volume thus increasing the thimble swept volumes during extraction. The thimble was sealed by the screw on caps and loaded into the thimble turntable. Conditions of extractions together with all GC/MSD analytical parameters were entered via the ChemStation. Five minutes of static extraction and 15 minutes of dynamic extraction at a density of 0.85 gm/mL was carried out at a temperature of 80^0 C. The SF CO_2 flow (liquid) was generally 1-2 mL/min (controlled by a variable heated restrictor) and a thimble swept volume of 3-10 was achieved. As the CO_2 expanded, the extractable was deposited onto a packed trap of octydecyl silane (ODS) kept at 10^0 C. After extraction, the ODS trap was rinsed by 1 mL hexane (nominal) into a sample vial. If required, an internal standard was added at this point prior to GC/MSD analysis. When operating under the Bridge, vials were weighed after the analysis to determine the exact volume of hexane.

Extract Analysis

In most cases extracts were analysed on the adjoining HP5890 Series 2 GC/5972 MSD. The GC was equipped with a 25 M HP-1 (0.2 mm i.d., 0.25 µm film). The MSD was operated either in full scan (from 40-450 amu) or SIM mode depending on the analyte concentration. For PAH analysis, GC conditions were: 50^0 C held for 1 min, first ramped at 25^0 C per min to 160^0 C, second ramped at 10^0 C to 300^0 C held for 5 min. One µl was injected splitless into the GC. Injector and transfer line were kept at 280^0 C and 300^0 C respectively. The MSD was tuned using standard AUTOTUNE parameters. Operating in a 2-step SIM mode provided sensitivity in the range of 0.05 µg/mL for PAH analysis. In addition to 25 native PAH compounds analysed, surrogate ions of d8-naphthalene, d10-acenaphthene, d10-phenanthrene, d12-chrysene, d12-perylene were monitored to assess extraction loss. The ion intensity of d14-terphenyl (internal standard, IS) was used in internal standard reporting.

To screen petroleum product extracts, a HP 5890 Series 2 GC/FID equipped with a 30 M RTX-1 column (0.32 mm i.d., 0.5-µm film) was also used. This column had a higher temperature limit at 320^0 C which was useful to elute high boiling components. The temperature program for diesel fuel screening was 50^0 C for 2 min, ramped at 10^0 C/min to 310^0 C and held for 10 min. Inlet and detector were held at 300^0

C and 320^0 C respectively. A 1-µl aliquot of the extract was injected splitless by the ALS. To quantitate the unresolved hydrocarbon hump, the chromatogram was integrated from C-10 to C-22 (nominally 10-24 min) manually using the manual integration function on the HP 3365 ChemStation (DOS-series).

Results and Discussion

Loss of analytes on the SFE trap

The standard trap that comes with the instrument has stainless steel(SS) beads and was recommended for extraction of semi-or non-volatile compounds because its inert surface would minimise any irreversible adsorption of the analytes (1). To evaluate the overall extraction process, a real diesel-contaminated soil sample from a sour gas processing plant (Nordegg, Alberta), well characterised from other extraction studies (2) was extracted using 1 min static/10 min dynamic conditions at density of 0.78 gm/mL and flow rate of 1.5 mL. The trap was maintained at 5^0 C while the extraction chamber was kept at 80^0 C. Toluene (1 mL nominal) was used to rinse the SS trap. The recovery was found to be 2000 µg/gm compared to the 'true' 5000 µg/gm. When the total ion chromatogram (TIC) was examined, there was evidence of light end loss of the diesel profile (figure 1).

To evaluate the trapping efficiency further, PAH was spiked onto a GF filter and extracted under identical conditions with the exception of trap temperature, which was lowered to 5^0 C. Again loss of lighter PAH, namely 2 to 3-ring PAH was evident. A series of experiments were carried out using trap temperatures of 0, -5^0 and -15^0 C. In all cases, some of the lighter 2-3 ring PAH were lost (figure 2). This was somewhat surprising because under moderate flow rate, PAH should be cold-trapped by the packing material alone without having to resort to any chemical adsorption effect. During extraction, at a flow rate of 1 mL/min (liquid CO_2), the gaseous flow rate was roughly at 100 mL/min and this apparently was too high for cold trapping to be effective. It was then decided to go onto a chemical trap which offered more 'stickiness' for the analytes. The octadecyl silane (ODS, 30-µm particle size) trap was selected and identical extractions were carried out. There was no loss of PAH or the lighter end of diesel at trapping temperatures as high as 10^0 C (figure 3).

The trap could be custom-packed with common sorbent material such as octyl (C8), cyano or unmodified silica, depending on the degree of chemical functionality required to trap the analyte. The only requirement being that particle size was not smaller than 15-µm for backpressure consideration and a melting point compatible with the highest trap temperature used during rinsing.

Selective Extraction Study

A unique feature of instrumental SFE is 'tunable' extraction in which the density of SF CO_2 can be varied reproducibly, achieving solvation power ranging from that of hexane (at density of 0.4 or so) to that of chloroform (at density of 0.9 gm/mL) (3). The potential of selectively extraction could be exploited by first starting with a relatively mild extraction conditions to remove the easily extractable constituents of the sample, then stepping up the conditions to effect the extraction of the components of interest. The analytes could then be isolated in a relatively clean fraction and analysed without any additional sample cleanup as in the case of non-discriminatory extraction process. Another advantage was by eliminating the bulk of the extractable in a preliminary extraction step, the trap would not be overloaded or even plugged for samples having a high extractable content.

To study the effect of SC CO_2 density, a hydrocarbon mixture from simulated distillation (SIMDIS) studies having a range of C-8 to C-40 was spiked onto a GF filter and allowed to 'age' for 4 hr. This was extracted by a 3-step process with densities of 0.4, 0.6 and 0.85 gm/mL (115, 149 and 329 bar). Chamber temperature was maintained at 65^0 C. Duration of each step was 0.5 min static and 10 min dynamic with a flow rate of 1.5 mL/min. Sweep volume was nominally 4. The ODS trap at each step was kept at 5^0, 10^0 and 15^0 C respectively. The resulting extracts were analysed by GC/MSD full scan to determine the distribution of hydrocarbon in each fraction.

Results indicated even at the 'mildest' condition (fraction 1, density 0.4 gm/mL), the entire range of C-8 to C-40 was extracted, in the second fraction only traces of C-36 and C-40 could be found. The third step did not extract anything further.

A 0.2 gm aliquot of the Nordegg soil was spiked with gasoline and extracted using the same procedure. The chromatograms indicated roughly half of the natural contaminant (diesel) eluted in the first fraction together with gasoline, the remaining half was extracted in fraction 2.

To see the distribution of PAH in a 2-step extraction of a real sample, a natural matrix reference soil certified for 15 PAH (Resource Technology Corp, distributed by Fisher Scientific) was extracted using a low density of 0.3 gm/mL for 10 min at 40^0 C, followed by extraction at 0.85 gm/mL for 20 min at 60^0 C. Analysis of the two fractions showed no clean fractionation: about 20-40 % of PAH was found in the first fraction.

Selective extraction is feasible if the physical characteristics of the sample such as particle size, porosity and amount of organics are well known and the components of interest differ widely in their extraction behaviour. In actual practice, it is difficult to implement because the extraction profile of analytes and background material are often unknown.

Rinsing of the trap

The trap temperature as described above could be adjusted to ensure quantitative trapping of the analytes. Upon completion of extraction, the trap was rinsed by up to 2 solvents into sample vials which, in most applications were ready for injection. The rinse rate, trap and nozzle rinsing temperature could all be varied. Rinse volumes of up to the capacity of the sample vial (1.8 mL) could be used or multiple rinsing carried out to miminise carryover. The trap functioned as a mini-HPLC column on which rough elution cuts could be performed, similar to fractionation on a cleanup column.

For simplicity and to lessen the number of samples to be analysed, a single rinsing of the trap would be desirable. To study the completeness of rinsing, PAH, was chosen because the higher molecular weight PAH with the affinity for ODS surface would be good indicators. A number of extractions were carried out in which PAH was spiked onto soil and filter paper and extracted at density of 0.85 gm/mL for 30 min. The trap was rinsed with 1, 1.5 mL of hexane and toluene.

Results indicated either hexane or toluene was adequate to elute PAH from the ODS trap, and that the second rinse generally recovered only less than 2% of PAH.

Accuracy of dispensing rinsing solvent

For quantitative analysis, the pre-injection volume needs to be known exactly. The volume of rinsing solvent is influenced by the void volume of the trap and whether the trap is dry or not at the beginning of the rinsing cycle. The system can compensate for the void volume if the type of trap is specified. A study was initiated to find out how accurate or consistent the system can dispense the rinsing solvent. By using the ODS trap that had a void volume of 0.58 mL, a series of 1-mL collection was made using tared 1.8 mL ALS vials. The amount of solvent dispensed was determined gravimetrically.

Results showed the volume of rinsing solvent was not constant. Up to about 7% of deviation of the specified volume was noted. This, however, compared well to typical GC/MSD precision of +/-8 to 10 % by internal standard quantitation. The weight of an empty ALS vial plus cap was actually quite constant, having a variation of +/-1 % within a batch. For practical purpose, one could weigh the extract after collection and the error due to the vial tare weight was minimal. Weighing was found to be a convenient way if the use of internal standard was not required. However, if hexane or volatile solvents were used for trap rinsing, caps needed to be put on to minimise drastic volume change from evaporation.

Recovery Study

To assess the accuracy of SFE, the Fisher reference soil was extracted in triplicates. The results are listed in table 1 with the certified values. Using a relatively short extraction, the total PAH recovery was 5707 ppm versus 6731 ppm as certified. There was a significant difference of the lighter 2-ring PAH as well as the heavier 6-ring PAH. The loss of relatively volatile naphthalene and substituted naphthalene probably occurred during collection due to blown-off from the ODS trap. The heavier PAH was not extracted quantitatively within the 15-min extraction; a second extraction generally recovered another 20-30 %. To extract these intractable PAH within a reasonable time, a matrix modifier was necessary.

The Nordegg soil was extracted in replicates. The mean value for 6 determinations was 5009 ppm diesel. This is in excellent agreement with 4986 ppm obtained by a Microwave Assisted Process (MAP) extraction (2). Precision expressed as percentage coefficient variation is 7.7 %.

For comparison to conventional soxhlet extraction, 3 pairs of 36-mm glassfibre filter discs were cut from exposed 8*10-in total suspended particulate (TSP) and size exclusion PM-10 filters collected from a diesel fuel burn exercise. The soot-laden filter discs were spiked with a surrogate PAH mixture and extracted using 5 min static/15 min dynamic at density of 0.85 gm/mL at 60^0 C. The extracts were spiked with d14-terphenyl before SIM analysis on GC/MSD. To evaluate the efficiency of extraction, each pair was extracted a second time by employing modifier: 0.5 mL methanol, 0.5 mL toluene and no modifier (as a control). Results were summarised in figure 4, which shows good agreement with standard ESD protocol using soxhlet extraction. The first 15-min extraction recovered about 85-90 %. The use of modifier seemed to have a significant effect on heavier PAH extraction: without modifier the second extraction yielded 8%, whereas using methanol and toluene yields 27 % and 19 % respectively (figure 5). This is in accordance with many published papers (4).

Conclusion

The HP7680T operated under the Bridge System provides unattended extraction and analyses for 8 samples with much better precision than conventional soxhlet extraction. Analysis of spiked and known material gives results comparable to conventional technique. The advantage of SFE lies clearly in the fast sample turnaround time: SFE extraction can usually be completed under 30 min and produces an injection-ready solution because of less sample workup. Coupled with a Bridge, spill samples can be completely characterised by performing selective extractions to obtain fractions ranging from non-polar ('hexane-extractable') to polar ('dichlormethane-extractable'), followed by GC/MSD qualitative and quantitative determinations.

List of Figures

Table

Reference

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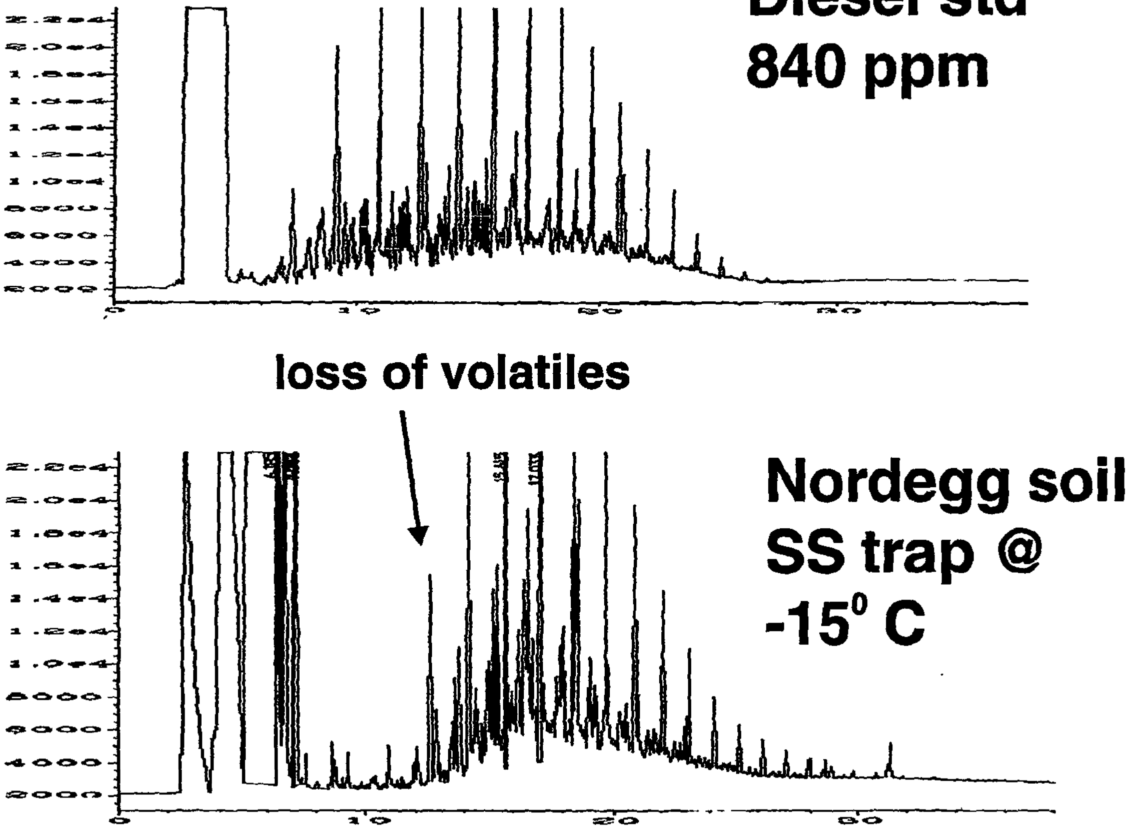
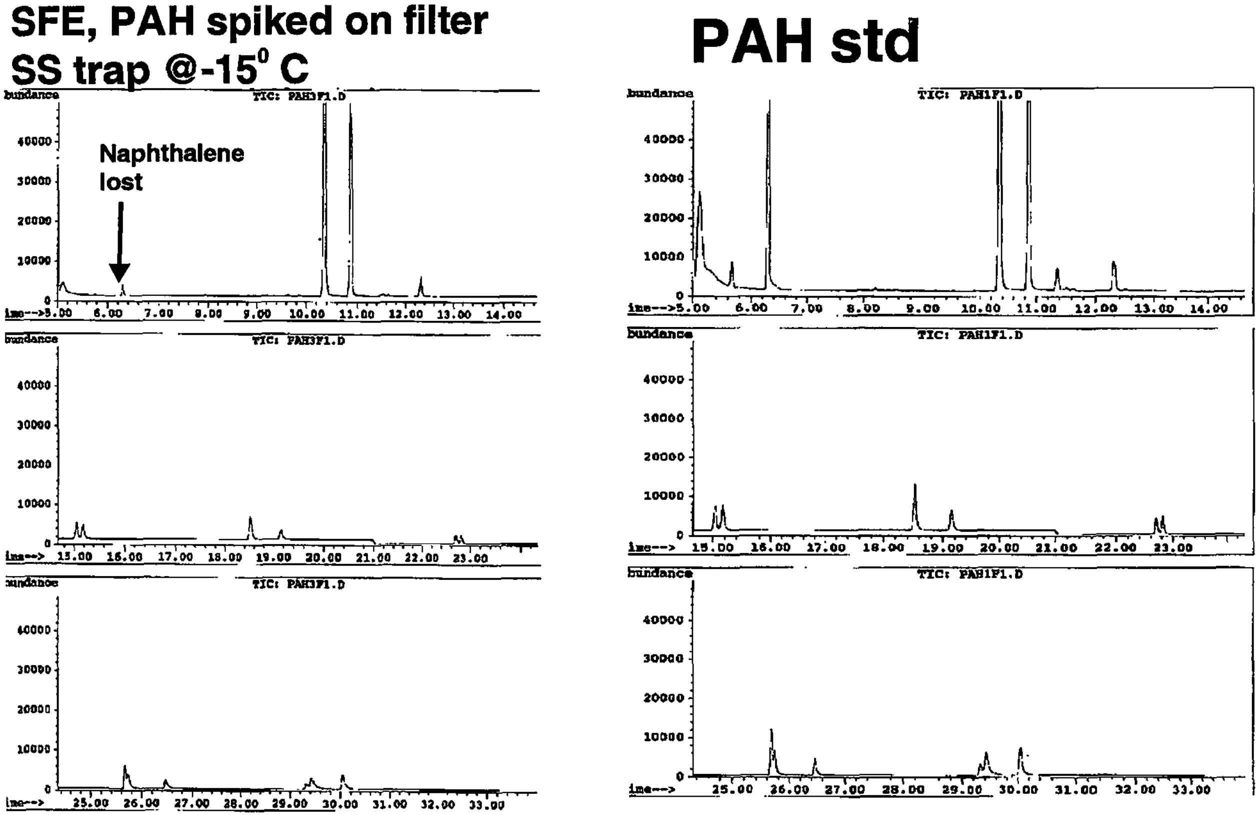
Figure 1



Diesel std
840 ppm

loss of volatiles

Nordegg soil
SS trap @
-15^{0} C

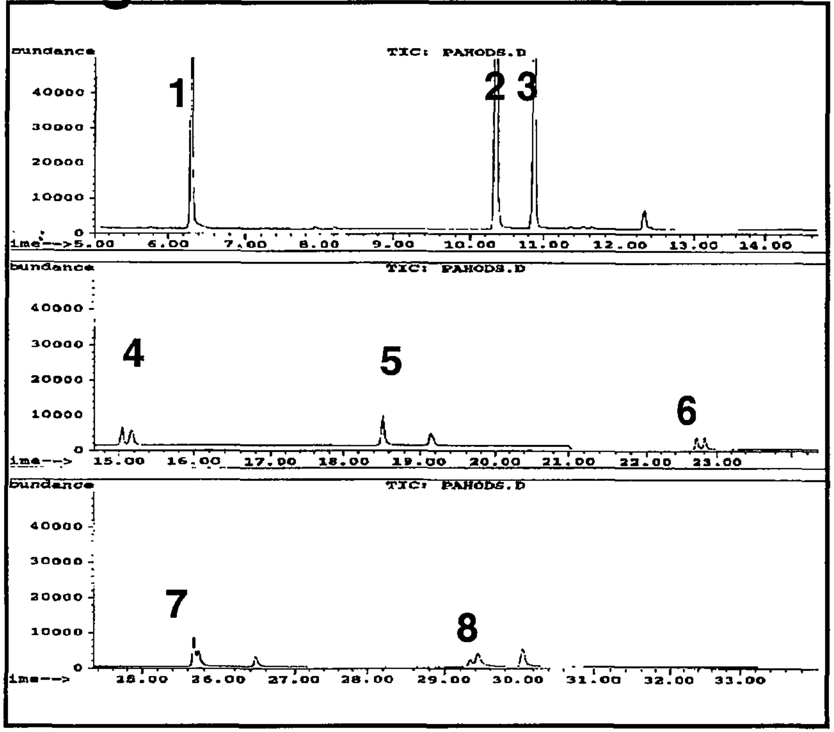


SFE, PAH spiked on filter SS trap @-15^0 C

PAH std

Figure 2

Figure 3



Recovery of PAH; ODS trap @ 10°C

1= Naphthalene, 93%
2=Acenaphthalene, 93%
3=Acenaphthene, 88%
4=Fluorene, 88%
5=Phenanthrene, 94%
6=Fluoranthene, 89%
7=Chrysene, 91%
8=Benzo(ghi)perylene, 92%

Figure 4: Comparison of Soxhlet and SFE extraction of PAH from filter cuttings

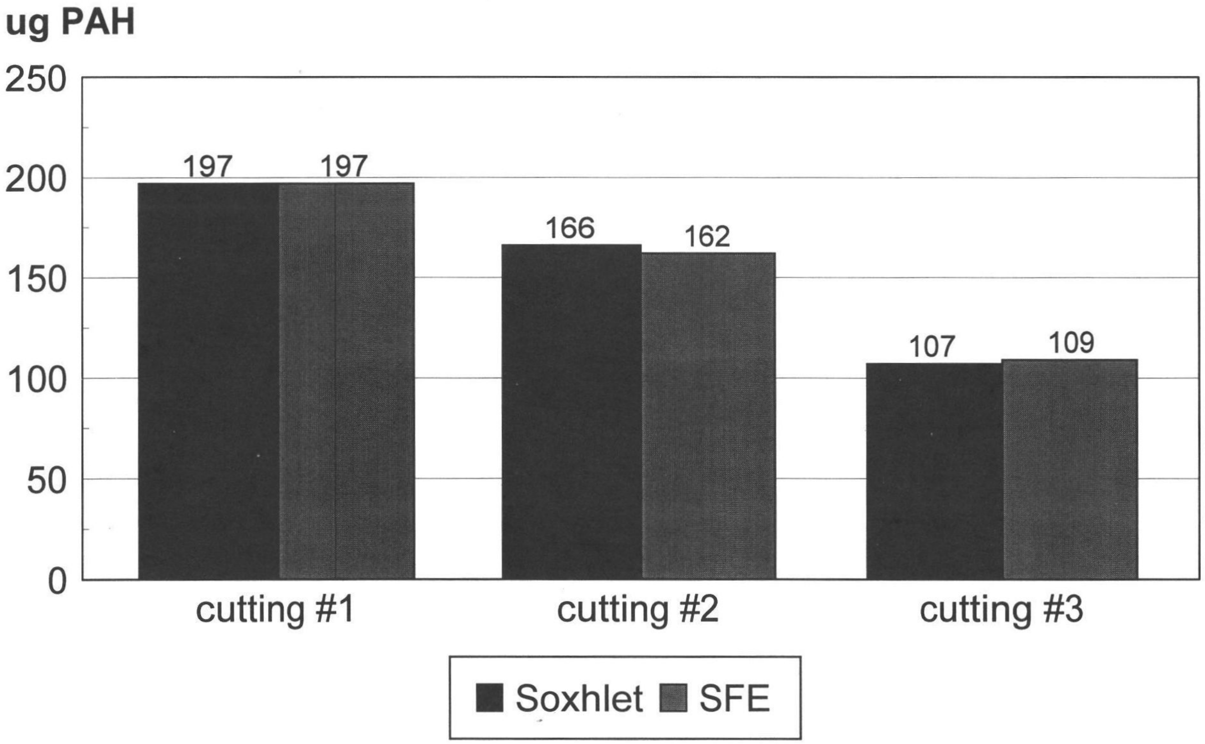


Figure 5: Use of modifier in SFE extraction of PAH from filter cuttings

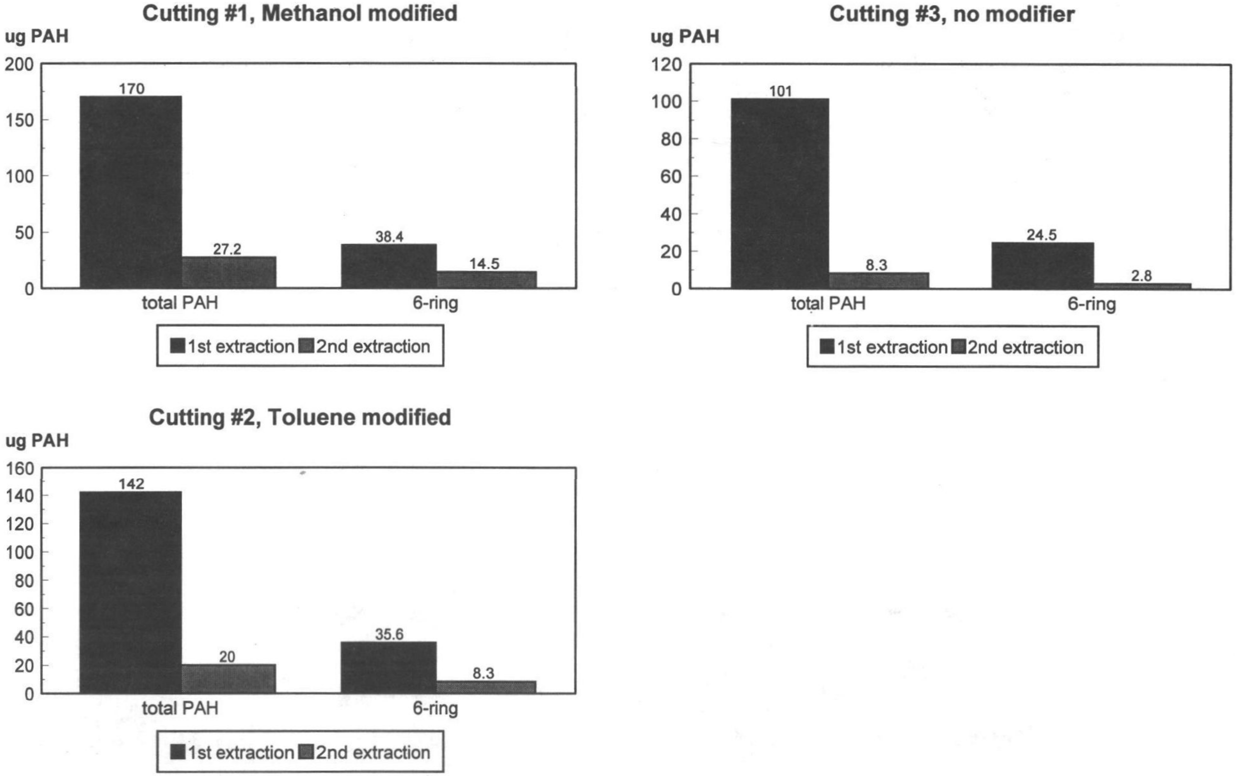


Table 1

SFE Extraction of PAH from a natural matrix reference material

CRM 103-100, Fisher Scientific

PAH	*Reference Value*	*SFE*			Mean	Standard Deviation	Precision, % (Coefficient of variation)
		trial 1	trial 2	trial 3			
NAPHTHALENE	35	3	2	5	3	1	42
2-METHYL NAPHTHALENE	60	5	5	7	6	1	25
ACENAPHTHENE	627	237	225	240	234	2	1
FLUORENE	443	308	320	317	315	6	2
PHENANTHRENE	1925	1770	1570	1670	1670	71	4
ANTHRACENE	431	381	380	385	382	3	1
FLUORANTHRENE	1426	1391	1420	1375	1395	11	1
PYRENE	1075	1103	1090	1156	1116	37	3
BENZ(A)ANTHRACENE	264	258	306	323	296	46	16
CHRYSENE	316	250	226	240	239	7	3
BENZO(a)PYRENE	97	52	43	38	44	10	22
INDENO(1,2,3-CD)PYRENE	32	9	7	5	7	3	40
Sum	6731	5767	5594	5761	5707		

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The Use of Thermal Extraction in Spill Response

Abstract

Thermal extraction (TE) is a potential method for quick on-site screening for spill chemicals. This paper reports on the evaluation of two instruments, the Tekmar 5000 on-line sample concentrator and the CDS EA 600 Environmental Analyser. Both instruments were optimised in their primary role for desorption of sorbent cartridges in air monitoring surveys. In addition, each instrument was adapted for TE of solid samples. Although similar in principle in their operation, they differ in the intermediate trapping of desorbed analytes. A selected number of chemicals were spiked onto a variety of matrices and the feasibility of using TE was studied. Performance evaluation, such as precision, detection limit and comparison to conventional wet extraction methods were made. Finally the advantages and disadvantages of TE will be presented and discussed.

Introduction

Methodologies for determining spilled chemicals on solid samples traditionally involves a lengthy solvent extraction and cleanup prior to gas chromatography (GC) or gas chromatography/mass spectrometry (GC/MS) analysis. For on-site emergencies response work, this limits the sample turn-around time plus the requirement for fume-hood work area and solvent storage/disposal.

Because of the universal nature of extraction, the analytes of interest are often extracted together with background materials that might interfere with subsequent analysis. To minimise this, the raw extract often needs to be concentrated down and subjected to cleanup procedures which might involve fractionation on a silica gel column as in the case of polyaromatic hydrocarbon (PAH) analysis; or multi-stage column cleanup as in the case of dioxin/polychlorinated biphenyl (PCB) analysis. In each of these steps, the volume of the eluate often needs to be reduced by rotary evaporation or blow-down by a gentle stream of nitrogen. Generally, the sample turn-around time is in the order of 2-3 days for a batch of 6-8 samples.

TE Technique

For quick screening of spilled chemicals, a viable solventless extraction technique is by thermal means. The solid sample is weighed into a furnace, which is heated up rapidly while purged by a stream of helium. The temperature used is selected to be high enough to desorb the analyte, yet not so high as to volatilize the humic acid or cause the pyrolysis of the matrix. The helium purge gas carries the analyte into an internal trap of tenax maintained at ambient temperature (in the CDS unit) or a cryogenic trap consisting of an open-bore or glass bead-filled tubing (Tekmar). After 6-12 minutes of desorption, the accumulated analytes on the secondary trap are in turn rapidly desorbed into the GC and analysed in the usual manner. Analytes amenable to this technique can be volatile compounds from soils or sorbent tubes such as those used in industrial hygiene methods. Semi-or non-volatile analytes can also be thermally desorbed from any solid matrix such as soil, soot samples collected on filters or wipe samples of contaminated surfaces. Compared to wet extraction methods in which the analytes are diluted in solvents, TE delivers the analytes of interest directly to the analytical instrument without any dilution and hence offers potentially much higher sensitivity.

Experimental

For this work, two desorption systems were investigated. Both instruments were originally designed to handle sorbent tubes for volatile compounds. However, they were both flexible enough to allow direct thermal desorption work to be carried out. Detailed description of each instrument is given as follows:

Tekmar 5000 is an automatic desorber for sorbent tubes used in ambient air monitoring, emission studies and industrial hygiene analysis (1 to 3). The furnace accepts sorbent tubes 5/8-in diameter which accommodates solid samples easily and was used to conduct most of the thermal desorption work in this study. An alternate furnace is also available for tubes 1/4-in diameter. For thermal extraction of solid samples, an aliquot of 10-100 mg was weighed onto a small piece of glass-fibre filter, loosely rolled up and inserted into the furnace. A prepurge of 1 min was used to purge out any moisture and entrained air. The furnace was heated up to 225 ^{0} C (tenax sorbent tubes) or up to 300 ^{0} C for soil samples under a flow of helium of 20 mL/min. The desorbed analytes were swept into an internal cryogenic trap (C1) maintained at a low temperature to trap the analytes. In this study the open-bore trap was used. After 6-10 min of desorption, the flow to C1 was reversed, the trapped analytes were swept via a heated nickel transfer line onto another cryogenic trap C2 consisting of a length of uncoated fuse silica tubing which functions as a cryogenic focussing device to improve resolution of light compounds on the GC. The GC was a HP 5890 equipped with a flame ionisation detector (FID) and a DB 5 megabore column. For semi-volatile desorption studies, a Restek RTX-1 column (30 M, 0.32 mm, 0.5-µm film) was used to resolve PCB or PAH. The split injector was operated at a split ratio of 10:1. Data output was on a HP 3396 electronic integrator via the built-in INET port. Quantitation was by means of external standard method in which peak area of the analyte was compared to that of a standard. Instrumental parameters are summarised below:

Furnace	5/8 in. * 7 in.
Prepurge	1 min at 20 mL/min
Internal trap, C1	1/16 in. open bore or glass bead-filled
Desorb	8 min at purge flow 20 mL/min, 225 ^{0} C for tenax tube, 300 ^{0} C for soil
Transfer	2 min at 300 ^{0} C
Cryofocus, C2	40 ^{0} C; inject: 1 min at 300 ^{0} C
Valve	280 ^{0} C; Line 300 ^{0} C; Injector 300 ^{0} C
Bakeout	250 ^{0} C for 8 min
GC column	Volatiles: 50 m HP 1 * 0.32 mm fused silica, 1-µm film; Semi-volatiles: 30 m RTX 5 * 0.32 mm fused silica, 0.5-µm film
Program	40 ^{0} C for 3 min, 25 ^{0} C/min to 300 ^{0} C held 5 min
Carrier	Helium at 50 cm/sec; nominal column flow 5 mL/min (nominal)
Detector	FID, 300 ^{0} C, range 10 exp-12; attenuation 2

CDS EA-600 Environmental Analyser is a compact integrated PAT/thermal desorption/GC system for environmental samples (4). Occupying a space only 24-in wide (roughly 75% the footprint of a normal laboratory GC), the system is well-suited for the limited bench space in a mobile laboratory. The integral GC accepts standard-sized capillary columns and is equipped with a tandem Tremetrics (Austin, Texas) photo-ionisation detector (PID)/FID detector. The PAT/thermal desorption module can analyse water, soil and air samples and hence is very versatile for emergency field work. Although primarily a PAT/GC system, the optional cartridge desorption module can accommodate 1/4-in diameter sorbent tubes used in air monitoring. Fine particulate samples can also be weighed into empty glass tubes and inserted by the desorption probe into the furnace. Desorbed analytes can go directly into the GC or through an internal tenax trap similar to PAT operations (as in this study). Instrumental parameters are summarised below.

CDS Desorption

Trap rest	35 ^{0} C
Trap initial	35 ^{0} C, 5 min
Cartridge rest	50 ^{0} C, 1 min
Cartridge purge	200 ^{0} C, 5 min
Desorb temp	200 ^{0} C, 2 min
Bake trap	225 ^{0} C, 4 min
Focus	180 ^{0} C
Valve oven	200 ^{0} C
Transfer line	200 ^{0} C

GC

Column	SE-54 (Alltech), 30 M, 0.53-mm, 1.5-µm film
Oven	35 ^{0} C for 3 min, ramped @ 10 ^{0} C/min to 225 ^{0} C held 3 min
Detector	PID/FID, 270 ^{0} C
Head pressure	8 psi
Column flow	10 mL/min (nominal)
Purge flow	25 mL/min

Data Station A/D	HP3365 ChemStation (DOS-series), HP 35900 board

For air sampling, tenax tubes were packed by tap-filling blank glass tubes (Supelco, 3*1/4-in) with about 0.5 gm of tenax-GC. The tubes were conditioned before use by purging at 240 ^{0} C under 50 mL/min of ultrapure helium for 4-hr on a tube conditioner (Dynatherm). They were sealed in screw-top glass tubes (Supelco) to exclude any infiltration of outside air. After collection, the tube was attached to the desorption probe through which purging helium flows. The probe was inserted into the cartridge desorber situated on top of the PeakMaster EV (the PAT module of the system). The trap was purged at a cartridge rest temperature of 50 ^{0} C to get rid of any adsorbed moisture and air in the sorbent. The cartridge furnace was then heated up to 200 ^{0} C and the analytes on the tenax tube sample purged into an internal WeTrap/tenax trap (the WeTrap was an optional tenax pre-trap on the system that removed up to 90 % of water when performing PAT at elevated temperature. For this work, the WeTrap was not used and kept at 250 ^{0} C because evaluated samples did not contain excessive amounts of moisture. After 5 min of cartridge purging, the internal tenax trap was heated up to 200 ^{0} C (desorb trap) for 2 min. The gas flow was routed by a heated 8-port valve and entered the GC via a heated transfer line. Trapping of the volatiles were entirely done on the liquid film of the GC column during trap desorption; as peak shape and resolution for the early eluting peaks were acceptable; the cryofocus module was not used in this study.

At the end of the analysis, the tenax trap was heated up to 225 ^{0} C to bake out any residual organics so the tube was ready for the next collection. The desorption module was cooled down by a stream of house air to reduce the waiting period.

Results and Discussions

Although similar in their concept in heating solid samples to vaporise the analytes, followed by concentrating and delivering them to an analytical instrument, each instrument differs in the manner the analytes are captured before analysis and hence will be discussed separately.

Tekmar

The instrument under study was one of the early models and found to have a few design flaws which were subsequently fixed . The most serious was an infiltration of laboratory air through the trap vent. During standby, the desorb gas was cut off and the internal trap was opened to the outside atmosphere through the trap vent. Volatiles in air could be concentrated by passive diffusion onto the internal trap. Depending on the duration of standby, high and non-reproducible background peaks were present in tube blank runs. This problem was fixed by attaching a 600-mg charcoal sorbent tube in front of the tube vent to scrub out any volatiles in laboratory air. This measure drastically reduced the background peaks in blanks. Another problem was to winding of the heating element of the tube furnace: ours had the heating elements around the outlet end of the furnace. As a result, samples were subjected to uneven heating and had to be loaded into the outlet end of the furnace, rather than the more convenient inlet end at the front of the instrument.

Cryogenic trapping The standard internal trap C1 was an 10*1/16-in open-bore nickel tubing cooled by liquid nitrogen down to as low as -150 ^{0} C. This took place before the tube furnace was heated up. A desorption flow of 10-30 mL/min was used in this study: a low flow rate and C1 temperature of -150 ^{0} C was used to desorb tenax tube in which volatiles were collected. High flow rate of up to 30 mL and C1 temperature up to 40 ^{0} C was used to evaluate semi-volatile desorption studies. The rationale was that a low flow rate and low C1 temperature allowed better trapping of volatiles on C1 without breakthrough, whereas in semi-volatile work, a relatively high C1 temperature and high flow rate would minimise adsorption loss on C1 and permit higher swept volumes of the tube furnace, leading to a better transfer of analytes to the GC. For semi-volatiles, the temperature of C1 was determined by the boiling point of analytes in mind, e.g. C1 was kept at 10 ^{0} C for PAH desorption. The most volatile PAH (naphthalene and the methylated analogue) were still retained on C1.
For very volatile compounds, another cryogenic trap C2 could be used to sharpen the resolution and peak shape of the early eluting compounds. This was a simple piece of fused silica tubing cooled by liquid nitrogen. The entire assembly was housed in a separate module attached above the GC injection port. In this study, using gasoline vapour as a model mixture, peak shape and resolution were compared at various C2 temperatures. It was found at -100 ^{0} C there were significant loss of volatiles as they were desorbed, and C2 as high as 40 ^{0} C did not result in poorer peak shape and resolution (Figure 1). At this relatively high temperature, trapping of analytes as they were transferred

from C1 to C2 was entirely done by the liquid phase of the GC column at ambient temperature only. Keeping C2 at 40 ^{0} C also saved cryogen consumption. The reason for analyte loss at C2 of -100 ^{0} C could be ice formation on a relatively small volume or blown-off of the volatile organics.

Sorbent cartridge About 2 gm Tenax-GC (Alltech, 35/60 mesh) was packed into 5/8*7-in SS tubes and held between glass wool and retained by metal springs made from paper clips. Although the tenax-GC was baked at 250 ^{0} C furnace before use, the tubes still needed to be cleaned before use. After activation, the tubes needed to be properly stored to minimise the background. Tekmar provided aluminum shipping tubes capped with dual O-rings seals. Background chromatograms before and after proper conditioning are shown in Figure 2.
Extreme care had to be taken because high and variable backgrounds occurred readily by careless handling or even from dirty sample container that the tubes had come into contact with. Tenax-GC is superior to other polymeric sorbents in that it has a relatively high temperature limit (380 ^{0} C) and freedom from forming a variety of artifacts (reference 5).

Thermal desorption of solid samples Originally designed for sorbent tube desorption analysis, the furnace for 5/8-in tube is easily accessible and wide enough to accommodate soil or filter samples. To study the feasibility of thermal desorption for these types of sample, various analytes were spiked onto glass-fibre filter and soils to simulate emergency response samples. Figure 3 shows the thermal desorption/GC chromatogram of a glassfibre (GF) filter analysed straight from the box without any prior treatment. The chromatogram shows both the strength and weakness of the present system: superior sensitivity of TE in that the entire desorbate was delivered to the GC without any dilution; the weakness being the complex profile would render detection of minor constituents adsorbed on the filter very difficult. The same filter after being heated in an oven at 140 ^{0} C for 4-hr shows much cleaner background.

Volatile Organic Compounds (VOC) on Charcoal Volatile organics in air are traditionally collected on charcoal sorbent tubes and solvent extracted by carbon disulphide and analysed by GC/FID. To evaluate if TE can be used to desorb the VOC, a 100-mg aliquot of charcoal from a SKC coconut charcoal sorbent tube was spiked with a NIOSH VOC mixture (50 ng per VOC component) used to quantitate indoor air pollution. It was loosely wrapped on a small piece of GF filter and desorbed at 280 ° C. As expected, there was no recovery, meaning TE cannot provide the energy alone to free the VOC from the charcoal surface.

PAH For semi-volatile desorption work, the heating zones needed to be at the highest temperature permitted by the instrument to minimise any condensation. The max temperature for the tube furnace, C1, transfer line were 350 ° C whereas the 8-port switching valve could not be operated continuously above 300 ° C without shortening its life expectancy of the valve seals. This evidently limited the range of PAH that can be desorbed. A chromatogram for a PAH standard spiked onto a GF filter is shown in figure 4. With the heating zones at 300 ° C, only 2-4 ring PAH could be detected. By raising the heating zones to 325 ° C, PAH desorption was still incomplete. The same figure shows the desorption of a certified PAH soil contaminated with wood preservatives. Despite a relatively small sample size of 2 mg, the chromatogram was complicated. In this technique, the analytes are freed from the surface binding forces by thermal means without the aid of solvation effects which occur during solvent extraction processes. Desorption of high molecular weight PAH, being adsorbed the strongest, would be more difficult and to an extent depending on the surface structure of the matrix. It was not known whether condensation occurred at some point in the flow path or a inadequate desorption temperature.

Diesel Figure 5 shows a desorption analysis of a diesel standard spiked on a filter and a diesel-contaminated soil sample from a sour gas processing plant at Nordegg, Alberta. Using a nominal sample size of 10 mg and a desorption temperature of 250 ° C for 8 min, the diesel concentration was found to be 2492 µg/gm (n=4; coefficient of variation CV=+/- 13.8%) compared with 5000 µg/gm by conventional hexane extraction.

Because of the multi-stage trapping and relatively long flow path, sample carry-over could be a problem especially with very dirty samples. A desorption blank after the Nordegg soil runs show 5-10 % carryover. The carry-over could be minimised by using a very small sample size for a preliminary screening before arriving at the optimal weight. Incorporating a bake-out step after desorption, or interspersing blank runs with samples were all good insurance against cross contamination.

Other spill chemicals To investigate the applicability of TE, a variety of chemicals such as Aroclor mixtures, glycols, acetic anhydride, vinyl acetate were spiked onto different soil matrices (soil, sand, etc.) to simulate spill samples (figure 7). Again, unless the matrices are fairly clean, the resulting chromatograms were hard to assess because of the universal nature of FID detectors.

Linearity This was evaluated by adding known amounts of diesel to a GF filter and desorbed. It appears the desorption yield is linear up to 100 µg of diesel (Figure 6).

Detection limit The minimum amount detectable was limited by the analytical instrument, in this case a GC/FID and the weight of samples that could be accommodated by the dimension of the furnace. A GC/FID typically has sensitivity around 5-10 ng. For a typical sample weight of 100 mg, this means the thermal desorption/GC/FID system has detection limits in the 5 ng/100 mg or 50 ng/gm (ppb) range. The real limitation, however lies with the background: the thermal desorption chromatograms for real samples usually are so complex that a selective detector such as a mass spectrometer is almost mandatory.

CDS

The sample flow path is not nearly as complicated as for the Tekmar unit. For this study, the desorption module was inserted into the flow path ahead of the internal tenax trap so analytes desorbed from the sorbent tube sample were concentrated in the tenax trap as in the PAT mode.

Air monitoring Typical tenax tube samples from air monitoring using an AirCon 2 high volume sampler are shown in figure 8. A sampling rate of 1 L/min was used. Some commercially available ready-packed tubes such as the MSA mix bed tenax/carbon molecular sieve(CMS) were also evaluated. This cartridge was sealed in an outer glass tube and was ready to use as received. The background was acceptable.

Stepwise desorption study Since the extent and nature of desorption are dependent on the desorption temperature, a study was carried out to investigate if a stepwise desorption could be used to differentiate a more volatile component from a less volatile one. This has a potential of fingerprinting different spilled chemicals based on their boiling range. Equal amounts of gasoline and diesel (0.8 µg) were spiked onto a piece of glass fibre filter and thermally desorbed at 1st desorption/2nd desorption temperatures of 50 ° C/200 ° C and 75 ° C/200 ° C. In both cases the gasoline and diesel were desorbed during the first desorption, whereas the second desorption recovered only an additional 20-40 %. The stepwise desorption was not successful because the sample was not 'aged' sufficiently so as to minimise evaporation loss of gasoline. For some components differ widely in volatility, stepwise desorption can be a useful screening technique if the spilled chemicals bear distinct thermal desorption profiles.

Detection limit and precision study Finally, to assess the precision of TE, a VOC mixture of 45 chemicals including alkanes, alkenes, aromatics and chlorinated hydrocarbons were spiked onto GF filter at 5 ng per component and desorbed. Five replicate runs were made at a desorption temperature of 250 ° C. Precision was found to be about 23 %(CV). The chromatogram (figure 9) shows a reasonable signal/noise ratio of each peak of 5 ng, this probably represents the detection limit of TE on the CDS instrument.

Conclusion

Both instruments were evaluated in the more tradition role of sorbent cartridge analysis and found to work well. Some design problems of an early production model of Tekmar desorption instrument have been identified and corrected. Feasibility studies were carried out to desorb soil/filter samples as a viable field screening technique. Extensive optimisation of both instruments were conducted. Recovery studies were conducted using artificially spiked samples using a selected number of common spill chemicals. Real samples were also run to assess the limitation and usefulness of TE. Recovery for diesel range fuel was determined to be about 50 % with a precision of 14 %. By far, the most severe limitation came from the high and variable background of actual samples: a GC with non selective detector was inadequate for trace desorption analysis. Minimum detectable quantity is 5 ng of 'desorbable', which translates to 0.5 ppm for a 10-mg sample size. Although lacking the high temperature requirement to perform TE for semi-volatile compounds, for relatively clean backgrounds and high analyte concentrations as typically encountered in a spill situation, TE analysis is potentially useful as a screening tool. On the described instrumentation, a TE analysis takes typically 45-min per sample plus its versatility in handling a variety of sample matrices are important assets to spill responders.

List of Figures

Reference

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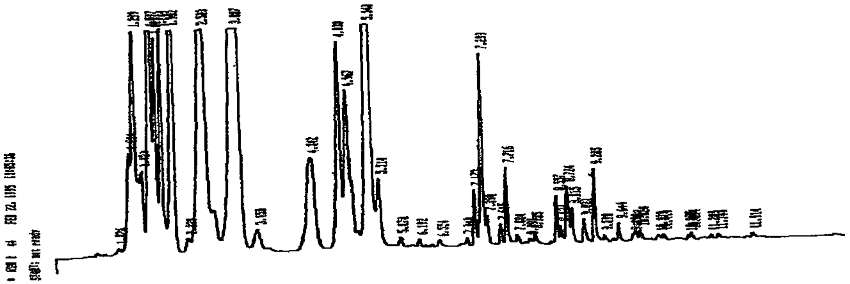
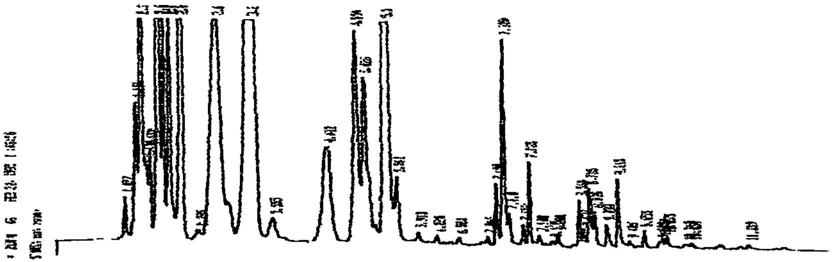
5. W. Bertsch, R. Chang, Journal of Chromatographic Science, p 175, Vol 12, Apr 1974.

Figure 1

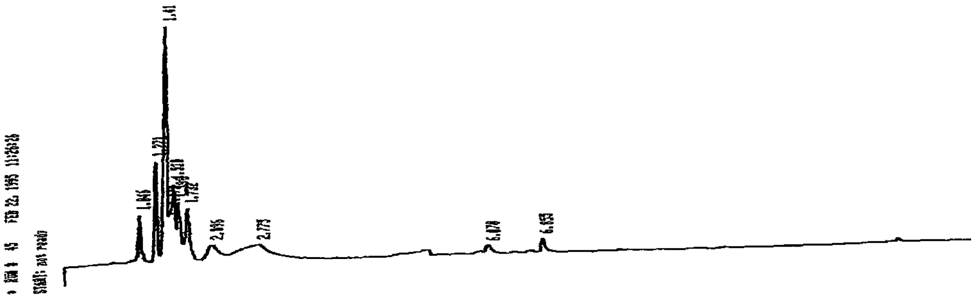
C1/C2
-100°c/40°c



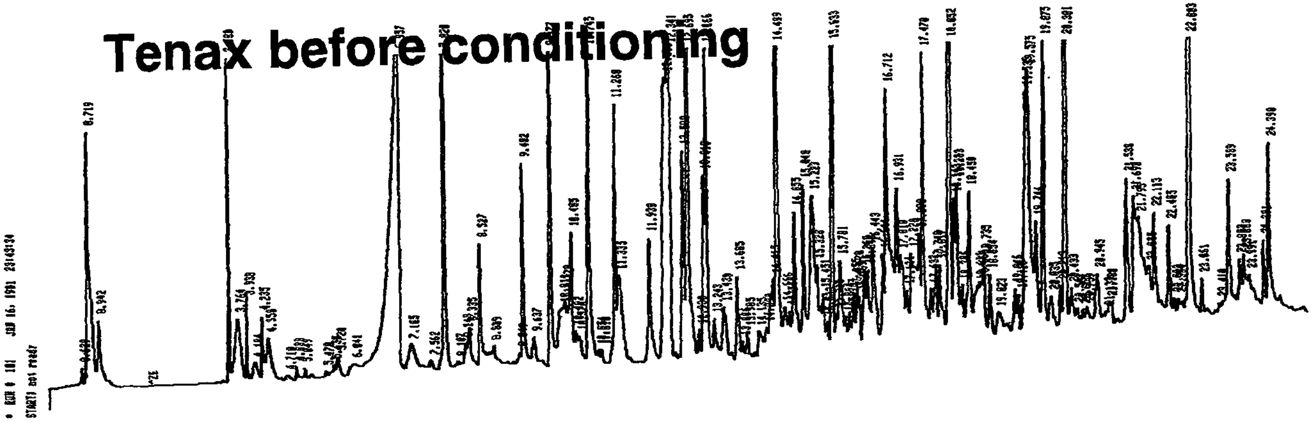
-100°c/0°c



-100°c/-100°c



Tenax before conditioning



After conditioning

Figure 2

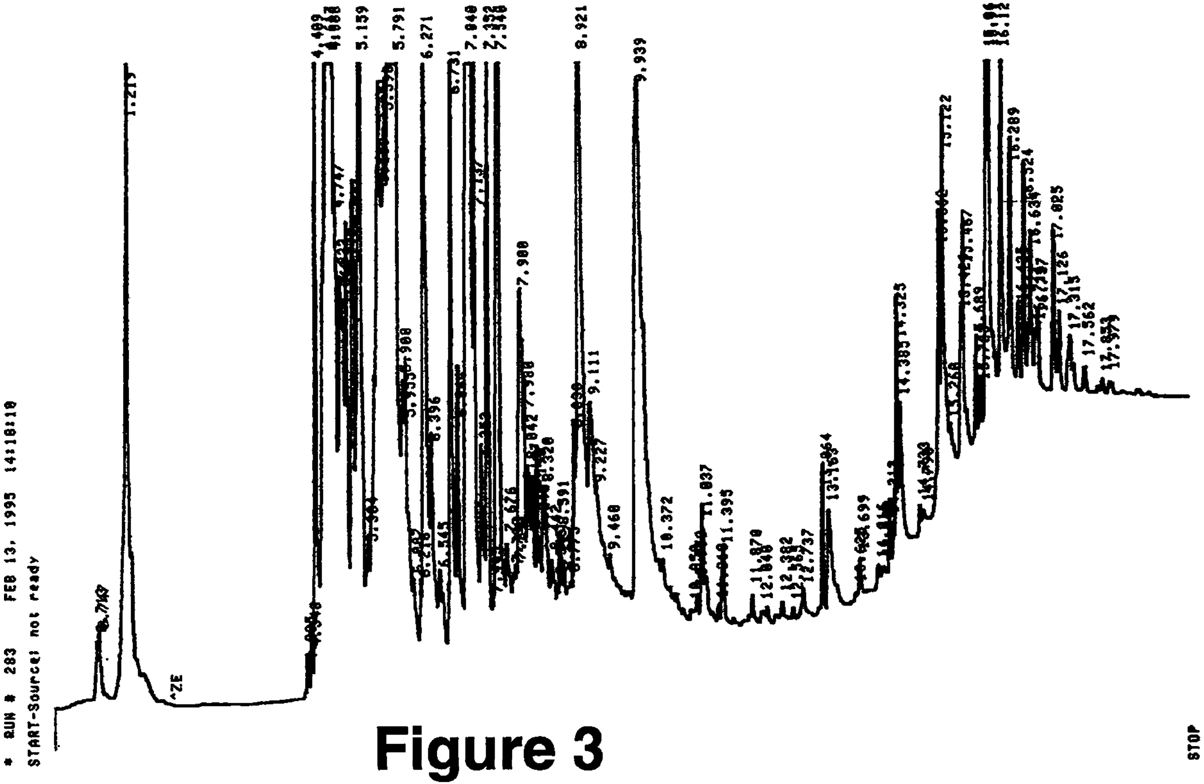

* RUN # 283 FEB 13, 1995 14:18:18
START-Source: not ready
^ZE
4.409
5.159
5.791
6.271
6.731
7.040
6.396
6.545
7.626
7.980
8.320
8.591
8.921
9.111
9.227
9.460
9.939
10.372
11.037
11.395
12.737
13.964
14.385
15.122
15.260
15.467
16.12
16.289
16.324
17.025
17.126
17.562
STOP

Figure 3

Figure 4

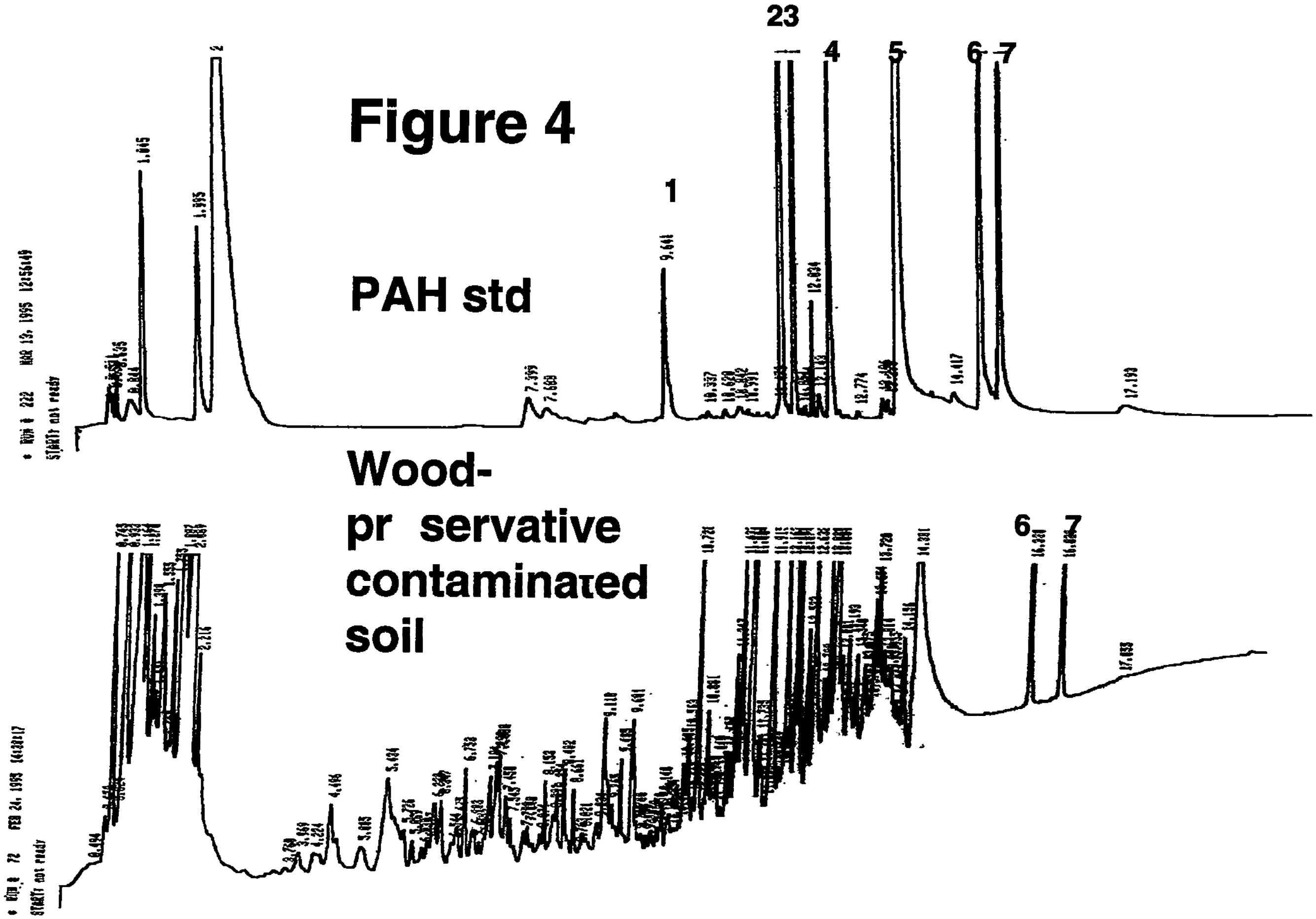


Figure 5

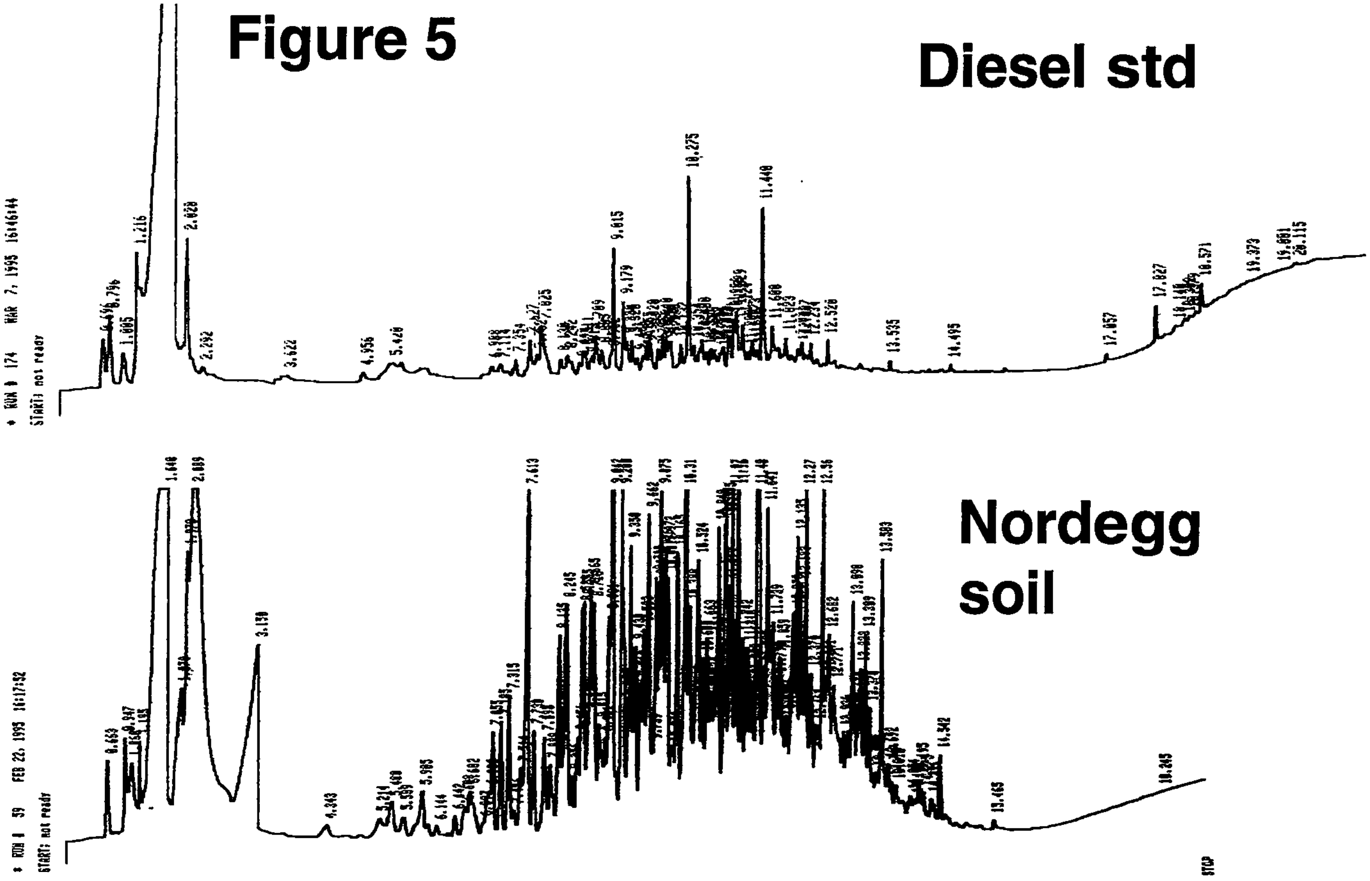
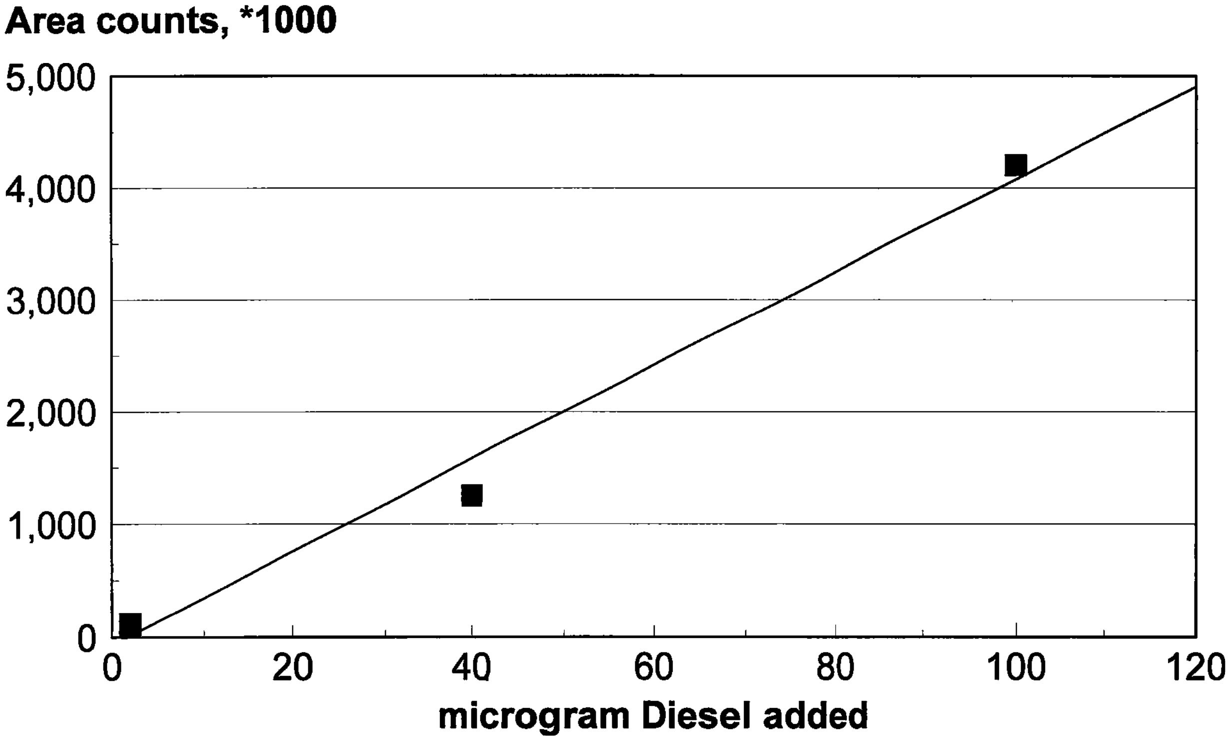
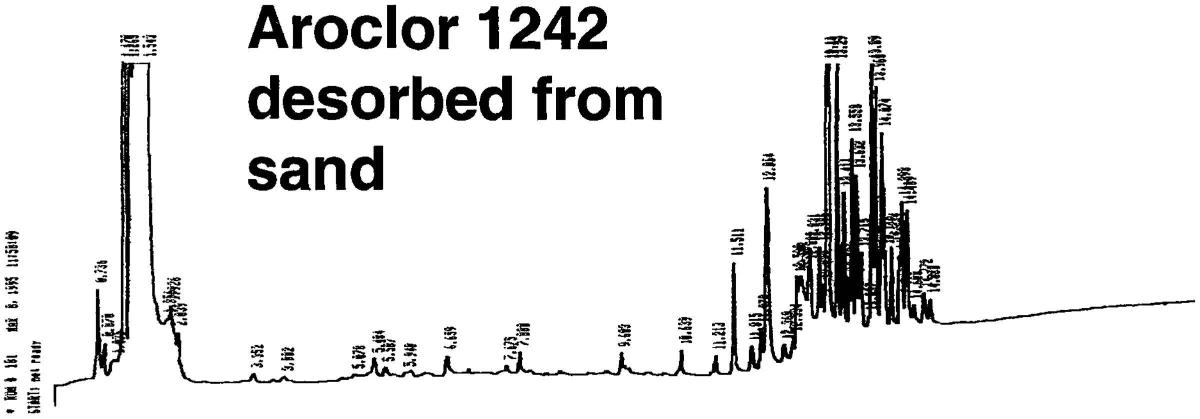
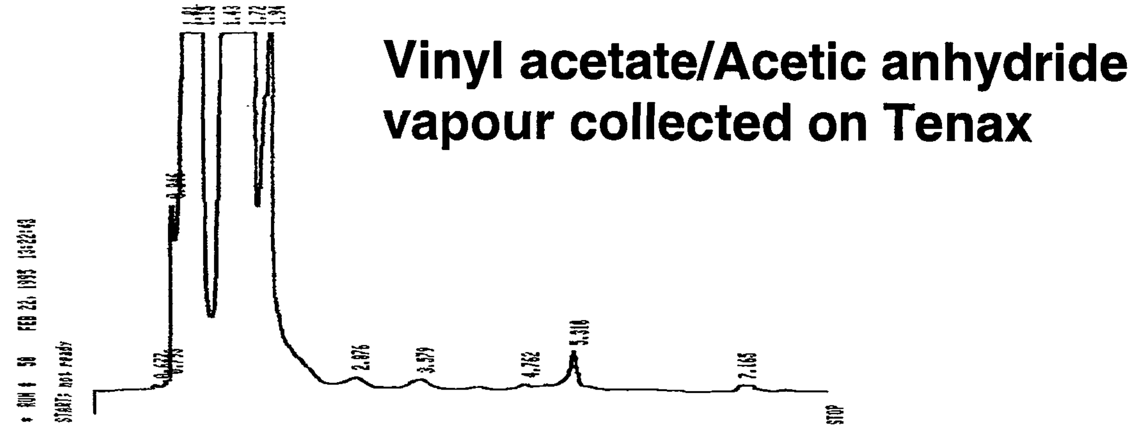

Diesel std
Nordegg soil
RUN # 174 MAR 7, 1995 16:46:44
START: not ready
1.216
2.020
9.015
9.179
10.275
11.440
12.520
13.535
14.495
17.057
17.827
18.571
19.373
20.115
RUN # 59 FEB 22, 1995 16:17:52
START: not ready
1.446
2.089
3.150
4.343
7.613
10.31
12.27
12.36
13.583
14.342
15.465
18.845
STOP

Figure 6: Thermal desorption linearity test, filter spiked with Diesel





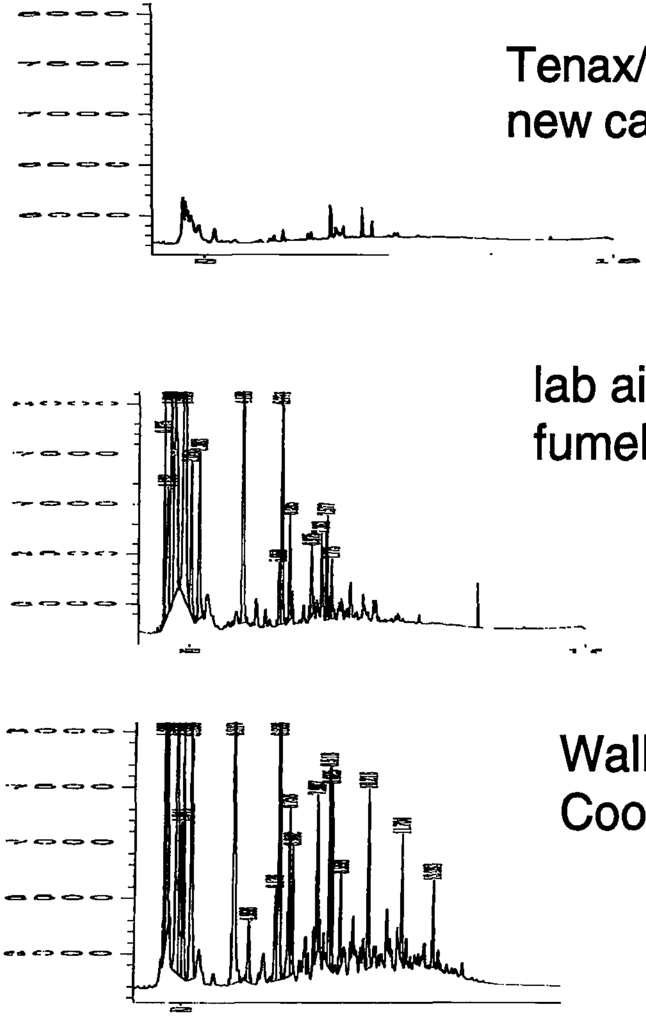
Aroclor 1242 desorbed from sand



Vinyl acetate/Acetic anhydride vapour collected on Tenax

Figure 7

Figure 8



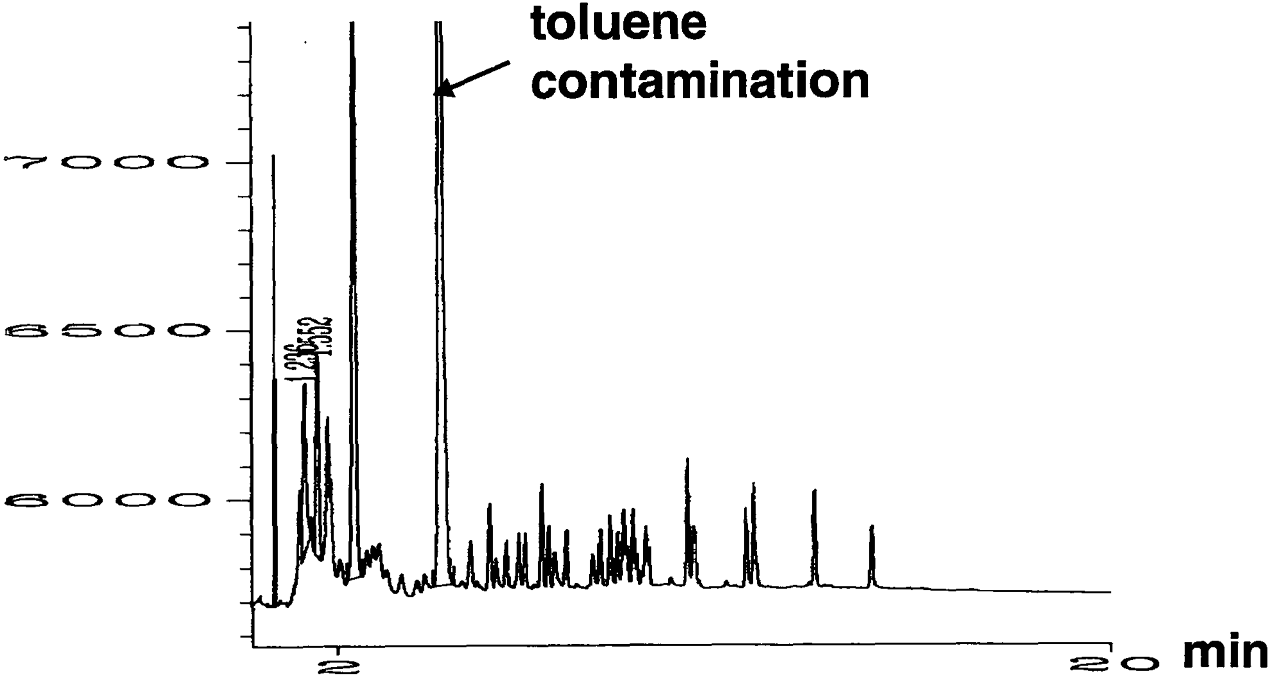
Tenax/CMS
new cartridge

lab air near
fumehood

Walk-in
Cooler

Figure 9

VOC mix on tenax/CMS



toluene contamination

Validation of a Successive Correction Modeling Technique: A Method to Identify and Quantify Sources of Air Emissions Detected by the TAGA 6000E

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ABSTRACT

The U.S. Environmental Protection Agency's Environmental Response Team (U.S. EPA/ERT) was requested by Region VI to verify or refute periodic exceedances of the short-term thresholds of several volatile organic compounds (VOCs) near a petroleum recovery Superfund site. This request lead to a series of responses and services for which the U.S. EPA/ERT performed on and off site. One such service was to provide routine mobile monitoring runs for airborne VOCs during extreme atmospheric conditions (i.e., morning inversions). Another service was to apply available models to evaluate the impact of site emissions.

During a routine ambient air mobile monitoring run for VOCs within a residential neighborhood, a plume was detected adjacent to a hazardous waste site containing contaminated subsurface impoundments. The site was expected to emit several of the same compounds as those detected in the plume. Region VI then requested the U.S. EPA/ERT to identify the source(s) responsible for the elevated concentrations.

A successive correction technique (SCT)[1], developed to set up and run several Fugitive Dust Model[2] (FDM) input files sequentially, was used to determine the emission rates necessary, at the sources of concern, to produce the ambient concentrations detected during mobile monitoring. After several investigative modeling runs using the SCT, it was found that an adjacent excavation site was the most likely candidate responsible for the majority of the impact. The source term was obtained and its impact on a nearby neighborhood was evaluated.

INTRODUCTION

The Sciex^{TM} Trace Atmospheric Gas Analyzer (TAGA) 6000E was used to sample and analyze VOCs in the ambient air of the neighborhood surrounding the Superfund site. Vinyl chloride (VNCL) and 1,1,2-trichloroethane were detected on several occasions by the TAGA during mobile monitoring along the roads of the neighborhood. Although the same conclusions were reached with regards to both compounds, only the results for VNCL will be discussed in detail.

Early one morning, a plume was detected in the eastern part of a residential area marked in Figure 1. Several possible mechanisms responsible for these emissions were: barometric pumping of the gases in the impoundments; volatilization from a creek which entered from the southwestern end of the site and had originated from the direction of petroleum operations; volatilization from a groundwater treatment facility; fugitive emissions from the excavation activities that occurred on the adjacent site which ensued beneath a clamshell with a carbon adsorption air handling unit; or emissions from petroleum operations a half mile away. Other sources were located nearby. All known possible sources were analyzed and the sources that produced the impact similar to the concentrations detected by the TAGA were maintained for further evaluation.

MOBILE MONITORING

Mobile monitoring was conducted using the TAGA, a mass spectrometer/mass spectrometer (MS/MS). The TAGA is a real-time, direct-air sampling laboratory instrument which is mounted in a vehicle (bus). The TAGA MS/MS utilizes the technique of triple quadrupole MS/MS to differentiate and quantitate compounds.

The TAGA performs mobile ambient air monitoring using a direct-air sampling system along roads adjacent to suspected sources to detect emissions originating from these locations. Outside ambient air is continuously drawn through a port in the wall of the TAGA bus. As the mobile monitoring proceeds, the operator presses letter keys (flags) sequentially to denote events or locations during the monitoring. Flags A through D are provided on Figure 1 to denote the location of intersections along South Drive.

For this study, the TAGA collected and determined the concentrations of eight selected VOCs, in the parent ion/daughter ion mode, at 2.25 second intervals during mobile monitoring at the receptors of interest. Therefore, every 2.25 seconds, the TAGA provided ambient concentrations of eight compounds. This provided a robust data field for the modeling analysis.

STATIONARY SAMPLING

Two gas chromatographs (GCs) were used as stationary samplers to help locate possible sources. Only one sampling station is depicted in Figure 1. The other is to the south of the groundwater treatment facility. The stationary samplers were each equipped with a flame ionization detector. Due to the variability of the plume, the concentrations detected were lower than those detected by the TAGA. Additionally, the longer sampling period, along with the proximity of the samplers with respect to the suspected sources, limited their ability to resolve locations of the sources. However, they could be used as way-points, to determine if the source was upwind or downwind (with respect to the average wind conditions).

MODELING

Traditional receptor models use the chemical and physical characteristics of gases measured at the source and the receptor to qualitate and quantitate source contributions to receptor concentrations. Receptor models quantify contributions from each of the sources but when several sources emit the same compounds, its accuracy is limited. The difference between it and traditional receptor models is that receptor models use known source terms to discern the responsible source, while this technique uses meteorology and source/receptor geometry to locate the source and ascertain its release rate.

In this study, the SCT solved the Gaussian dispersion equations within the FDM in an attempt to obtain the emission rate of a source and the rate distribution across the source. The SCT may be adapted for other models to utilize the most appropriate algorithms for the situation at hand (such as the Industrial Source Complex Short Term [ISCST] model for Industrial sources.)

However, the FDM was selected for the SCT (in this case) because of its ability to simulate the sources at Superfund sites, namely: the ability to simulate rectangular area sources of varying length and width dimensions; calculate emissions from irregularly oriented line sources; calculate ambient air concentrations for receptors located directly above the source; and to calculate concentrations using meteorological data provided in several formats. The FDM model uses a line-source algorithm recommended [3] to predict emissions from area sources with close proximity to receptors.

The model was set up to calculate concentrations at locations along the route that the TAGA traveled during its mobile sampling runs. A Global Positioning System was used to determine the location of the TAGA relative to the suspected sources.[4] During the sampling runs, however, specific locations were determined using flags (as described above). The locations along the route were broken down into discrete receptors approximately one meter apart. The model was run independently for each source and predicted concentrations were obtained at the receptors. During modeling, those sources that produced a plume within the region consistent with the TAGA results were retained. The emission rate was then adjusted (or factored) to produce concentrations similar to the measured values and the model was rerun. After the sources were evaluated individually, they were combined in a single model run. The emission rates were then adjusted so that the receptor concentrations predicted by the model matched those measured by the TAGA.

The emission rates were factored with the use of spreadsheet software that was programmed to compare the results of the model to the results of the TAGA. The program located the peaks (local maxima) and included concentration information spanning two standard deviations on either side of those peaks to match predicted and measured plumes. A ratio of the average values across the two standard deviations of both data sets was used to adjust the emission rate(s), where:

$$\frac{\textit{Avg. TAGA Concentration } (C_A)}{\textit{Avg. Predicted Concentration } (C_P)} = \frac{\textit{Actual Emission Rate } (E_A)}{\textit{Predicted Emission Rate } (E_P)}$$

where E_P was assumed to be equal to 1 g/s for the first approximation of the emission rate — making the correction step easier. This allows for an estimation of the emission rate through:

$$\frac{C_A}{C_P} = E_A$$

The value for E_A is then the first correction made to the first approximation. The drawback in the above procedure is that the equality assumes that the plume is produced by a single source, because the average across what is assumed to be the a single plume detected by the TAGA is compared with the average across a single plume generated by the model. Therefore, after each (suspected) individual source was identified, the model was run again and the results were again compared with the TAGA data. Then, the (model) emission rates were readjusted to produce receptor concentrations that matched the measured (TAGA) values.

The spreadsheet program interacted with the FDM model in a batch (iterative) mode so that the only input required was the name of the file that contained the TAGA data of interest. Meteorological and source location/dimension data were included in the original input file of the FDM model and interaction allowed the modeler to supervise the isolation of the individual plumes in the TAGA data. The predicted emission rate could then be used to evaluate the impact of the pollutants on other receptors.

CASE STUDY

The objective of this study was to identify the emission sources by utilizing a dispersion model and to estimate the impact of the plume on the neighborhood. Traditional receptor models were found to be inadequate. Therefore, the FDM was selected to simulate all the potential sources. Several model runs were made using unitized emissions from each of the suspected and known source locations. Air emission information was available on the impoundments, but the rates were too low to produce the concentrations detected. It was possible that the impoundments may have released emissions at a higher rate than previously measured. Additionally, no data were available on the three suspected sources; therefore, all sources were represented by a unity first approximation.

The first approximation (unity) emission rate was used in conjunction with meteorological data collected on site. The following conditions were present when the plume was first detected by the TAGA: stability=Class E, wind speed=1.4 m/s, and wind direction=180°. These values indicate winds orthogonal to South Drive and dispersion-restrictive flows. If a significant source of air emissions were present on site during this time, a well defined plume would be expected along South Drive (as happened). The emission rates were determined using the SCT modeling procedure discussed earlier along with the results from the TAGA.

The FDM output from each scenario was analyzed numerically and then reviewed by an objective observer. First, the TAGA data and model predicted data were scrutinized mathematically according to the plume dimensions. Then, both data sets were plotted and compared visually. The emissions of those sources that passed (as possible contributors) were then scaled and the model rerun for the individual sources and rechecked. Finally, the candidate sources were combined and rerun. Various combinations were evaluated and the most likely candidates (and their emission rates) reported.

The impoundments were represented in the model by area sources broken down to adequately represent the dimension of the source. Several other suspected sources were simulated with point, line, or area sources (as necessary). These are marked in Figure 1 with numbers 1 through 6. After the emission rates were determined for each source, they were kept constant for verification with subsequent TAGA data sets and the evaluation of the impact on the community. Then the (confirmed) emission rates were used to predict the worst-case ambient air concentrations possible during the episode.

RESULTS

The TAGA measured concentrations of VNCL along (east to west) South Drive are provided in Figure 2. Flags (labeled A through D) indicate the locations of the intersections sighted on the site map (Figure 1). There are two Gaussian-shaped plumes evident; the weaker plume, whose maximum is slightly greater than the detection limit, is located on the western portion of the street (between A and B), while the stronger plume is located on the eastern portion of the street (between C and D). The maximum concentration of the large plume was 35 parts per billion by volume (ppbv), while the smaller plume's maximum was 4 ppbv.

Since each source was simulated separately and in different combinations, several concentration plots for South Drive were generated for the study. Most of the impoundments were immediately dismissed as possible sources because of their relatively wide or misplaced plumes produced by the model runs. The predicted South Drive VNCL concentrations from the creek (located at 3 on the site map) are provided in Figure 3. Comparing this figure with Figure 2, it is clear that the creek is not a major source for the plume detected by the TAGA. However, it does produce a plume within the zone between the A and B labels on South Drive. Additionally, the results from stationary sampler stations indicated that some emissions did originate from the direction of the creek (on some occasions), so emission rates that produced concentrations commensurate with those values reported in the plume between A and B were retained. The predicted South Drive VNCL concentrations from the groundwater treatment facility (located at number 4 on the site map) are provided in Figure 4. The concentration curve is similar in appearance and location to the smaller plume in Figure 2. Therefore, the groundwater treatment facility is an assumed source of VNCL. The predicted South Drive VNCL concentrations from the carbon adsorption unit at the excavation site are provided in Figure 5. There is a large plume located between C and D. This plume is similar to the plume found in Figure 2 between C and D; thus the carbon adsorption unit is assumed to be the source. A petroleum operation located a half mile away (labeled number 6 on the site map) was also evaluated. Predicted concentrations on South Drive are provided in Figure 6. These concentrations do not correlate well with the measured values; therefore, this source was disregarded.

After several iterations (and modifications) of the model run using the SCT, the predicted concentrations yielded results similar to the measured values and the following emission rates (Q) were realized:

$Q_{\text{excav}}=0.5$ g/s $\quad Q_{\text{water treat}}=0.004$ g/s $\quad Q_{\text{creek}}=0.0005$ g/m-s

The values of the emission rates were then held constant for subsequent (traditional) FDM model runs. The results were verified against subsequent TAGA sampling runs and then used to evaluate the possible impact on the neighborhood. A verification run is illustrated in Figure 7, where the predicted concentrations are superimposed onto measured ones. Again, the emission rates were determined by the earlier TAGA sampling run, the model was run using new meteorological data, and the results were compared with the results of the TAGA sampling run concurrent with the meteorological data.

Additional model runs were made to obtain the worst-case impact possible at the residents that day. In doing so, the more restrictive atmospheric conditions that occurred that day were used, namely: stability=Class F, wind speed=1 m/s, and wind direction=180° (limited dispersion). A summary of the source combinations, the maximum values, and their locations can be found below.

Maximum Off-site Concentrations of Vinyl Chloride
for Each Suspected Emission Source

Sources	X (m)	Y (m)	Concentration (ppbv)
All	139.2	165.0	163.8
Excavation	139.2	165.0	163.8
Water treatment	179.0	165.0	14.9
Creek	-298.3	165.0	7.9

m = meters (locations relative the origin marked on Figure 1)
ppbv = parts per billion (by volume)
ALL = Excavation, Water Treatment, and Creek Emissions

The largest maximum predicted concentration was 163.8 ppbv and was produced by every model run that included the excavation site. This maximum was located directly downwind of the excavation site. The maximums from the water treatment facility and the creek were 14.9 ppbv and 7.86 ppbv, respectively. A two dimensional plot of concentration isopleths are provided in Figure 8.

CONCLUSIONS

Receptor models were found to be ineffective for this study. Therefore, a SCT was developed and successfully employed to meet the objectives. The results of the SCT implied that the majority of the emissions were released at the location of the excavation carbon adsorption air handling unit and the minority of the emissions were released from the locations of the groundwater treatment facility and the creek. Confirmation of these results was provided later by traditional runs of the FDM model after the source terms were estimated (and held constant) and compared with data from subsequent TAGA mobile monitoring runs. Additional confirmation was provided with stationary (point) samplers. This confirmation was consistent for the 1,1,2-trichloroethane (not reported here) and the VNCL detected by the TAGA along South Drive. This gave credence to the results of the worst-case impact evaluation.

Maintenance logs from the adjacent excavation site indicated that the carbon adsorption unit did indeed fail and was subsequently replaced. The groundwater treatment facility was later tested and found to emit VOCs during a pump cycle. Repairs were made to the system sealing these releases. TAGA runs made subsequent to the repairs did not reveal plumes as large and as well-defined as those present on the day that the plume was detected on South Drive. No confirmation has been provided on the creek.

Due to the success of the SCT used with the FDM model, it is recommended for use with the TAGA as a means of identifying sources and quantifying emissions at Superfund sites that emit these and similar VOCs.

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3. J.S. Touma, Review and Evaluation of Area Source Dispersion Algorithms for Emission Sources at Superfund Sites, EPA-450/4-89-02, U.S. Environmental Protection Agency, Research Triangle Park, 1989.

4. J. Zhuang, G.M. Zarus, et. al., "An Integrated Information System for Mobile Monitoring," 86th Annual Meeting and Exhibition of the Air and Waste Management Association, A1118, Denver, 1993.

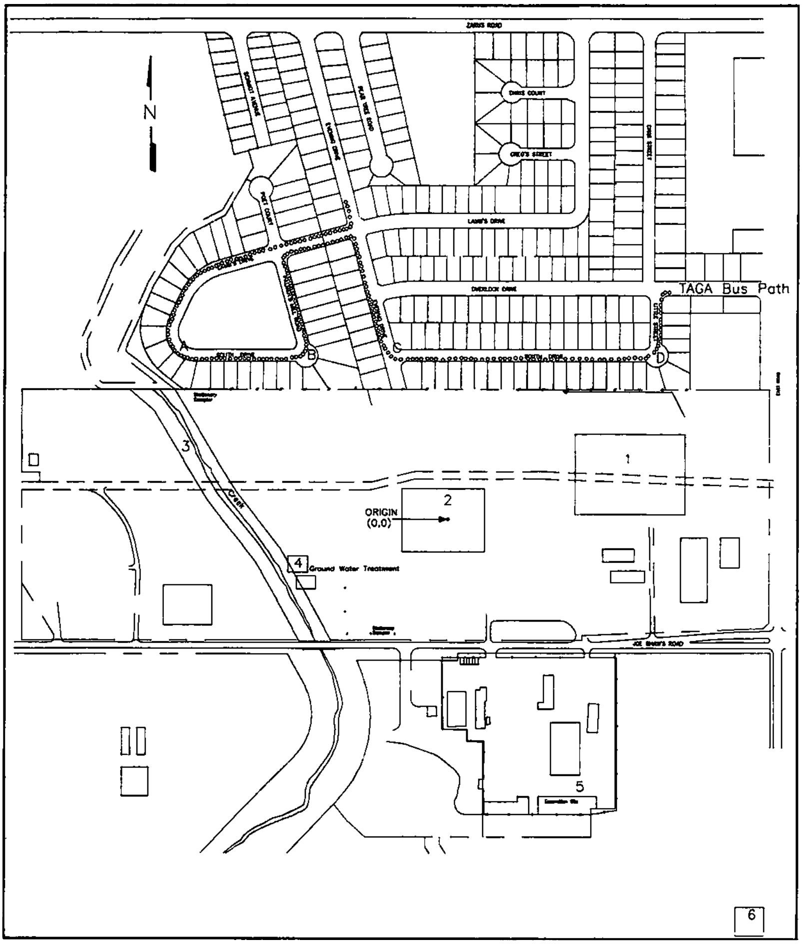

Figure 1. TAGA Mobile Monitoring Path through a Residential Neighborhood.

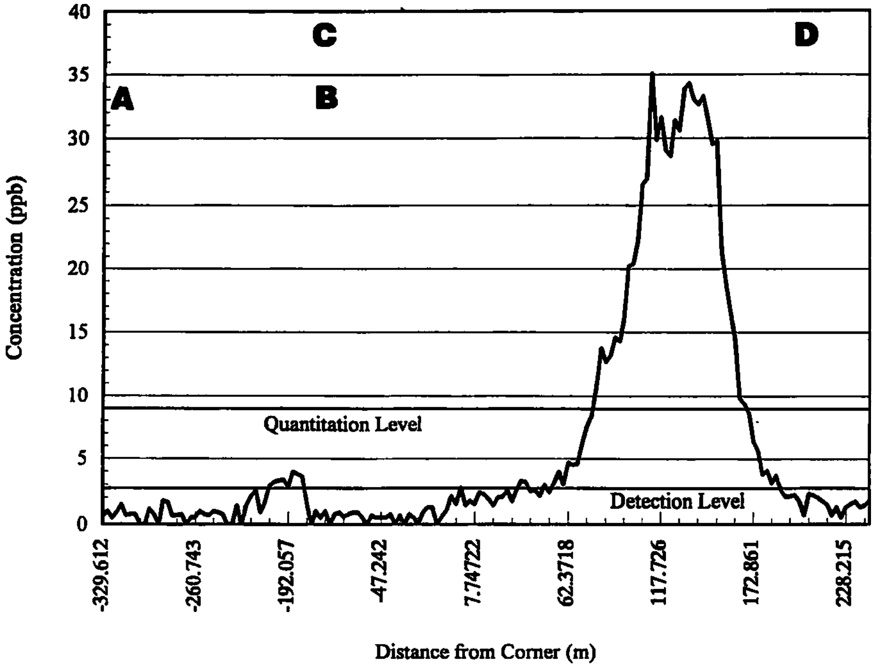

Figure 2. Vinyl Chloride Concentrations Measured on South Drive by the TAGA, with Locations Relative to the Evening Drive-South Drive Intersection.

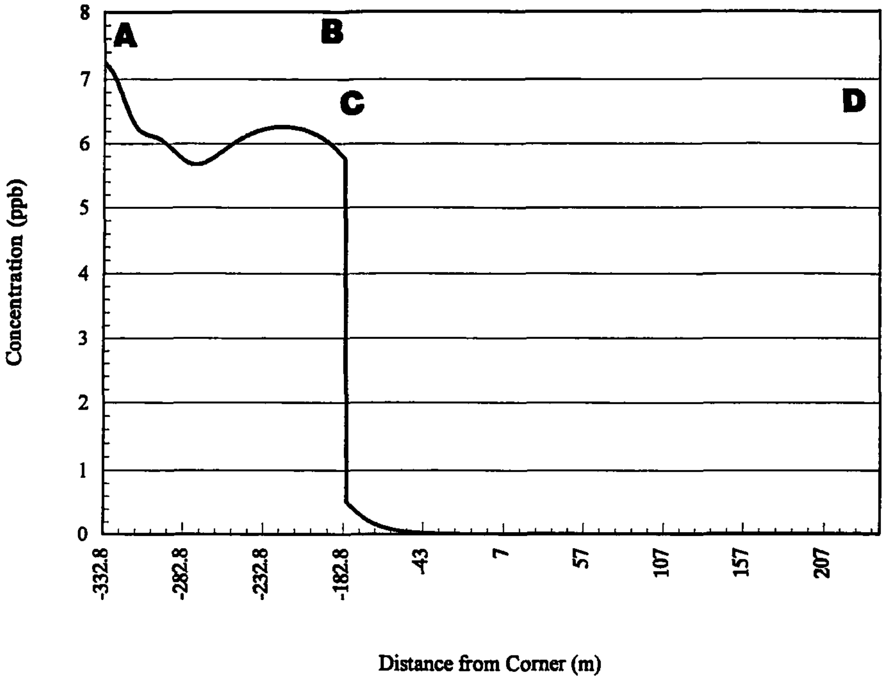

Figure 3. Predicted Vinyl Chloride for South Drive Produced by the Creek, with Locations Relative to the Evening Drive-South Drive Intersection.

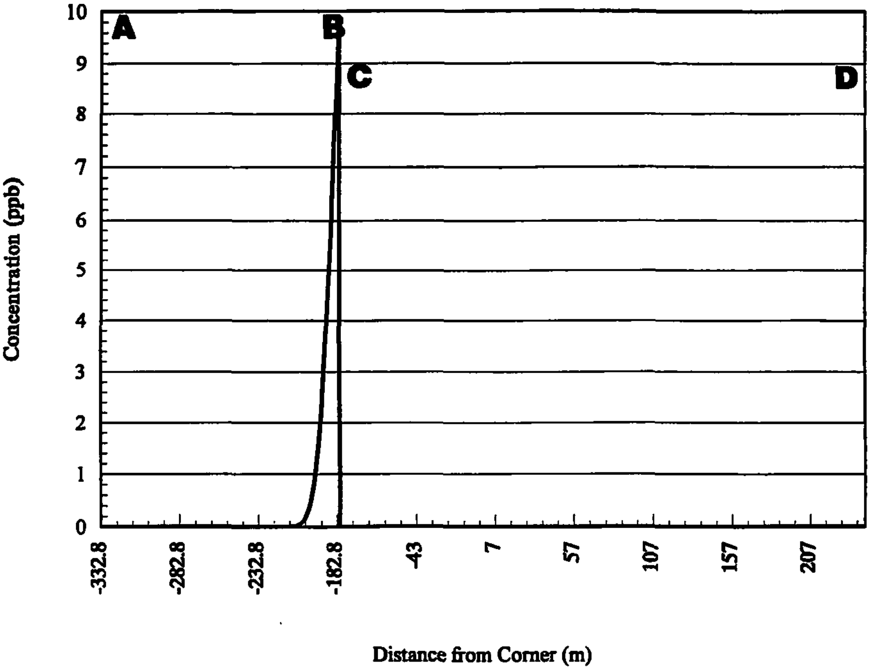

Figure 4. Predicted Vinyl Chloride Concentrations for South Drive Produced by the Water Treatment Facility, with Locations Relative to the Evening Drive-South Drive Intersection.

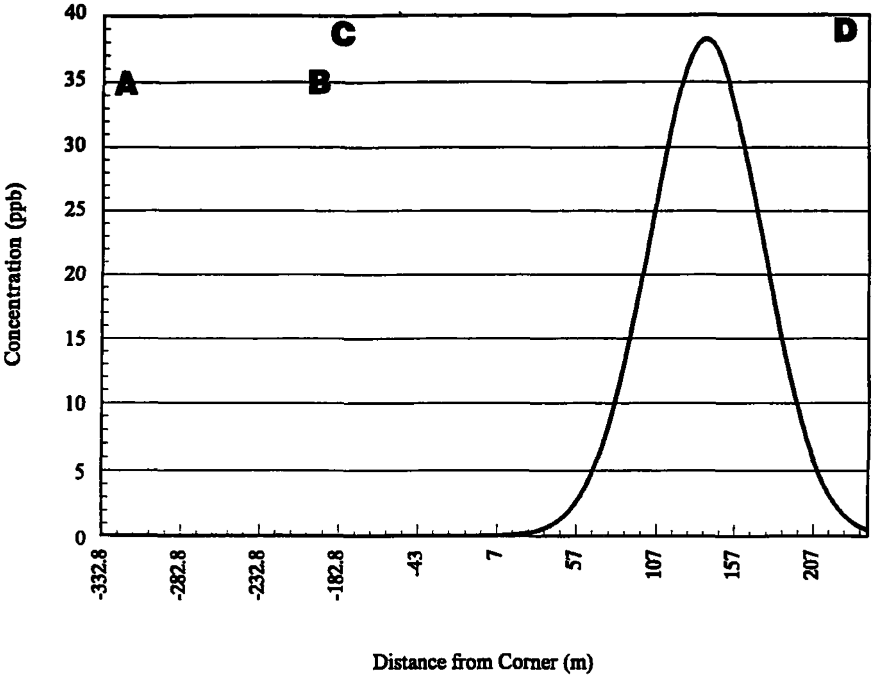

Figure 5. **Predicted Vinyl Chloride Concentrations for South Drive Produced by the Excavation Site, with Locations Relative to the Evening Drive-South Drive Intersection.**

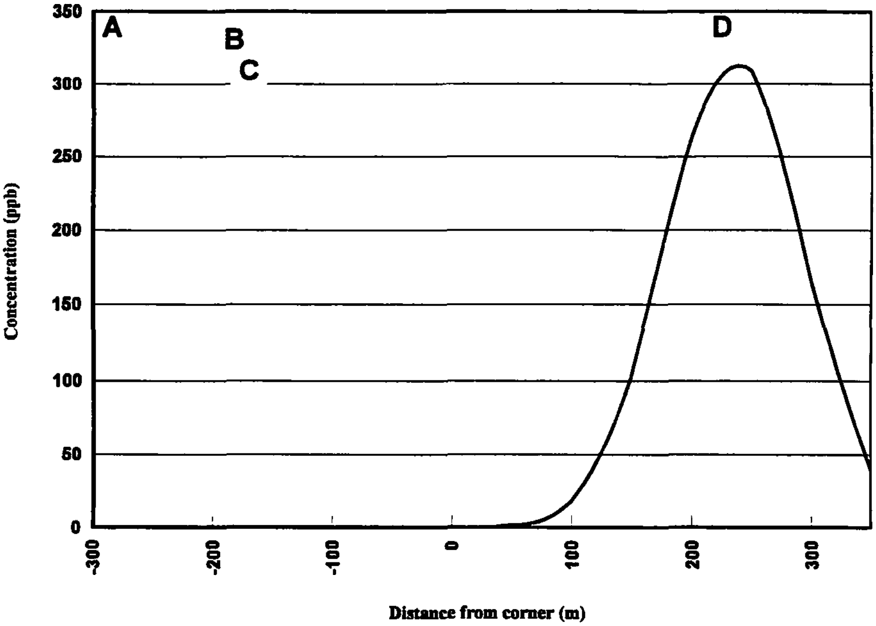

Figure 6. Predicted Vinyl Chloride Concentrations for South Drive Produced by the Petroleum Operations One Half Mile to the South of the Site.

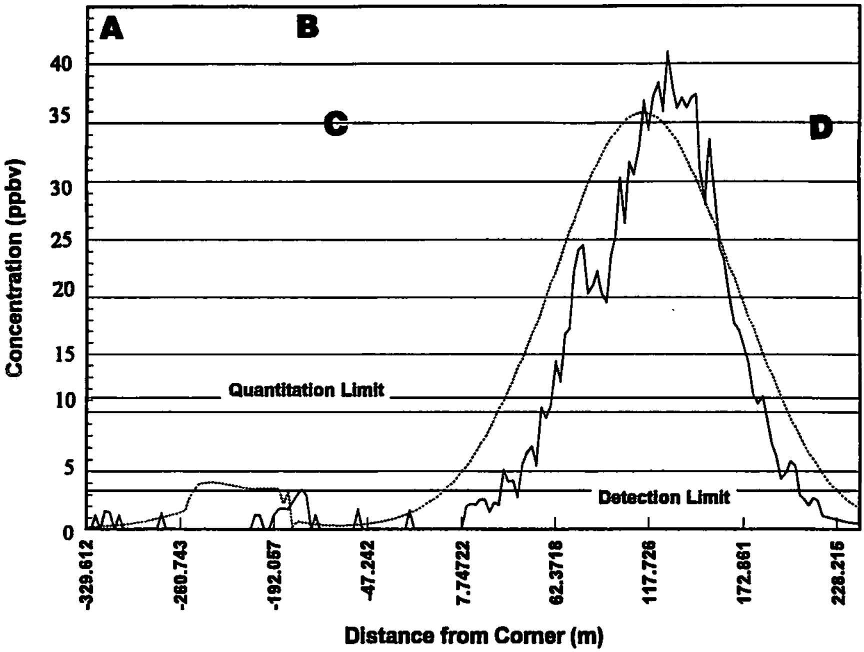

Figure 7. Predicted Versus Measured Concentrations of Vinyl Chloride along South Drive Using Actual Conditions Acquired during a Mobile Monitoring Run, with Locations Relative to the Evening Drive-South Drive Intersection.

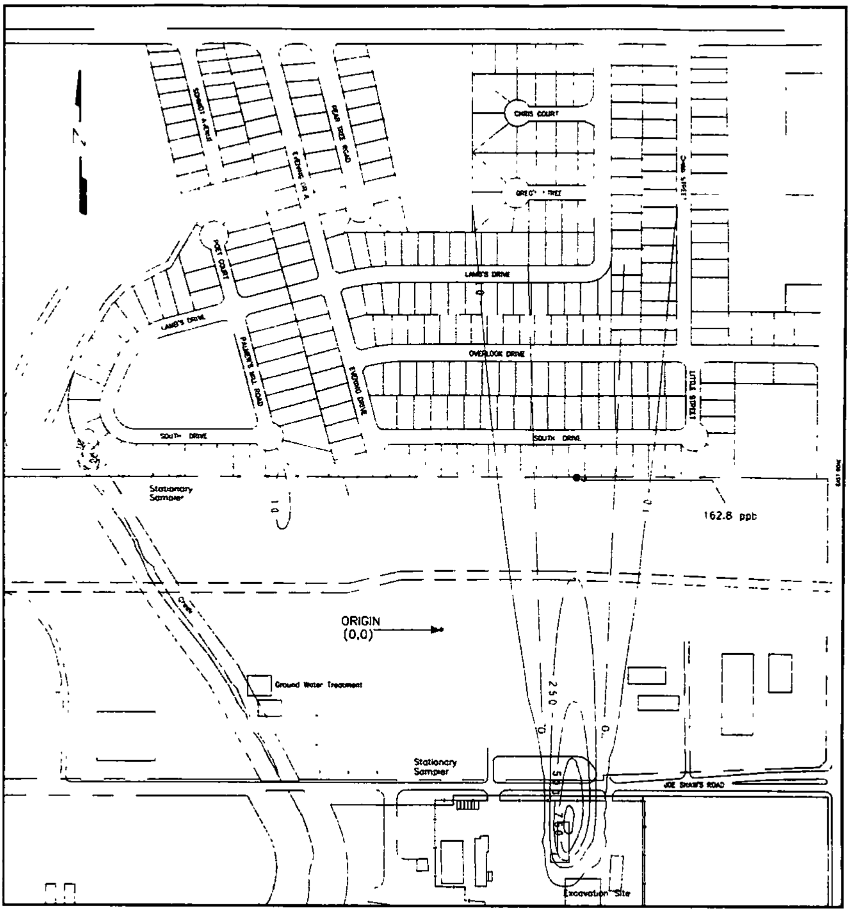

Figure 8. Concentration Contours from the Petroleum Recovery Superfund Site, Assuming the Worst-case Meteorological Conditions that Occurred During the Day of the Release.

A High-Tech Solution for Evaluating the Impact of Volatile Air Emissions from Petroleum Recovery and Refining Sites: A Superfund Case Study

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ABSTRACT

The use of several technologies in the field has lead to the development of a strategy for evaluating the presence and migration of volatile air emissions from petroleum recovery and refining facilities. A mix of technologies provided successful evaluation of volatile organic compounds (VOCs) in the air pathway. Evaluation of these technologies is provided for a case study. Recommendations of the approach established through this study are generalized for similar studies.

For the study in mention, the U.S. Environmental Protection Agency's Environmental Response Team (U.S. EPA/ERT) was requested by U.S. EPA Region VI to verify or refute the presence of volatile organic air emissions at a petroleum recovery hazardous waste (PRHW) site. Several environmental protection and public health organizations inevitably became involved with the evaluation, including: Region VI of the U.S. EPA, the Agency for Toxic Substances and Disease Registry (ATSDR), and the U.S. EPA/ERT. Each group brought a unique expertise which helped to identify the sources, to determine their emission rates, to evaluate the impact, and to monitor the ambient concentrations during remedial activities. The results of the study allowed the groups to establish some generalizations about the technologies and to reduce the overload of information received during site evaluation using several technologies. This report describes several of the successful technologies used at the PRHW site and some of the results obtained.

INTRODUCTION

Several technologies were employed to estimate the air emissions from a PRHW site and evaluate their impact on a surrounding neighborhood.[1] Figure 1 is a site map—indicating the proximity of the adjacent neighborhood. Each singular technology provided its own insight into understanding the nature of the emissions, their origins, and their fate. However, the abundance of data received was sometimes overwhelming.[2] Therefore, the technologies were each evaluated for their efficacy in estimating the impact of volatile air emissions measured from petroleum refining and recovery sites in general. The strategy outlined in Figure 2 is to:

1) Provide fenceline monitoring.
2) Provide neighborhood monitoring.
3) Identify and quantify sources.
4) Predict exposure.

A description of the technologies involved to meet these ends is reviewed in the following sections.

A mobile mass spectrometer/mass spectrometer (MS/MS) was found to be successful with quantifying the concentrations of VOCs at a single location over time, at several locations while in transit, and of discrete samples collected in bags. A portable gas chromatograph (GC) capillary column provided a quick response to facilitate the analysis of several soil gas samples in a short time frame. An argon ionization detector (AID) GC was used to provide confirmation of the vinyl chloride concentrations detected by the MS/MS analysis of discrete air samples. It provided a precise estimation of the quantities but required a longer time than the capillary column GC to conduct the analysis.

Flame ionization detector (FID) GCs were found to be sufficient for perimeter monitoring. If placed correctly, these GCs provide continuous monitoring of ambient concentrations of VOCs both upwind and downwind of the suspected sources.

Surface flux emissions can be collected using an isolation flux chamber. This sampling procedure collects emissions from the surface of an impoundment with minimal interference with the natural flux that occurs across the surface. Air dispersion modeling analysis was found to be a successful tool to fill in the gaps when samples were not available. Models can help evaluate the impact of the emissions on neighborhoods or to ascertain the location and the rate of the emissions associated with operations on or nearby the site.

Compounds that have been successfully evaluated at petroleum recovery and refining sites in particular include:

benzene bis(2-chloroethyl)ether 1,2-dichloroethene
toluene styrene methylene chloride
1,1,2-trichloroethane vinyl chloride

Other airborne compounds that have been successfully evaluated in the field include:

trichloroethylene trichloroethane tetrachloroethane
methylene chloride toluene 1,3-dichloropropane

Several other technologies were employed on the PRHW site. An evaluation of the data received from this site, suggested that the integration of several technologies can be used to successfully evaluate the long-term and short-term air impact of VOC emissions typical of petroleum recovery and refining sites on the ambient air quality in and around the region surrounding the sites.

BACKGROUND

Major industrial operations ensued on this PRHW site prior to being ranked on the National Priorities List (NPL). These operations included the distilling of petroleum feedstock to produce fuels, recovery of petrochemicals from styrene tars, and the recovery of other chemicals from vinyl chloride still bottoms. Storage pits were constructed to support the styrene tar processing operations. Fifteen pits were constructed and eventually closed. Closure was obtained by removing any of the free liquids, mixing in soil and calcined clay with the residues, and, finally, covering the pits with clean soil. When migration of compounds through the air pathway became a concern, the U.S. EPA Region VI, ATSDR, U.S. EPA/ERT, and Weston/REAC teamed to produce a comprehensive analysis of the air emissions. Several tasks were initiated using various technologies. The technologies employed successfully met the objectives discussed in this report. An integrated approach to evaluate volatile emissions from petroleum recovery and refining sites was then utilized. The integrated approach utilized the following steps:

1) Preliminary modeling to evaluate the necessary detection levels for analysis.
2) Perimeter monitoring to ensure the safety of the residents surrounding the site and to warn the operators of any elevated levels that may warrant a shut-down.
3) Random sampling of suspected long-term emission sources.
4) Judgmental sampling (spot-checking) of short-term emission sources.
5) Mobile monitoring of the neighborhood to ensure residential safety, evaluate off-site migration, and investigate possible off-site sources.

6) Confirmatory analysis using portable high-tech instrumentation to validate the presence of compounds detected by the routinely used instrumentation.
7) Modeling of short- and long-term emissions to provide concentration (and potential exposure) data at locations not routinely sampled or during periods in which sampling cannot be performed.

MS/MS MOBILE MONITORING AND SAMPLE ANALYSIS

The Sciex^{TM} Trace Atmospheric Gas Analyzer 6000E MS/MS (TAGA) is a real-time, direct-air sampling, laboratory instrument mounted in a vehicle. The TAGA has demonstrated the following analytical capabilities:

1) Direct-air sampling and analysis of VOCs in the ambient air at the part-per-billion by volume (ppbv) level while mobile monitoring along roads.
2) Direct-air sampling and analysis of VOCs of the indoor air of houses and buildings to determine whether contaminants are migrating from an adjacent site into the structures.
3) Rapid analysis of gas samples collected in bags in order to support extent of contamination studies conducted at or near sources of VOCs.
4) Direct-air sampling and analysis of VOCs in the ambient air monitored in industrial settings.

The general theory of the TAGA utilizes the technique of triple quadrupole MS/MS to differentiate and quantitate compounds. The analysis procedure involves multiple sequential steps. The initial step in the MS/MS process involves simultaneous chemical ionization of the compounds present in a sample of ambient air to allow ions (parent ions) to be formed. The parent ions with different mass-to-charge (m/z) ratios are separated by the first quadrupole (the first MS of the MS/MS system). The parent ions selected in the first quadrupole are accelerated through a cloud of uncharged argon atoms. A portion of the parent ions entering the second quadrupole fragment as they collide with the argon atoms forming daughter ions. The daughter ions are separated according to their m/z ratios by the third quadrupole (the second MS of the MS/MS system) and then counted by an electron multiplier.[3]

The TAGA performs mobile, ambient air monitoring using a direct-air sampling system along roads adjacent to suspected sources to detect emissions originating from these locations. Outside ambient air is continuously drawn from a port in the wall of the TAGA bus, through a glass splitter, and into the ionization source through a heated transfer line.

As the TAGA mobile monitoring proceeds, the operator presses the letter keys (flags) sequentially to denote events or locations during the monitoring. One set of measurements for each ion monitored by the TAGA is called a sequence. An example of a mobile monitoring sequence file for the PRS site is provided in Figure 3. The figure reveals vinyl chloride concentrations (ordinate) along the road adjacent to the site. Flags A through D are also labeled in the figure and indicate locations of landmarks on the TAGA's sampling route. They correspond with the locations marked in Figure 1. A Global Positioning System (GPS) was used in tandem with a Geographical Information System (GIS) to accurately depict the TAGA's location. The specifics of this system are discussed later.

The TAGA performs stationary, ambient air monitoring with or without a Teflon hose. When the Teflon hose is not in use, the monitoring is conducted identically to the mobile monitoring except that the bus is not in motion. With the Teflon hose, one end is connected to the sampling port on the TAGA bus and the distal end is moved to an area of concern and the sample is pulled into the TAGA. This technique allowed for the real-time analysis of the ambient air in areas on the site (within 300 ft of the TAGA) that were not physically accessible to the bus for mobile monitoring.

The TAGA analyzes bag samples by directly connecting the sample bag to the heated transfer line of the TAGA and allowing the sample to be drawn directly from the source. This technique allows for the analysis of discreet samples from areas that are not physically accessible to the bus or the Teflon hose and allows for several ambient samples to be collected simultaneously. The only drawback experienced with the TAGA was the inability to distinguish 1,2-dichloroethane from vinyl chloride. Vinyl chloride and 1,2-dichloroethane can form similar parent ions in the first quadrupole and are both identified as vinyl chloride. This problem was resolved through confirmatory analysis.

GC/FID FENCELINE MONITORING

Several GCs were used within the Air Quality Monitoring Stations (AQMSs) located along the periphery of the site. The AQMSs were designed to provide real-time air quality monitoring data. They are comprised of a monitoring system which includes a MINICAM™ GC equipped with an FID and connected to an ambient air sampling system, that is manifolded to a span gas for daily quality assurance checks. Each GC is equipped with a three-bed sorption tube for concentration of the ambient air analytes prior to thermal injection onto the GC column. A GC analysis, based on an 8-minute sample aliquot, is performed every 13 minutes.

Data from each analysis is printed out at each station, archived on a floppy disk, and transmitted to the site control room and the Regional command post station. All of the AQMS units were calibrated from standard gas blends that contain the target compounds. These GCs provided a warning system that alerted the site manager when elevated levels of compounds were detected in the ambient air that would cause an exceedence in the 12- or 24-hour thresholds. Due to co-elution of certain compounds — an inability to delineate two similar responding compounds — the system often created false positive detections for vinyl chloride. However, the warning system reduced the mobilization of the TAGA. A sample printout of a reduced AQMS data file is provided in Figure 4.

MICROCHIP GC DATA VALIDATION

The Microsensor Technology, Inc. Model P200 is a dual capillary column, dual microchip thermal conductivity detector (μTCDs) field portable GC. An internal sampling pump pulls a vapor phase sample through a fixed sampling loop.

Once injected into the GC system, the sample components are separated by the dual capillary analytical columns and detected by the dual μTCDs. This system allows the use of "correlation chromatography" techniques. In a sense, the dual detection and identification is similar to having both an analytical column and confirmation column present in one unit. This increases the level of confidence in the identification of a particular compound.

A software package has been developed using correlation chromatography to enhance identification routines.[4] As a result, compounds present in the library but not present in available calibration standards can be tentatively identified based on library values alone. This is a useful function when specific calibration standards are not readily available or where the exact composition of site contaminants are not well defined.[5] Only VOCs in the vapor phase can be injected into the P200 GC.

The concentrator can be used to concentrate air samples prior to analysis. Detection limits for air samples using a 100-fold concentration factor range from 20-100 ppb. This device provided quick analysis of grab samples on the PRS site when used to confirm the TAGA analysis, but had some difficulty when only trace amounts of VOCs were present.

GC/AID DATA VALIDATION

A Sentex™ Sentograph GC/AID was used to confirm the presence of vinyl chloride in bag and ambient air samples analyzed by the AQMS and the TAGA. This GC/AID has an internal sample concentrator. Both the pump and the concentrator trap are controlled and operated by the computer. The GC/AID provides good separation between the peaks associated with vinyl chloride and 1,2-dichloroethane. This separation ensures identification of the vinyl chloride. The distinction is important because 1,2-dichloroethane often forms vinyl chloride in the ionization chamber within an MS/MS. The computer operated concentrator coupled with the inclusion of a packed column allows this GC/AID to successfully quantify vinyl chloride in the bag and ambient air samples. Resolution of vinyl chloride via this GC/AID confirms its presence in the samples analyzed by the MS/MS. Another advantage of this GC/AID is that it is not subject to the same co-elution that is experienced with the GC/FIDs. This provides a method to check the GC/FIDs during operation. Specific information on GC/AID operation may be found in Kaelin (1991).[6]

FLUX CHAMBER SAMPLING

An isolation flux sampler is a stainless steel dome that is placed on a surface to directly measure the emissions which pass through it. It offers several advantages to other means of emission rate determination such as: 1) directly measuring the emissions by allowing only those emissions which pass through a certain known area to be captured; 2) a design that provides sufficient mixing so that the sample collected is indicative of the emissions; 3) an evacuated chamber surrounding the interior cavity which insulates the inner cavity and minimizes solar heating; 4) a construction of stainless steel to eliminate any photochemical oxidation that may occur; 5) a purging with ultra-pure air to maintain an even mixture of clean air/emitted gas; and 6) containing a valve to allow any excess air to escape to ensure against pressurization.

Proper random sampling of the suspected source ensures that the actual average source emissions are represented by the average flux sample emission rates.[7] The determination of the random sample location for an area source involves three steps: 1) the area source is divided into cells (or grids); 2) the number of samples is calculated for the source (where the number of samples is proportional to the area of the source); and 3) the sample cells are randomly selected. The samples are taken somewhere near the center of each grid. These steps are illustrated in Figure 5.

The flux rate of contaminants from the ground are calculated using the concentrations determined in the effluent gas of the flux chamber. The concentration of the constituents in the effluent gas is determined by analysis using one of the analytical methods described above. In an effort to receive the analytical results in the field and to ensure the reliability of the data, several methods were used: the TAGA MS/MS was the primary instrument used to quantify the target compounds in the samples; the Sentex™ GC/AID was used to confirm the presence of vinyl chloride in the samples; and some samples were collected in SUMMA™ evacuated canisters for laboratory confirmation.

Flux chamber sampling was performed on the PRS site to determine the average emission rates of the buried waste lagoons along with the variability of those emissions over time and in response to weather conditions. The surface flux emissions over six days for one of the lagoons is reported in Figure 6. Flux measurements collected from all of the lagoons revealed spacial variability similar to that shown in the figure. The abscissa denotes the sample location. Due to these spacial and temporal variabilities a 95 percent upper confidence level (UCL) of the concentrations from each lagoon was used to calculate emission rates; thereby producing (estimated) emission rates that were conservative enough to ensure that exposures were not underestimated.

GPS/GIS

The tandem use of A Global Positioning System (GPS) and a Global Information System (GIS) enhances a scientists ability to evaluate data collected at a variety of locations at different times.[8] Such a system employed during mobile monitoring, provides the opportunity to reanimate the sampling run with validated data after the rigors of data collection is over. At the PRHW site, a Trimble™ GIS Surveyor GPS was used to determine the location of the TAGA while in transit. Two GPS receivers are required to accurately calculate position because of selective availability and atmospheric effects. The manufacturers suggested accuracy of this system is 1 to 2 cm. A 16-channel base station was erected at the command post on the site. The location of the antenna was surveyed in from known control points on the site. The base station received transmissions from all available satellites above 10° (from the horizon) at one-second intervals. A twin system was placed on the TAGA bus, also recording transmissions once-per-second. After the sampling runs were completed each day, the data from both GPS units were downloaded to a lap top personal computer and processed. The processing calculates the TAGA's and the base station's positions by trigonometry, giving weight to those satellites with a better signal. The processor then corrects the positions of the TAGA by comparing the TAGA's location, calculated at any time, with the position calculated by the stationary receiver (base station) at the same time.

The final values were then imported into a Map Info™ GIS and overlaid onto a map of the site and the local neighborhood. A portion of a mobile monitoring run is provided in Figure 1. The path marked along the map (along South Drive) corresponds to the concentrations analyzed by the TAGA and reported in Figure 3. The accuracy of the GPS system was not determined because other methods of surveying the TAGA were not performed. However, the GPS locations were consistent (varied less than 1 meter) with each sequential mobile sampling run. Flags were keyed at specific locations along the TAGA run and stored in the TAGA database and corresponded to specific times. These times matched the times (well) in the location files recorded by the GPS. The times documented in the TAGA flagged files and the GPS files suggested a variance of less than 2 meters.

These values assisted with locating positions of potential sources using air dispersion modeling.

A sample output of the GPS from an 8-hour sampling run is provided in Figure 7. The dots represent GPS locations received every second. Different scales are provided in the figure to reveal the relative accuracies of the successive runs. Notice the inaccuracies between, not the successive runs, but, rather, the runs and the map. This is due to conversion errors associated with importing a digitized map using three control points. Due to the inaccuracies within the maps, the GPS was also used to redraw the portions of the map where more precision was required. Also notice the wider spaces between some of the dots. This indicates times when the TAGA bus is returning (traveling at a higher speed than when sampling) for post calibration after a run is completed. The image to the left (zoomed in) indicates stationary sampling near a subsurface impoundment. This cluster of dots varies less than a few feet on average. Some of these dots are spread out because the bus had to turn around to resume its mobile sampling.

AIR DISPERSION MODELING

Air modeling was used throughout the life of this project. Preliminary modeling was used to estimate the levels of contaminants in the ambient air. This information was used to determine the levels of personal protection required to operate on the site and to determine the proper instrumentation and media with which to collect and analyze the ambient air.

The Fugitive Dust Model (FDM), operated in the gaseous dispersion mode, was utilized at this site for numerous reasons, including: the ability to simulate rectangular area sources of varying length and width dimensions; the ability to calculate emissions from irregularly oriented line sources; the ability to calculate ambient air concentrations for receptors located directly above the source; and the ability to calculate concentrations using large meteorological data sets provided in several formats. The FDM uses an integrated line-source algorithm recommended [9] to predict emissions from area sources located in close proximity to receptors.

After samples were collected and analyzed, the FDM was used to estimate long-term exposures. The information obtained from the site investigation and the sample analysis was used in conjunction with 5 years of meteorological data to calculate long-term average and worst-case hourly concentrations at each of the receptors. The data were then used to calculate risks. The long-term average concentrations of vinyl chloride from the PRHW site are provided in Figure 8; this implies that much of the air pathway exposure potential remains on site, assuming that the emissions from the site do not exceed the 95 percent UCL (ie: the site conditions remain stable/intense activity does not ensue).

The Chemical Mass Balance (CMB7) model was used to resolve the contribution from each of the sources on the ambient air. The CMB7 model uses the chemical composition of an ambient air sample to estimate the contribution of different sources to the measured pollutant concentrations.[10]

A new method using the FDM was developed for locating and quantifying emission sources.[11] The method uses an iterative technique which successively corrects the emission rates of all the suspected sources and matches the predicted downwind concentrations with those collected by a monitoring device. Those sources that produce plumes which do not match the detected concentrations are eliminated. The method uses principles similar to the inversion algorithm[12] in that the downwind concentrations are used to derive a source term in the Gaussian dispersion equation. The difference between the new method and traditional receptor models is that receptor models use known source terms to discern the responsible source while this technique uses meteorology and source/receptor geometry to locate the source and ascertain its release rate.

This technique was found to work well using the mobile monitoring data collected by the TAGA. The concentrations collected along the road to the north of the PRHW site, plotted in Figure 3, indicated two plumes present in a neighborhood — the larger to the right of flag D and the smaller to the left of flag B. After several iterative[9] FDM model runs, three sources were identified and confirmed. The results of the model runs for the three suspected sources on receptors located along the road that the TAGA conducted sampling are plotted in Figure 9. These results were confirmed via a simultaneous monitoring run by the TAGA, also plotted in the figure. The results helped to find equipment that failed or operations in need of repair.

RESULTS

Detailed site investigations have lead to the development of a network of technologies that provides an excellent source of information to evaluate air pathway transport and fate of emissions indicative of petroleum recovery and refining facilities. The preceding technologies were used successfully to evaluate the impact at the PRHW site. The inclusion of several technologies allowed for direct measurement of ambient or source emissions for the use in estimation of short-term and long-term impacts, at the perimeter of the site to allow for quick response to releases, and off-site at impacted populations to ensure that receptors were not being exposed to unacceptable levels of VOCs. Implementation of a mix of technologies resulted in identifying a significant source of on-site emissions which were reduced using engineering controls;

quick identification of a failed air pollution control device which resulted in an immediate site shut-down; and data at receptor locations that provided residents with reliable information about the air quality in their neighborhood.

In conclusion, the incorporation of the techniques mentioned are recommended for use on petroleum recovery and refining sites. The TAGA provides a robust data set for identifying plumes and is a quick and efficient tool for analyzing grab samples containing trace amounts of VOCs. The Sentex™ GC/AID and Microchip GC are excellent equipment for field confirmation for analytically difficult compounds. Data collected and analyzed by the various techniques can be related using models. Models can also estimate exposures in regions where no sampling was performed, thereby leading to a full evaluation of the air pathway. Geo-coding the site, the samples, and the modeling results allows for integration via a GIS system, allowing scientists to reanimate (or re-observe) the sampling to uncover locations of possible sources and to compare data collected via different methods.

The mention of trade names does not necessarily imply endorsement.

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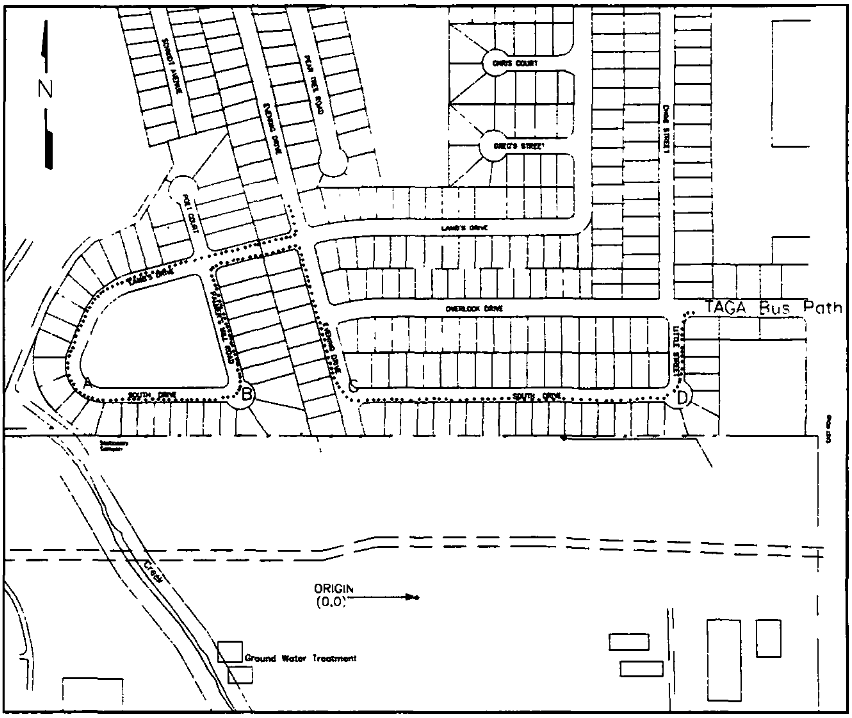

Figure 1. The Petroleum Recovery Superfund Site Map and Adjacent Residential Neighborhood.

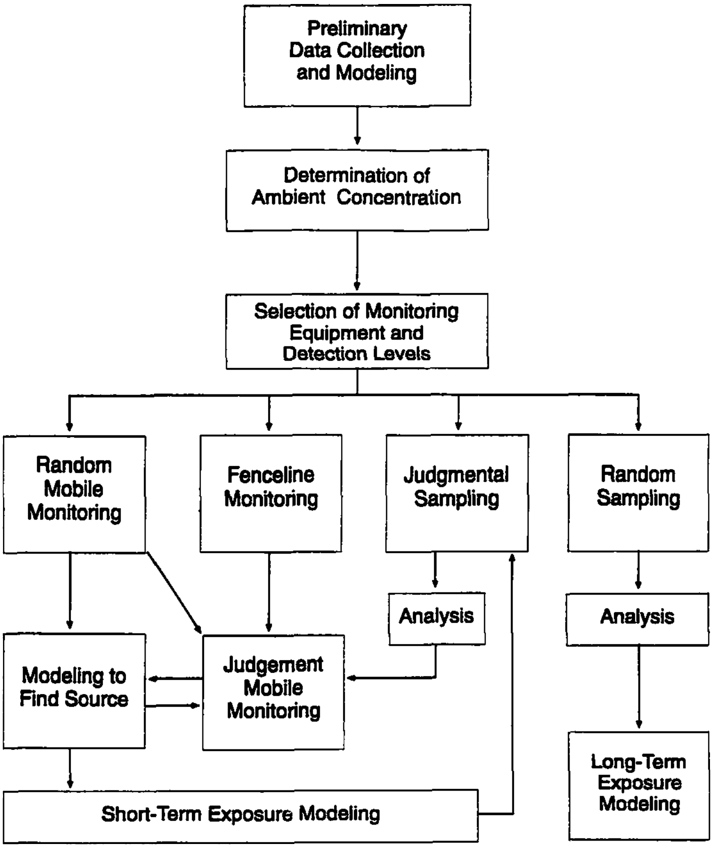

Figure 2. Impact Assessment Flow Diagram (using High-Tech Monitoring Instrumentation).

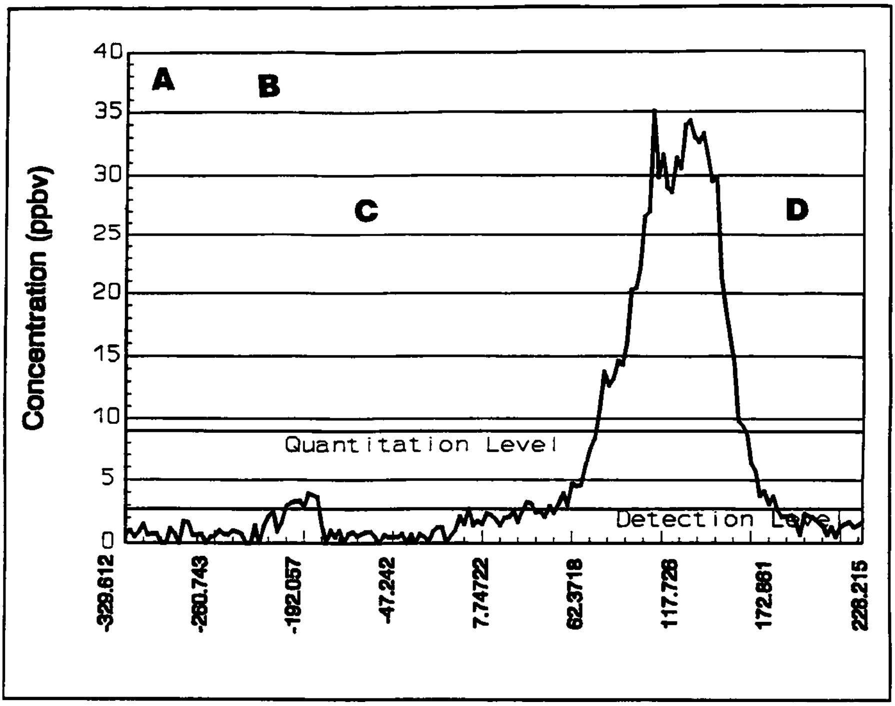

Figure 3. Vinyl Chloride Concentrations Measured on South Drive by the TAGA.

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                AQMS Ethylene Dichloride DATA (RAW) - BRIO SUPERFUND SITE
                                   15-MINUTE AVERAGES
 DATE   TIME     ED-1      ED-2      ED-3      ED-4      ED-5      ED-6      ED-7
YYMMDD   CST      ppb       ppb       ppb       ppb       ppb       ppb       ppb
------------------------------------------------------------------------------------
950305 1115       0         0         0         0         1         1         0
950305 1130       0         0         0         0         0         0         0
950305 1145       0         0         0         0         0         0         0
950305 1160       0         0         0         0         1        13         0
950305 1215       0         0         0         0         0x        0         0
950305 1230       0         0         0         0         0         8         0
950305 1245       0         0         0         0         0        22         0
950305 1260       0         0z        0         0z        0z        0         0   950305
950305 1330       0m        0m        0m        0m        0m        0m        0m
950305 1345       0m        0m        0m        0m        0m        0m        0m
950305 1360       0m        0m        0m        0m        0m        0m        0m
950305 1415       0m        0m        0m        0m        0m        0m        0m
950305 1430       0m        0m        0m        0m        0m        0m        0m
950305 1445       0m        0m        0m        0m        0m        0m        0m
950305 1460       0m        0m        0m        0m        0m        0m        0m
950305 1515       0m        0m        0m        0m        0m        0m        0m
950305 1530       0m        0m        0m        0m        0m        0m        0m
950305 1545       0m        0m        0m        0m        0m        0m        0m
950305 1560       0m        0m        0m        0m        0m        0m        0m
950305 1615       0m        0m        0m        0m        0m        0m        0m
950305 1630       0m        0m        0m        0m        0m        0m        0m
950305 1645       0m        0m        0m        0m        0m        0m        0m
950305 1660       0x        0         0         0         1         0x        0
950305 1715       0         0         0         0         1         2a        0
950305 1730       0         0         0         0         0         0x        0
950305 1745       0         0         0         0        14         0         2
950305 1760       0         0         0         0        32         0       345a
950305 1815       0         0         0         0        28a        0       317a
950305 1830       0         0         0         0        14a        0        20a
950305 1845       0         0         0         0         2a        0         2a
950305 1860       0         0         0         0         3         0        17a
950305 1915       0         9       247a      312a        2       226         1
950305 1930       3       217a       21a       83a        1        36         0
950305 1945       3       240a      378b       72a        6        37a       13
950305 1960       1         4a      158b      423b        2         8a        0
950305 2015       0       122b        8b       13b        1         6a        0
950305 2030       0         2b      119b        4b        1         1         0
950305 2045       0         1b        4b        2b        1         0         0
950305 2060       0         0b        6b        1b        1         0         0
950305 2115       0         1b        4b        1b        1         0         0
950305 2130       0         0b        1b        1b        1         0         0
950305 2145       0         0b        2b        1b        1         0         0
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Figure 4. Sample Output from the AQMS Stations (located at the Fenceline).

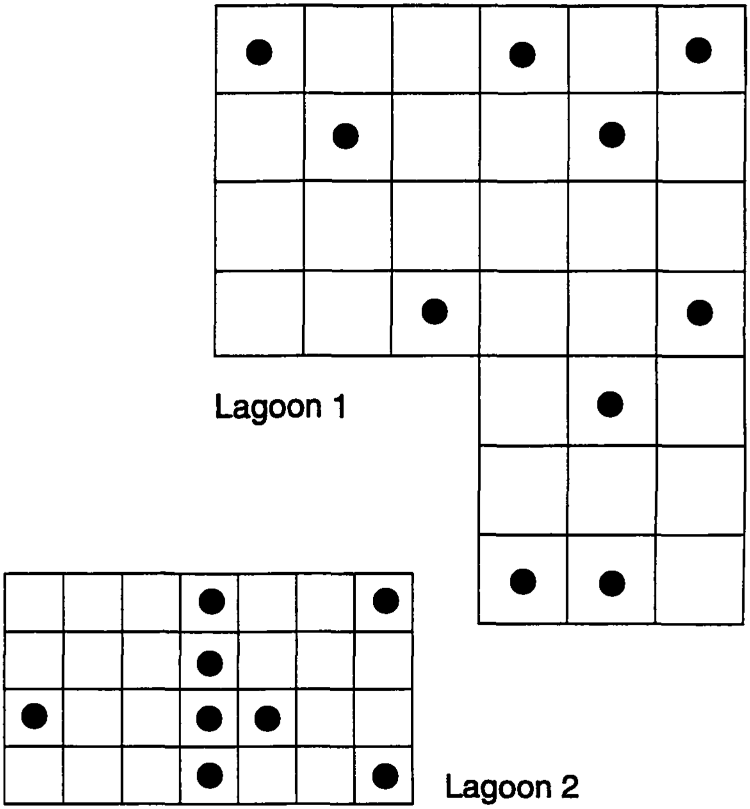

Figure 5. Random Locations for Flux Emission Sampling.

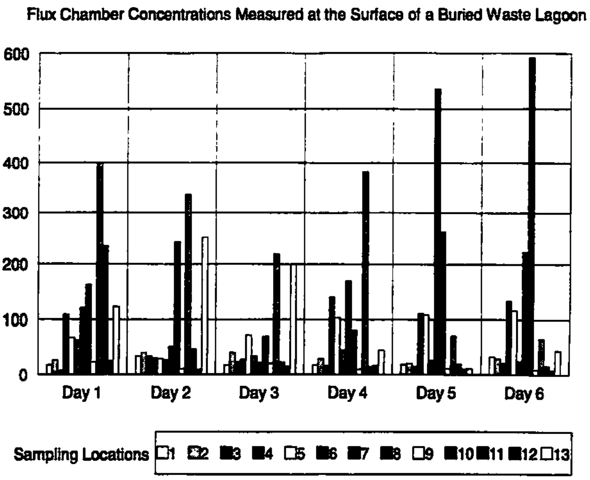

Figure 6. Flux Chamber Concentrations Measured at the Surface of a Buried Waste Lagoon (Concentrations Presented in Parts Per Billion by Volume [ppbv]).

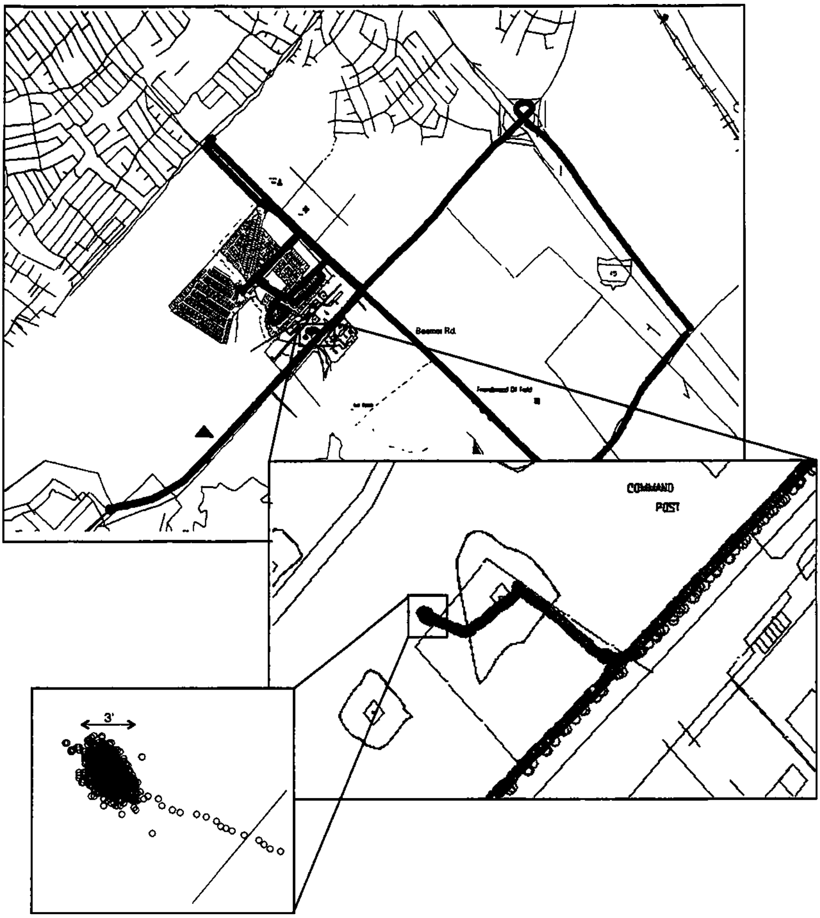

Figure 7. GPS Determined Locations of the TAGA Bus During Sampling Runs (at Different Levels of Resolution).

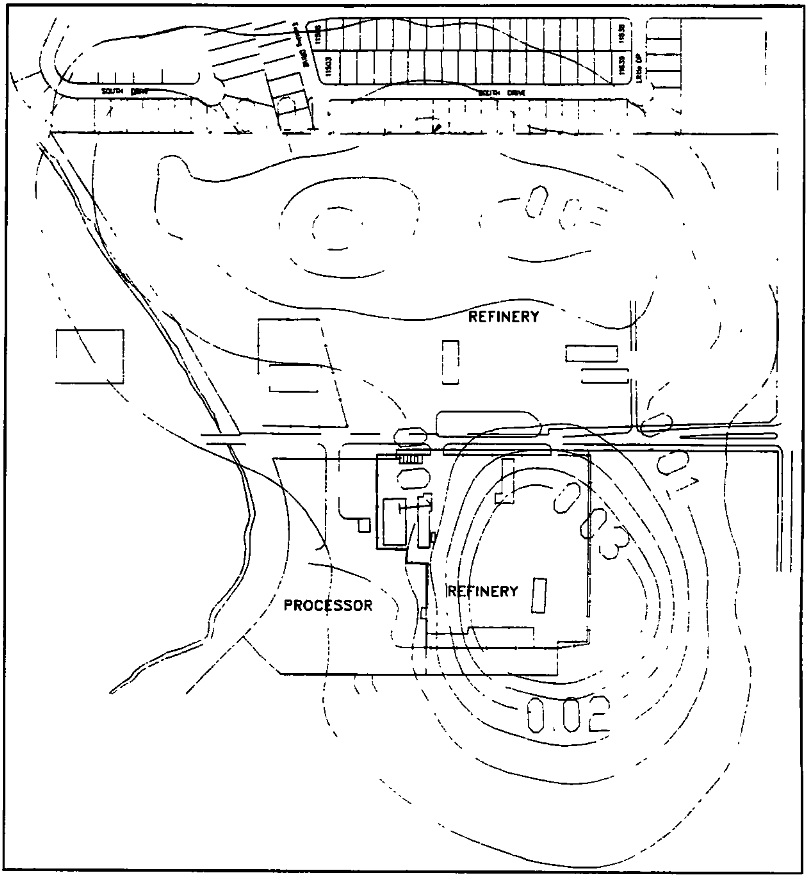

Figure 8. Long-Term Air Pathway Vinyl Chloride Exposure Concentrations (Isopleths Presented in Micrograms per Cubic Meter [$\mu g/m^3$]).

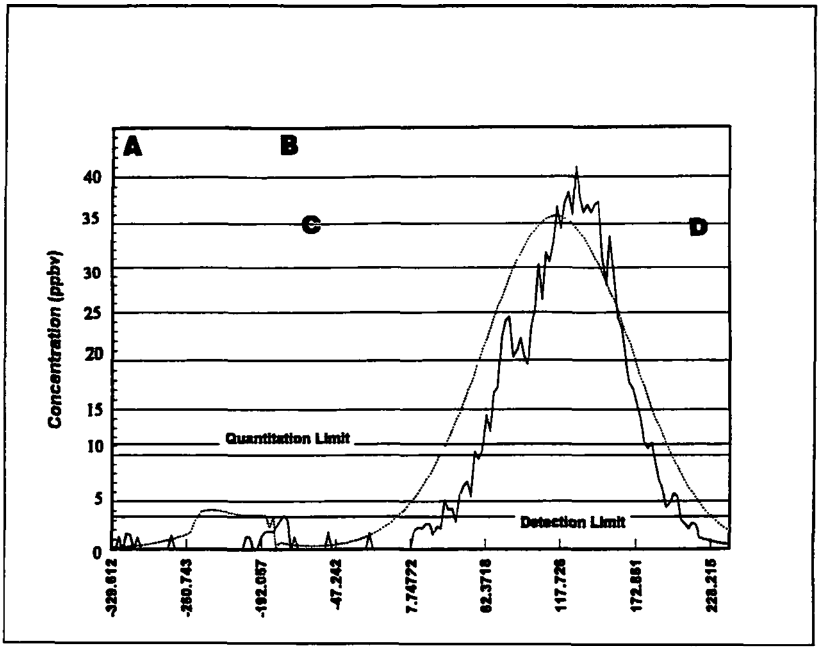

Figure 9. Predicted Versus Measured Concentrations of Vinyl Chloride along South Drive Using Actual Conditions Acquired during a Mobile Monitoring Run, with Locations Relative to the Evening Drive-South Drive Intersection.

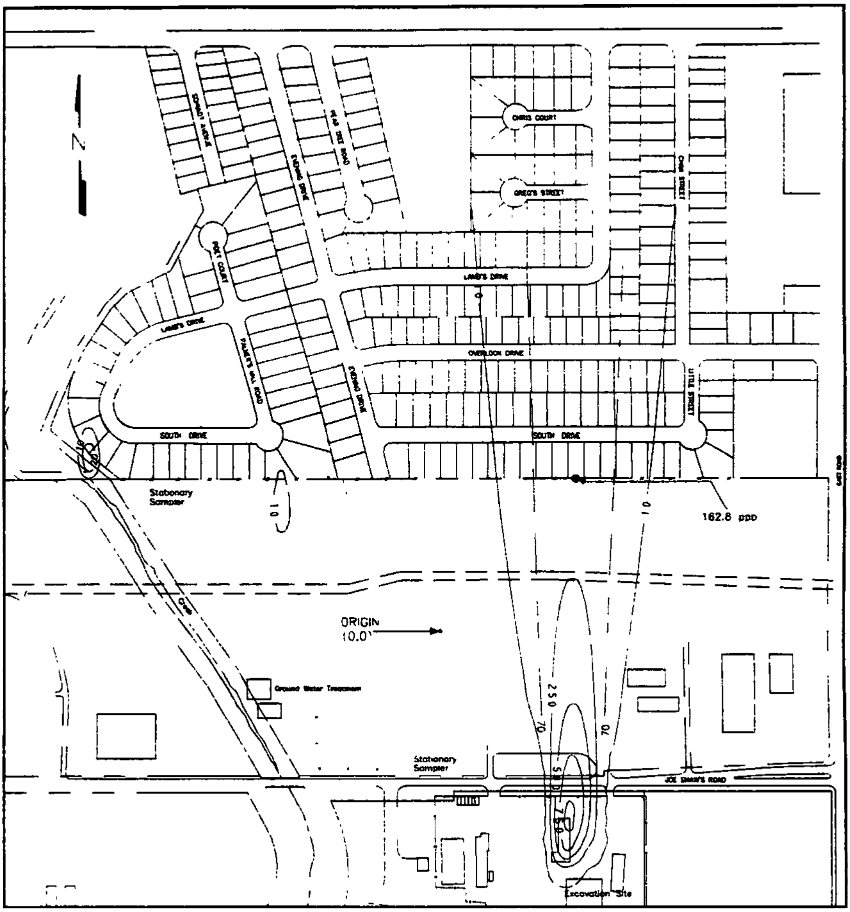

Figure 10. Concentration Contours from the Petroleum Recovery Superfund Site, Assuming the Worst-case Meteorological Conditions that Occurred During the Day of the Release.

On-Site Analysis of Sulphuric Acid Following the Train Derailment at Hervey-Jonction, Quebec

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Summary

On January 21st, 1995, near Hervey-Jonction, Quebec, 28 railway tank cars containing concentrated sulphuric acid derailed. Acid was spilled on the ground, in a nearby lake and river. At the request of the Environment Canada, Quebec Region, the analytical response vehicle of the Emergencies Science Division (ESD) was deployed to perform on-site analysis during the tank car removal operations. On-site analysis of soil and liquid samples was performed using field instruments.

Chronological Events

The incident occurred at 9:50 on January 21, 1995 within the Tawachiche ZEC (Zone d'exploitation contrôlée) in a wooded area, alongside Petit Lac Masketsi which flows into the Tawachiche River. Seventeen cars derailed and landed on the ground, parallel to the track with the spilled material affecting the surrounding soil. The eleven remaining cars were more scattered: one was found near the river, a few on the lake shore, others were partially submerged in the lake and finally, one car was totally submerged. It is suspected that the derailment occurred because of a broken track (from fatigue and/or cold temperatures). Environment Canada, Quebec Region, was contacted at 10:30 and arrived on site that afternoon. Some pH measurements were taken the same day and the lowest value obtained in the river was 2.7. It was decided to prohibit use of drinking water from wells located near the river until further notice. Operations to attempt neutralization of the river were started that day. By 20:00, all obvious leaks from tank cars were plugged and, by the next day, the population was allowed to drink water again.

The Emergencies Science Division (ESD) deployed the analytical response vehicle on January 24 at the request of the Quebec Region. The vehicle contained a variety of personal protection equipment, sampling tools and analytical instruments and was requested to provide timely on-site analytical results.

The total amount of concentrated acid spilled was 177,750 litres in the lake and river and 78,750 litres in the soil. Neutralization of the lake and river was conducted using calcium carbonate while tank cars were being emptied and removed. The soil was treated with sodium carbonate following removal of tank cars. By January 24, the track was repaired and clean-up operations took place from 06:00 to 18:00 to allow trains to travel at night. On January 31st, the last tank car was emptied and removed. The analytical response vehicle was demobilized on February 1st and ESD staff returned to Ottawa. On February 3rd, the Quebec Region team departed from the site, however they continued to conduct weekly visits to monitor the remediation operations.

Properties and Behaviour of Sulphuric Acid

Sulphuric acid (H_2SO_4) is a colourless, odourless, oily liquid and with a United Nations identification number of UN 1830. Its molecular weight is 98.1 g/mol. The acid involved in the present spill is of commercial grade and having a concentration >93.19%. The following table indicates some of the properties of the acid.

Table 1 - Properties of commercial grade sulphuric acid (data from EnviroTIPS manual)

Flammablility: not flammable or combustible
Human Health: mists and liquid are corrosive to tissue, by inhalation and contact, TLV: 1 mg/m^3, IDLH: 80 mg/m^3, STEL: 3 mg/m^3.
Environmental concerns: harmful to aquatic life in some species, in concentrations as low as 6 mg/L
State at 15°C, 1 atm: liquid
Melting point: -29.5°C, Boiling point: 279.4°C
Specific gravity at 15°C (water = 1) = 1.8354, at 25°C approx. 1.85
Solubility in water: completely miscible, with evolution of heat
Behaviour in water: sinks and reacts evolving heat, mixes slowly with water
Diffusivity in water at 25°C: 1.97 x 10-5 cm^2/s

TLV: Threshold Limit Value
IDLH: Immediately Dangerous to Life and Health
STEL: Short Term Exposure Limit.

When spilled in water, sulphuric acid mixes very slowly; concentrated acid solutions react violently. When spilled on soil, it will spread on the surface and penetrate into the soil at a rate dependent on the soil type and its water content. Downward transport of the liquid toward the groundwater table may cause environmental concerns. Because sulphuric acid is nonvolatile, dispersion in air is not a concern. Sulphuric acid is transported in tank cars as a nonpressurized liquid thus the force of gravity is the principle force governing the flow of the liquid from the leaking tank.

The amount of acid allowed in the environment is not regulated in Canada but there are guidelines for maximum sulphate concentration and pH. The recommended upper limit of sulphate is 500 mg/L, 150 mg/L is preferred. Freshwater toxicity indicates that minnows are seriously harmed or can be killed when exposed to a 6-8 mg/L concentration of sulphuric acid for 6 hours. Previous toxicity studies indicate that the toxic effect of sulphuric acid is primarily due to its acid strength. While a pH of 4.0 has caused gill irritation, pH 3.5 has caused death in sunfish, bass and carp. Generally, a pH of less than 4.5 is toxic to fish, however, a pH of less than 5.5 may be too toxic for other aquatic life. A pH of 4.5-5.0, is likely to be lethal to eggs and fry. Between 4.0-4.5, only a few fish survive. Below 3.5, it is very unlikely that any fish will survive more than a few hours (from EnviroTIPS manual).

Behaviour of Acid in Water

When spilled on water, the acid has been observed to sink and slowly mix with the water. The mixing of acid in the water can generally be described by classical diffusion equations. In rivers, the principal mixing agent is stream turbulence, while in calm water mixing takes place by molecular diffusion.

Estimate of pollutant concentration in a river downstream from a spill can be done using the turbulent diffusion model. The model assumes that the liquid or solid is neutrally buoyant and dissolves in water. Since sulphuric acid is denser than water, one can assume that the higher concentrations will be at the bottom.

No modelling has been carried out for molecular diffusion in still water but a nomogram has been prepared to define the average concentration within the hazard zone as a function of spill size but independent of time. These nomograms have been prepared in the EnviroTIPS manual series.

The average concentration of the pollutant, for a known volume of water and a known mass of spill, can be obtained using Figure 1 (from EnviroTIPS), assuming that the pollutant is spread evenly throughout the volume. In reality, since concentrated sulphuric acid is denser than water, the highest concentrations will lie at the bottom.

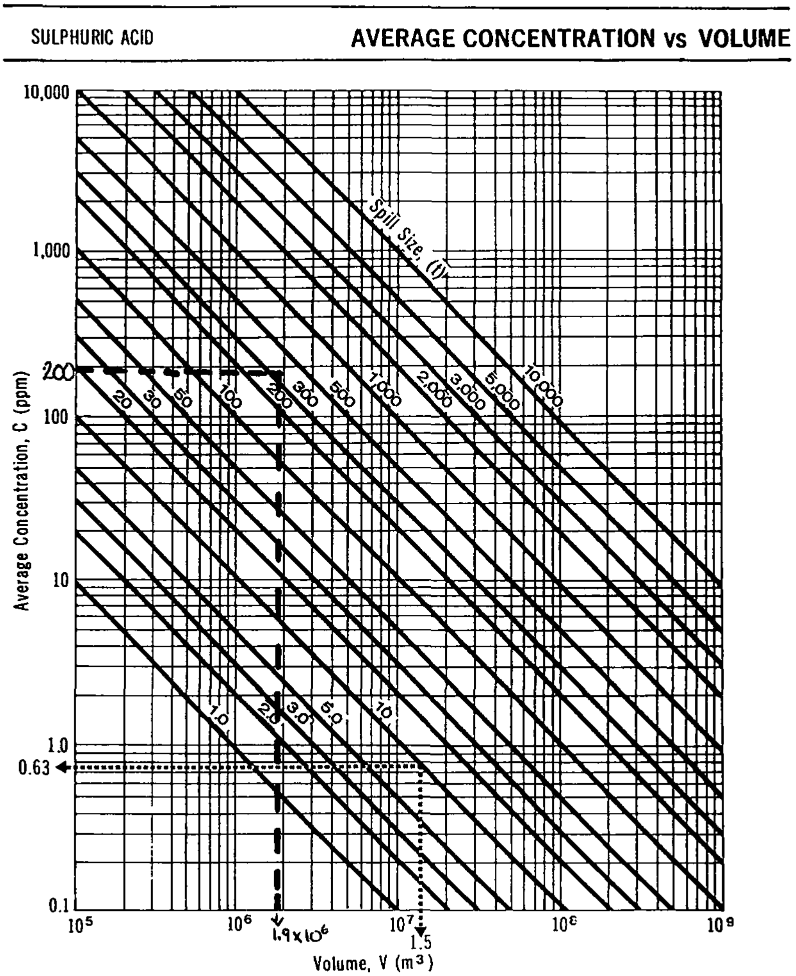
The following data was used: volume of water = 1.9 x 10^6 m^3, mass of sulphuric acid = 39 500 gallons or 179 567 Litres multiplied by the density (1.8354 g/mL) = 330 000 g L/mL x 1000 mL/L x 1 kg/1000 g = 330 000 kg = 330 tonne.

According to Figure 1, the average concentration should be approximately 200 ppm or 0.200 g/L. 1 mole = 98.1 g, therefore, 2.04 x 10^{-3} moles/L. The average pH would be 2.7.

Behaviour of Acid in Soil

Because of its miscibility with water, the rate of movement of sulphuric acid in soil will be affected. Dilution through mixture with water will decrease the viscosity with the effect of increasing the velocity of downward movement in the soil. During transport through the soil, the acid can dissolve some of the carbonate-based materials which will neutralize the acid to some degree. Upon reaching the groundwater table, the acid will

Figure 1 (From EnviroTIPS)



continue to move in the direction of groundwater flow and downward because of its density.

The soil which is found in the area of the spill is a clay till which is not very permeable (intrinsic permeability (k), 10^{-15} m^2) and has a porosity (n) of 0.55 m^3/ m^3. A nomogram for the penetration of sulphuric acid into the unsaturated zone above the groundwater table presents penetration time (tp) against depths of penetration (B), see Figure 2 (from EnviroTIPS). As can be seen, concentrated sulfuric acid does not penetrate the ground very fast (less than 1 cm in 100 days). Even assuming that dilution occurred because of the presence of snow, and that the solution is very dilute (close to that of water at 20°C), the penetration is about 8 cm in about 100 days. Another factor supporting the fact that there will be little penetration is that the soil is frozen and this will slow down the movement.

The penetration of sulphuric acid in the soil would be faster if the ground was more permeable, close to a silty sand (see figure 3). Assuming that the acid remained on the ground for 12 days following the spill, the liquid would have penetrated less than 1 m. The worst case condition would be a dilution to 60% at 4°C (on-site temperatures were always below 4°C) and the maximum penetration is still less than 2 metres. Extensive digging is therefore not required and would do more harm than anything else as discussed in a post-spill study conducted at Springhill, Nova Scotia, ten years after the event (reference, EE-86). Pumping of the liquid phase and neutralizing the first two to three feet of soil should be sufficient. Thawing of snow will carry all neutralization materials further down if there is any remaining acid material.

Experimental

The analysis of the various samples were conducted using pH paper, Horiba U-10 meter, DR/2000 Hach sulphate test, and acid-base titration. Most of the tests were conducted on samples brought back to the mobile laboratory but some measurements were carried out *in-situ*. Soil samples were collected using a trowel and were stored in glass jars with Teflon lined lids or mason jars with Teflon lining. Other solid samples were provided by the drilling company installing piezometers. River and lake water samples were collected using a Vandorn bottle or a bailer and then transferred to plastic polypropylene bottles. To optimize the analysis time, it was decided that the mobile provincial laboratory (Ministere de l'Environnement et de la Faune or MEF) would concentrate on the analysis of water and river samples whereas the ESD laboratory would conduct analysis on the soil samples. However, some river and lake samples collected in the area covered by federal jurisdiction were also analyzed. On-site quality control was implemented by the laboratories exchanging 5% or 1 out of 20 samples.

Sample preparation

Liquid samples were analyzed without further treatment whereas soil samples were filtered and extracted with deionized water and tests conducted on the extract. The extract was obtained by adding 100 mL of deionized water to the sample container using

Figure 2 (From EnviroTIPS)

SULPHURIC ACID

PENETRATION IN CLAY TILL

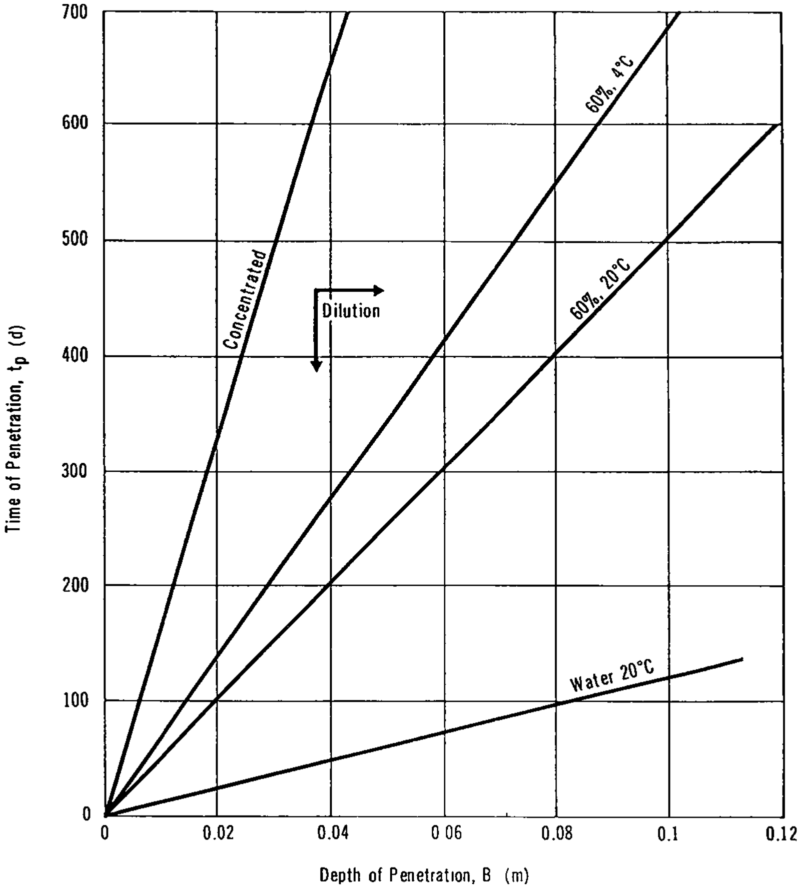
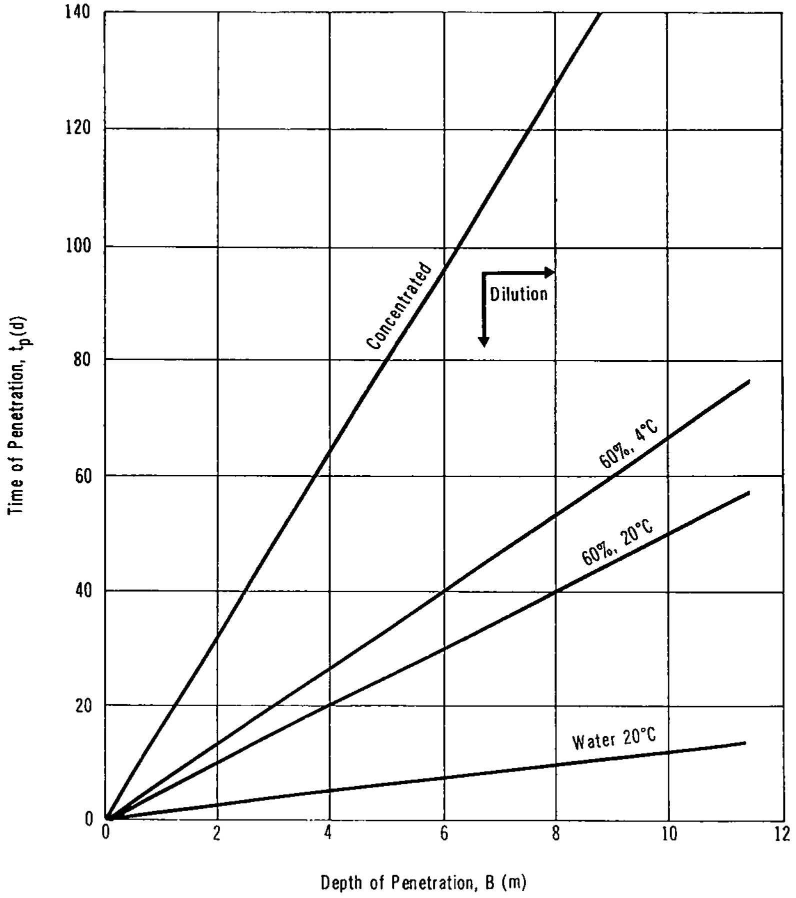


Figure 3 (From EnviroTIPS)

SULPHURIC ACID

PENETRATION IN SILTY SAND



a graduated cylinder (as much as 200 mL may be needed if the sample is peat or contains pine needles). A filtration apparatus of beakers and funnels was set-up. Whatman #1 was used to filter most samples, however, for peaty soil samples or those consisting of excessive pine needles, a commercial coffee filter was used as a preliminary filter. After filtering through #1, if the filter still contained solid matter, the extract was refiltered with Whatman #3. Pasteur pipets were used to transfer the sample to the filter funnel. The bottle was sealed and manually shaken for approximately one minute, venting was done as required.

pH paper test

EM Reagents, colorpHast pH 0-14 paper was used as a quick screening test on all samples (field laboratory and *in-situ*). The pH of the sample was measured as is with pH paper directly, if the sample was a dry solid, this test was not applicable. The test was also conducted on the soil extracts. Result was compared with a colour chart illustrated on the pH paper packaging box. This test was often conducted *in-situ* for water and wet soil samples.

Qualitative sulphate test

Some of the water samples were tested using $BaCl_2$ solution. In presence of sulphuric acid, the following reaction takes place:

$H_2SO_4 + BaCl_2$ (sln) $\rightarrow BaSO_4$ (white precipitate) + 2 HCl

Acid base test (PPAK method)

The acidity of the water was measured by conducted an acid-base titration following the method described in the Person-Portable Analytical Kit (PPAK) manual. In summary, 50 mL of the sample is titrated with 0.02N NaOH using phenolphthalein indicator, (a blank is also analyzed). The volume required to achieve neutralization is then multiplied by 19.5 to give a value in mg/L. The 19.5 multiplication factor is obtained using $M_1 \times V_1 = M_2 \times V_2$ where M is the concentration, V the volume, 1 corresponds to sodium hydroxide and 2 to sulphuric acid. The concentration of NaOH is known, the volume of NaOH is obtained from the burette and the volume of acid is 50 mL. M_2, which corresponds to the concentration of acid is obtained and divided by 2 since 1 mole of sulfuric acid corresponds to 2 equiv/L or 2. This value is multiplied by 98.1 g/mol (molecular weight of sulphuric acid) then by 1000 mg/g to convert the units to mg/L.

$H_2SO_4 + 2\ NaOH \rightarrow 2\ H_2O + Na_2SO_4$

Horiba U-10 water quality meter

The U-10 is a handheld, battery powered instrument cabable of simultaneously measuring pH, conductivity, turbidity, salinity, dissolved oxygen and temperature. In the present situation, however, only pH, conductivity and temperature were measured. The probe extension is 2 metres long and can be placed directly into liquids. The minimum sample required to perform testing with the Horiba U-10 is 20 mL and requires the sample to be placed in a small vial which is then placed directly on the appropriate sensor. Soil extracts and liquid samples were analyzed. The U-10 meter is easily calibrated using a commercially available pH 4 buffer solution andd the instrument's auto-calibration function. Repeated checks of the stability of the calibration has shown that the meter remains stable over the course of a day. After turning on the power, the instrument stabilizes within 2 minutes and is ready for use. Provided certain measures are taken to minimize the exposure of the electronic meter to the cold temperatures such as placing it in a protective container when not used, the instrument can operate in sub-zero temperatures.

Hach sulphate test

The sulphate content of some soil extracts and water samples was measured following the Hach method #8051 and using a Hach DR/2000 spectrophotometer. In summary, the wavelength dial of the DR/2000 was set to 450 nm, a powder pillow of barium chloride is added to the sample cell containing 25 mL of the sample. A second sample cell containing only the sample is prepared as a blank. After a reaction time of 5 minutes, the instrument is zeroed with the blank and then the sample concentration is measured. The result is automatically displayed as mg/L of sulphate ion. For samples having a pH between 0 and 5, the concentration of sulphate exceeds the upper limit of the instrument, thus the sample must be diluted prior to analysis. Consequently the concentration of the sulphate ion generated by the instrument must be corrected for the dilution factor.

On-site measurements

In-situ analysis of the water was concluded using the Horiba U-10 and pH paper. The indicator paper was used to measure pH at the water surface while the U-10 was used to obtain measurement at depths of up to 2 m. The U-10 was used directly in the river and at various locations on the lake through a hole in the ice. The only type of *in-situ* soil measurements were done by touching the soil with the pH paper. One of the tank cars was suspected to contain some water mixed with the acid. A Teflon bailer was used to collect a sample in the tank car and the pH was measured immediately on-site to establish the concentration of the acid.

Sampling and Monitoring

During the first three days, the main concern was the river which provided drinking water. The river was monitored using pH paper, a Metrohm Herisseau model E-58 pH meter or a waterproof EP-2 pH meter by Hanna Instruments. Visual observation of the soil areas was also done and visible liquid pools were pumped. With the arrival of the ESD mobile laboratory and additional personnel, a sample collection plan was developed and put into action. Figure 4 details the water sampling locations and tables 2 and 3 for the corresponding results. Soil surface sampling near areas where the spill occurred was done whereas in depth sampling was achieved when the contractor drilled boreholes to install piezometers (see figure 9). All soil samples were taken back to the field laboratory, extracted with deionized water and followed by analysis for pH, temperature,

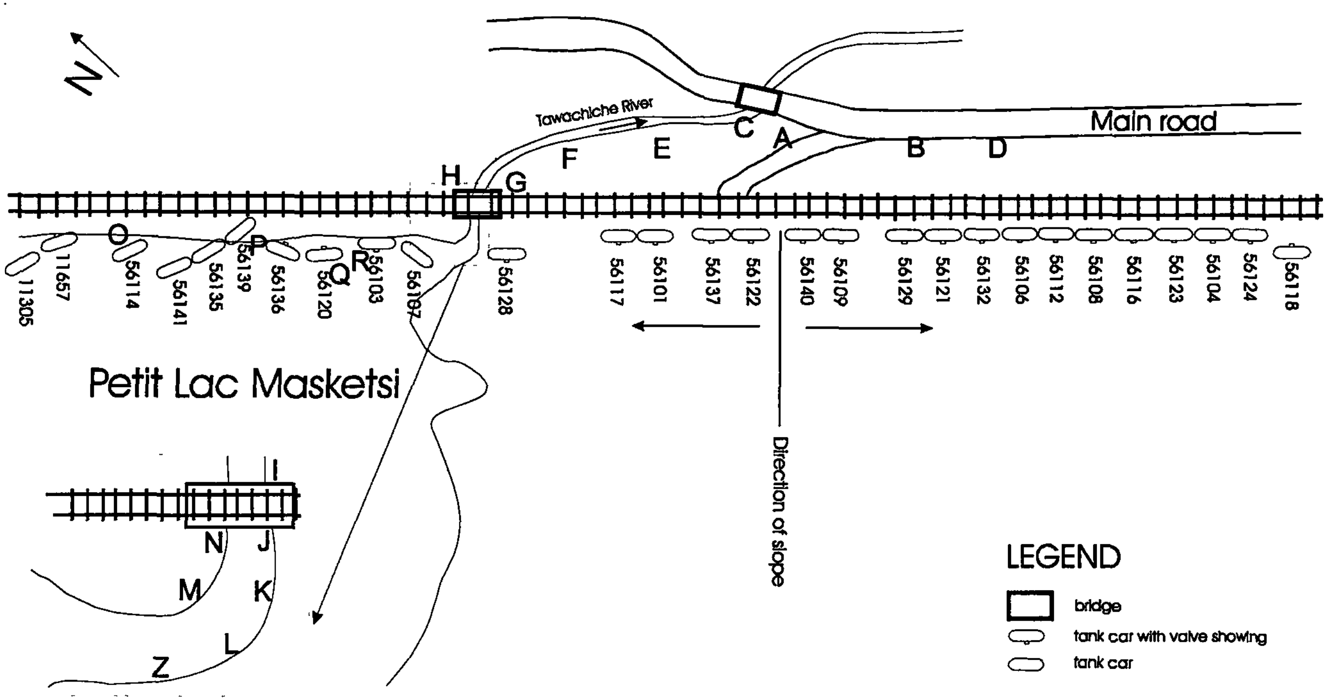


Figure 4 - Water sampling locations (indicated by a letter, refer to appropriate table for results).

Table 2 - pH values of water samples.

River					**Lake**			
Date	*Time*	*Location*	*pH*		*Date*	*Time*	*Location*	*pH*
21-Jan	n/a	C	3		22-Jan	11:30	O	7
23-Jan	1:00	C	3.9					
24-Jan	9:10	C	5		24-Jan	14:00	P	4.6-5.2
					25-Jan	10:20	P	5
23-Jan	8:00	E	4					
					24-Jan	14:10	Q	7
23-Jan	8:00	F	4		25-Jan	10:27	Q	5.1
23-Jan	8:00	G	3.8		24-Jan	14:25	R	7.6
					25-Jan	10:35	R	5.7
23-Jan	8:00	H	4.4					
23-Jan	15:45	I	4.2					
					Watertable			
23-Jan	15:45	J	4.4					
25-Jan	12:50	J	4		*Date*	*Time*	*Location*	*pH*
28-Jan		J	5.7					
					23-Jan	9:30	B	7.3
23-Jan	15:45	K	4		24-Jan	9:10	B	6.7-6.8
25-Jan	12:55	K	3.9		25-Jan	13:15	B	5.5
28-Jan		K	5.8					
					23-Jan	9:30	A	6.5
23-Jan	15:45	L	4		24-Jan	9:10	A	7.1-7.2
25-Jan	12:45	L	4.2		25-Jan	13:10	A	3.9
28-Jan		L	5.9					
23-Jan	15:45	M	3.7					
24-Jan	14:30	M	4.1		**Effluent**			
25-Jan	10:45	M	3.1					
					Date	*Time*	*Location*	*pH*
21-Jan	15:00	N	4		25-Jan	n/a	effluent	6.8
21-Jan	17:00	N	3.7					
21-Jan	18:50	N	2.7					
21-Jan	20:10	N	2.9					
22-Jan	10:10	N	4					
28-Jan	n/a	Z	5.7					
All data collected prior to January 25 was obtained using a Metrohm Herisseau model								
E-58 pH meter or a water proof EP-2 pH meter by Hanna instruments.								
The Horiba U-10 was used afterwards.								

Table 3 - Characterization of water samples

Date	*Sample #*	*Location*	*pH Horiba*	*Conductivity (mS/cm)*	*emperature (°C)*	*pH Paper*	*Titration (mg/L)*	*Conversion of titration to pH*	*Sulfates w/ Hach (mg/L)*	*Conversion of sulfates to pH*
25-Jan	W05	P	5.0	0.03	1.8	4--5	7.8	4.1	2	4.7
25-Jan	W16	Q	5.1	0.03	1.9	4--5	8.8	4.0	6	4.2
25-Jan	W14	R	5.7	0.3	1.6	4--5	9	4.0	6	4.2
25-Jan	W02	M	3.1	0.22	1.5	3--4	37	3.4	26	3.6
25-Jan	W07	L	4.2	0.11	3.8	4--5	17.8	3.7	14	3.8
25-Jan	W01	J	4.0	0.12	2.7	4	19.3	3.7	15	3.8
25-Jan	W04	K	3.9	0.12	2.3	4	19.1	3.7	13	3.9
25-Jan	W06	A	3.9	0.13	1.4	4	20.9	3.7	14	3.8
25-Jan	W13	B	5.5	0.03	0.4	5	22.4	3.6	10	4.0
25-Jan	background	Effluent	6.8	0.03	7.4	7	0.6		0	

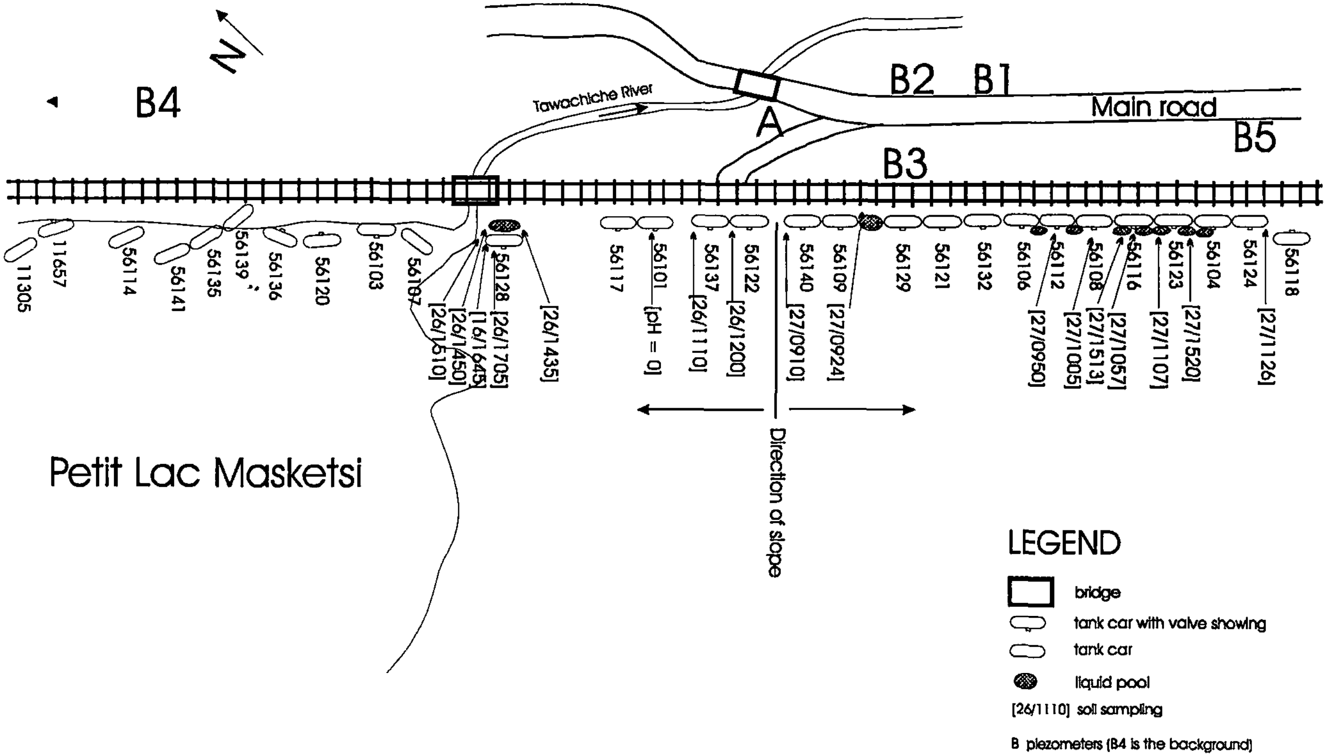


Figure 9 - Soil sampling and piezometers locations.

conductivity and sulphate content. Tables 4 and 5 show the detailed results of the analysis whereas figure 11 gives a visual appreciation of the extent of the contamination. Table 6 shows pH values obtained with both paper and pH meter. The values estimated with paper are very close to those obtained with the meter. It is not possible to establish a valid correlation because the pH paper gives a reading to the closest unit or gives a range and is not precise enough. However, the results indicate that pH paper is a useful and reliable screening tool.

Results

Only water samples collected January 25 were tested using the barium chloride solution. All results were negative, i.e. a precipitate could not be observed. We attribute this to the fact that $BaSO_4$ is soluble in sulfuric acid. To verify the effectiveness of the test, a 0.02N sulphuric acid solution was subjected to the test, it showed a positive result.

Table 2 lists the pH value for water samples. The pH of the river was between 2.7 and 4.4 until January 25. This can indicate a constant input of acidic liquid (possibly from rail car 56107 located in the lake) or efficient neutralization of the lake's output due to limestone application (limestone was applied beginning January 26). The pH of the lake near the shore became more acidic after a few days; it is possible that the acid which reached the bottom of the shallow section along the shore did not completely leak toward the center of the lake and some of it diffused upwards in the water column. By January 28, the pH in the bridge area had increased and stabilized around 5.7-5.9. A hole was dug at location B and a decrease in pH value was recorded. This could be an indication that acid from uphill had seeped through the soil and was starting to leak into the water table.

Table 3 contains results from the water samples collected by Environment Canada and taken to the ETC mobile laboratory. Four graphs were created from that data (figures 5 to 8). As can be seen, there are two points which never follow the trends, so it is suspected that the results are erroneous. By removing those data points from the graph, general trends can be observed. When pH is involved, a logarithmic curve can be seen, whereas for the graph involving sulphate content versus titration volume, a linear relationship is observed. In general, as the acidity increases (pH number decreases), so does the magnitude of the other parameters. The conductivity increases which is to be expected since more ions are present in solution when the acidity is increased. Both titration and sulphate content increase with a more acidic pH which is also normal because they represent the H^+ ion content and the sulphate ions present in solution. The relationship between sulphate and titration volume is linear. When the concentration of sulphate and the results from the titration are converted to pH value equivalent, the agreement between both parameters is very good, furthermore, these values also agree very well with the pH measured. In all instances, where there is a discrepancy between pH value and titration/sulphate, the latter values are higher. It is better to obtain a positive or more conservative bias during field testing.

Figure 9 indicates the various locations where piezometers were set-up and where soil samples were collected. Table 5 contains analysis results from boreholes dug by the

Table 4 - Soil Samples, collected by Environment Canada

Date	*Sample #*	*pH paper*	*pH of extract*	*Note*	*pH*	*Conductivity*	*Temperature*	*Sulphates w/ Hach*
					Horiba	*mS/cm*	*°C*	*mg/L*
26-Jan	26/1200	n/a	5	Clear extract	5.51	0.04	13.6	10
26-Jan	26/1110	1 to 2	1	Clear extract	0.22	over 100	15.5	36
26-Jan	26/1450	n/a	4 to 5	Clear extract	5.8	0.029	18.5	8
26-Jan	26/1435	n/a	4 to 5	Clear extract	4.87	0.127	18.4	29
26-Jan	26/1510	n/a	4 to 5	Clear extract	6.66	0.066	14.9	6
26-Jan	26/1645	5	4 to 5	Peat soil with needles (extract 200 mL), extract color apple	4.7	0.077	15.2	not measurable
26-Jan	26/1705	1	4 to 5	Peat soil with needles (extract 200 mL), extract color apple	5.1	0.115	15.5	6
27-Jan	27/0910	n/a	4 to 5	Clear extract	4	0.25	15.1	>75 (dilution 1/50 == 3mg)
27-Jan	27/0924	1 to 2	0 to 1	Very dark like maple syrup	0.9	over 100	15.3	dilution 1/5 == over 75
27-Jan	27/0950	1	0 to 1	Medium dark like cognac	1.1	57.6	15.2	not measurable
27-Jan	27/1005 (501)	1 to 2	0 to 1	Very, very dark like cola	1.8	5.45	14.7	not measurable
27-Jan	27/1005 sphaigne	1 to 2	0 to 1	Peat soil with needles (extract 200 mL), extract color cognac)	1.3	28.4	14.9	not measurable
27-Jan	27/1057	4 to 5	4	Almost clear	5.5	0.026	14.9	8
27-Jan	27/1107	4 to 5	4 to 5	Almost clear	4.7	0.033	15.1	8
27-Jan	27/1126	4 to 5	5 to 5	Clear extract	5.4	0.043	15.9	12
27-Jan	27/1513	4 to 5	6 to 5	Clear extract	5.6	0.038	16.5	9
27-Jan	27/1520	4 to 5	4 to 5	Soil became muddy upon addition of water (extract 200	5.5	0.046	14.4	not measurable
28-Jan	240195C	n/a	0 to 1	Clear extract	0.42	over 100	18	not measurable
28-Jan	240195D	n/a	0 to 1	Clear extract	1.02	60.3	18.3	not measurable
28-Jan	240195E	n/a	5 to 6	Clear extract	5.6	0.081	18.3	not measurable

Figure 5 - pH versus conductivity

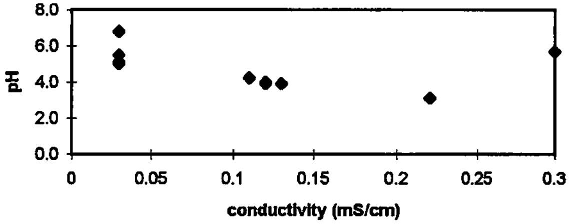


Figure 6 - pH versus titration

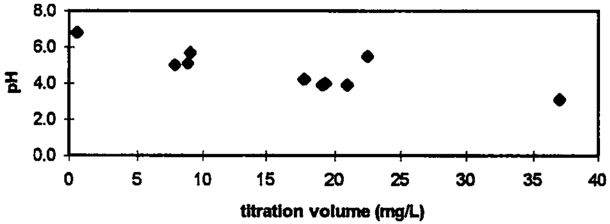


Figure 7 - pH versus sulphate content

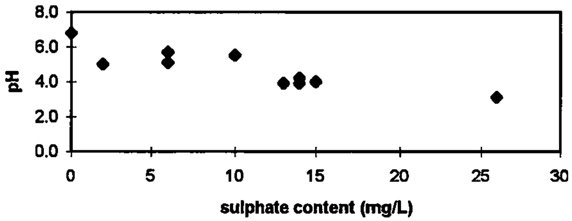


Figure 8 - sulphate content versus titration

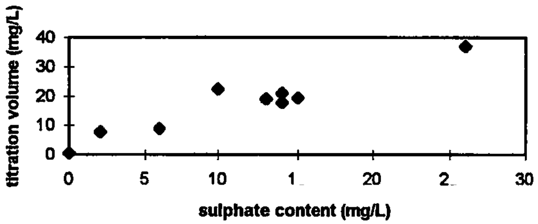


Table 5 - Samples from drilling holes

All samples provided by Groupe TS except for background sample which was provided by MEF.

Date	*Sample #*	*Depth*	*Borehole*	*pH of extract*	*Nature of the sample*	*pH*	*Conductivity*	*Temperature*	*Sulphates*
						Horiba	mS/cm	°C	mg/L
26-Jan	Background soil					5.7			
26-Jan	F1-CF1	2-2.5'	B1	5 to 6	sand	7.6	0.147	15.4	16
26-Jan	F1-CF2	3-3.5'	B1	5	sand	7.3	0.063	15.5	16
26-Jan	F1-CF4	6-7'	B1	5	sand	7.0	0.06	14.8	7
26-Jan	F1-CF5	8-9.5'	B1	5	sand	6.8	0.058	16.2	9
26-Jan	F1-CF6	11.5-12'	B1	5	sand	7.0	0.049	13.8	8
28-Jan	F3CF1	3-3'4"	B3	4 to 5	crushed rock	5.7	0.101	11.2	not measured
28-Jan	F3-CF2	4-7'2"	B3	7	sand	6.6	0.028	13.2	not measured
28-Jan	ROC F3	4-6'	B3	6 to 7	rock	6.4	0.025	12.3	not measured
28-Jan	F4-CF1	n/a	B4	5 to 6	soil / background	5.9	0.172	18.3	not measured
28-Jan	F5-CF1	2-2'8"	B5	5	soil	4.5	0.083	18.7	not measured
28-Jan	F5-CF3	7'5"-9'2"	B5	6	soil	7.1	0.134	18.5	not measured
28-Jan	F1E950128		B1		water table	6.0	0.084	10.7°C	5

Table 6 - Comparison of pH values obtained with pH paper and Horiba U-10

Sample #	pH paper	*pH*
F1CF-4	5	7.0
F1-CF1	5 to 6	7.6
F1-CF2	5	7.3
F1-CF5	5	6.8
F1-CF6	5	7.0
26/1200	5	5.5
26/1110	1	0.2
26/1450	4 to 5	5.8
26/1435	4 to 5	4.9
26/1510	4 to 5	4.9
26/1645	4 to 5	4.7
26/1705	4 to 5	5.1
27/0910	4 to 5	4.0
27/0924	0 to 1	0.9
27/0950	0 to 1	1.1
27/1005(501)	0 to 1	1.8
27/1005 (sphaigne)	0 to 1	1.3
27/1057	4	5.5
27/1107	4 to 5	4.7
27/1126	5 to 5	5.4
27/1513	6 to 5	5.6
27/1520	4 to 5	5.5
F3CF1	4 to 5	5.7
ROC F3	6 to 7	6.4
F3-CF2	7	6.6
F4-CF1	5 to 6	5.9
240195C	0 to 1	0.4
240195D	0 to 1	1.0
240195E	5 to 6	5.6
F5-CF1	5	4.5
F5-CF3	6	7.1
F1E950128	5	6.0
W05	4–5	5.0
W16	4–5	5.1
W14	4–5	5.7
W02	3–4	3.1
W07	4–5	4.2
W01	4	4.0
W04	4	3.9
W06	4	3.9
W13	5	5.5
blanc	7	6.8
Centre petite baie (MEF)	7	6.8
Affluent (MEF)	7	6.8
Sous le pont (lecture directe)	4	4.0
W12	4	3.7

consultant. The soil in this area is naturally slightly acidic (pH 5.7) and the background borehole B4 (sample F4) gave a pH around 5.9. Most of the samples have a pH with similar acidity or lower than the background soil. The only exception is B5 (sample F5-CF1) which shows a pH of 4.5, this can be caused by some acid leaking through the water table. Figure 3 shows the pH values obtained by collecting surface samples of soil. The acid does not appear to move in an horizontal manner because the pH of the soil about 0.5 metre around the liquid pools is normal. The acidic values (between 0 and 2) were obtained from soil soaked with acid whereas the other numbers came from samples which appeared untouched. The detailed analysis of these samples is shown in Table 4. Again the more acidic the sample, the higher the conductivity value and sulphate content. Figure 10 shows the relashionship between pH and conductivity for the soil samples. Conductivity could be used to estimate acidity of samples which have a pH value between 1 and 4. Below and above those values, there is full or no conductivity (respectively) and no extrapolation can be done. Most samples are "sandy" and produce a clear extract which can be tested for sulphates. The darker extracts which usually come from peat soils, produce a dark extract which cannot be analyzed by the Hach colorimetric test because the color of the solution interferes.

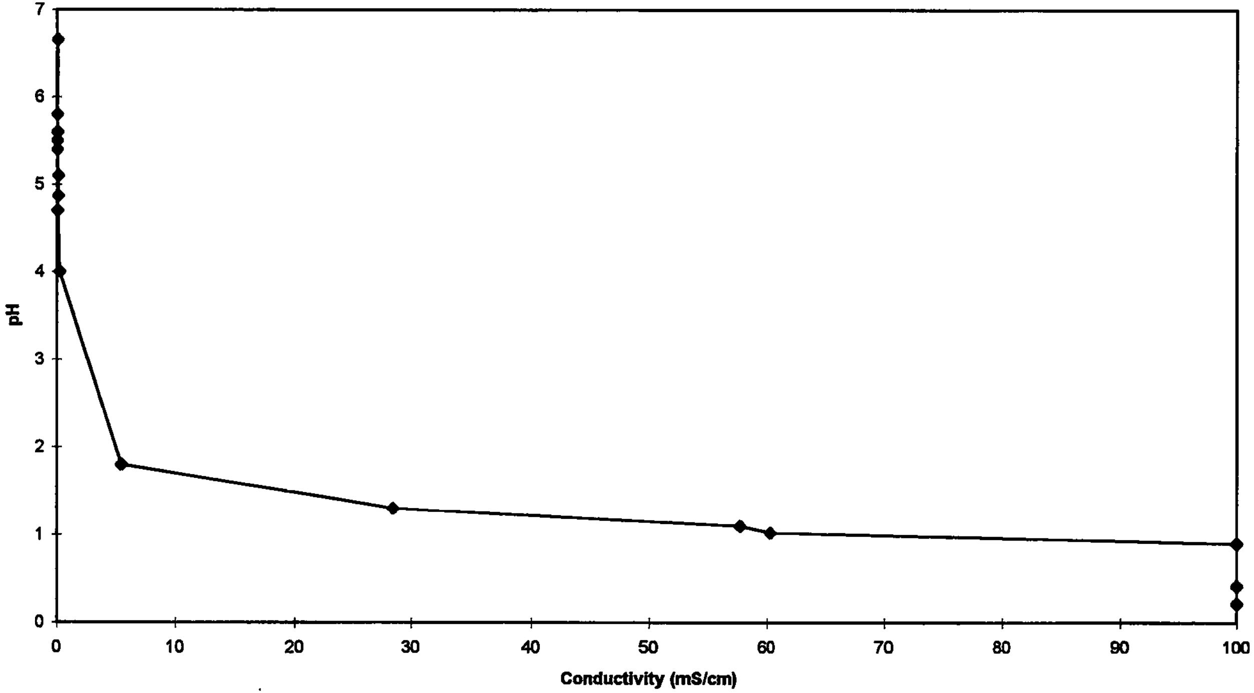
Figure 12 indicates locations where the lake water was tested in-situ. The pH values were close to normal, between 5.8 and 6.3 (pH of lake surface everywhere else was 6.4). The U-10 probe operated very well at temperatures down to 1.1°C. Figure 5 indicates results of similar tests performed after the tanks were pulled out of the water by a few feet and the top valve leaked for about 30 seconds. The pH was quite acidic near the 56141 tank car and the water around it generally more acidic than previously measured. Since concentrated sulphuric acid is heavier than water, the effect was more pronounced near the bottom. The samples temperatures varied between 8.7°C and 11.4°C; two explanations are possible for this phenomenon, the first being that some water penetrated the tank and created an exothermic reaction which warmed up the liquid, the second being that the temperature sensor of the probe heated up when rinsed with water between samples. The latter explanation seems more plausible. The pH of the samples collected from the tank varied between 0 and 0.4 at the surface. A composite sample (multi-level in the tank) also gave a pH near 0, considering that there were no holes or water intakes in the tank, it can be assumed that the concentration of the whole tank was still very close to that of concentrated acid.

Discussion

Figure 14 is a schematic representation of the lake's cross-section. Some pH measurements were taken by the MEF at various depths. This allowed to estimate that if all the acid present in the lake is stirred or completely mixed, the final pH will be 3.2. This corresponds to 67,356 litres which was a very conservative number because each tank car contains approximately 49,210 litres and there was at least the content of 1.5 tank cars spilled in the lake. To bring the lake to a viable pH for all aquatic life (pH 5.5), 87 tonnes of calcium hydroxide would be required.

The final amount of acid poured in the lake was 39,500 gallons or 179,000 litres. Assuming that the initial concentration of sulphuric acid is 17.8 M or 1750 g/L, and that

Figure 10 - Relationship between pH and conductivity for soil samples



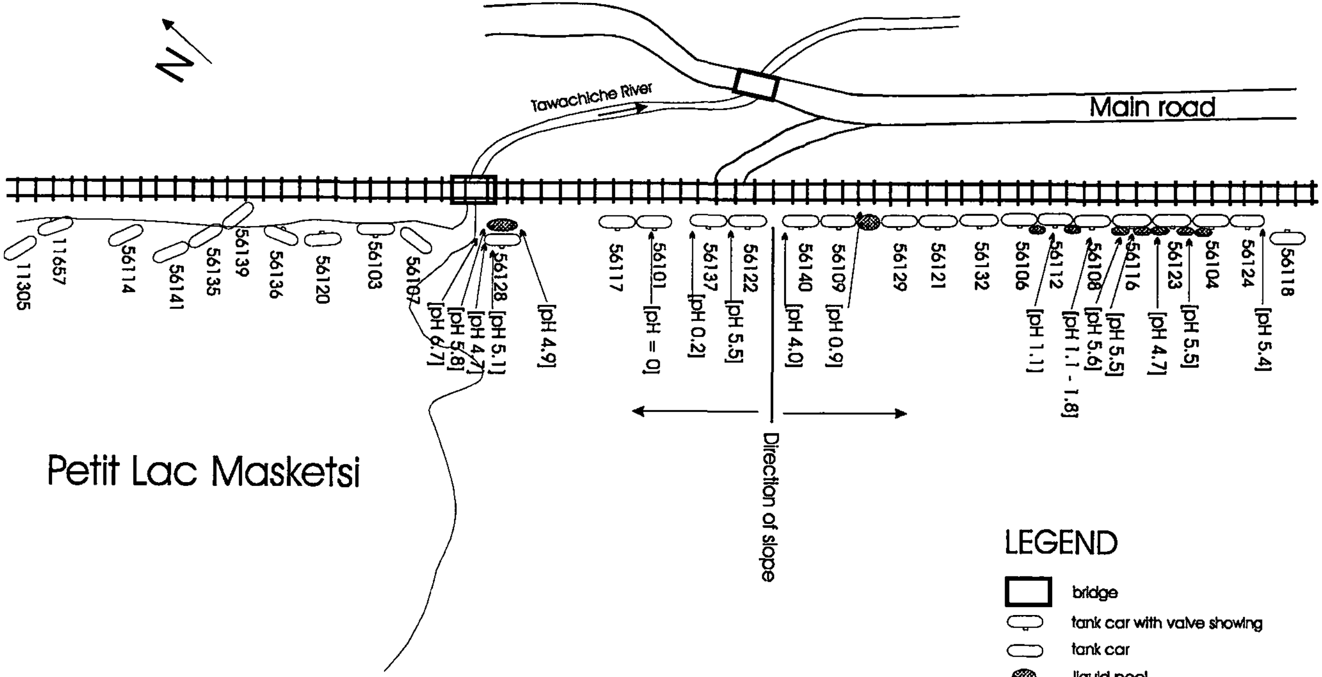


Figure 11 - Extent of soil contamination.

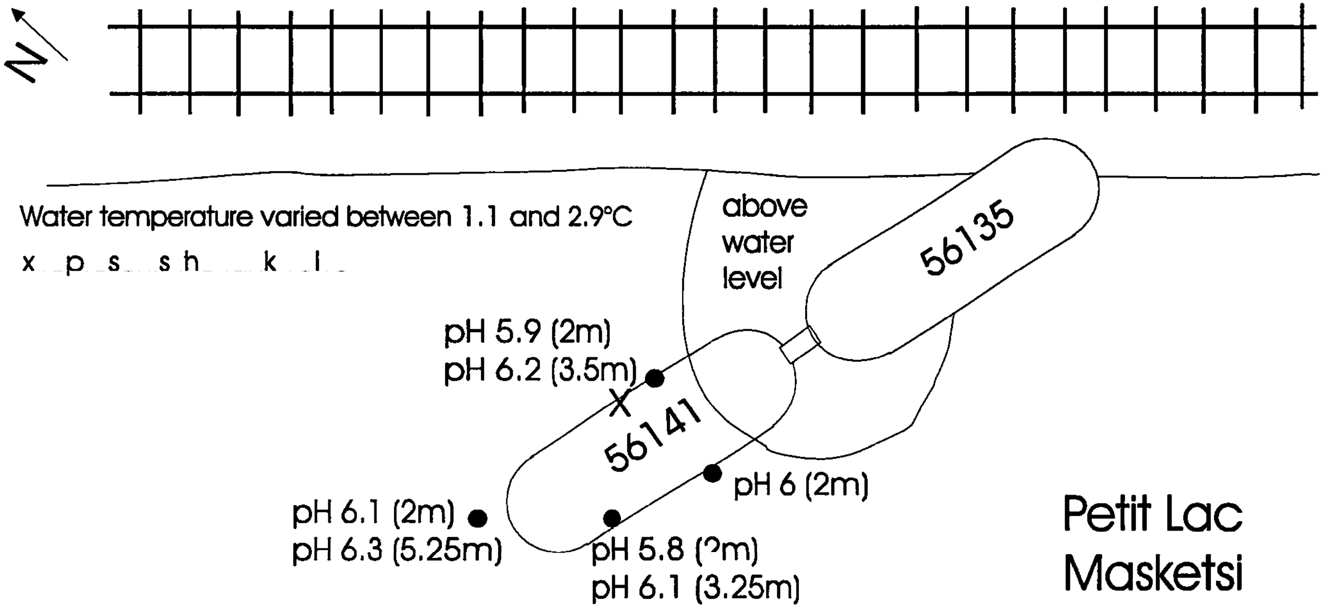


Figure 12 - In-situ measurements at various depths near the 56141 tank car before complete removal from the lake.

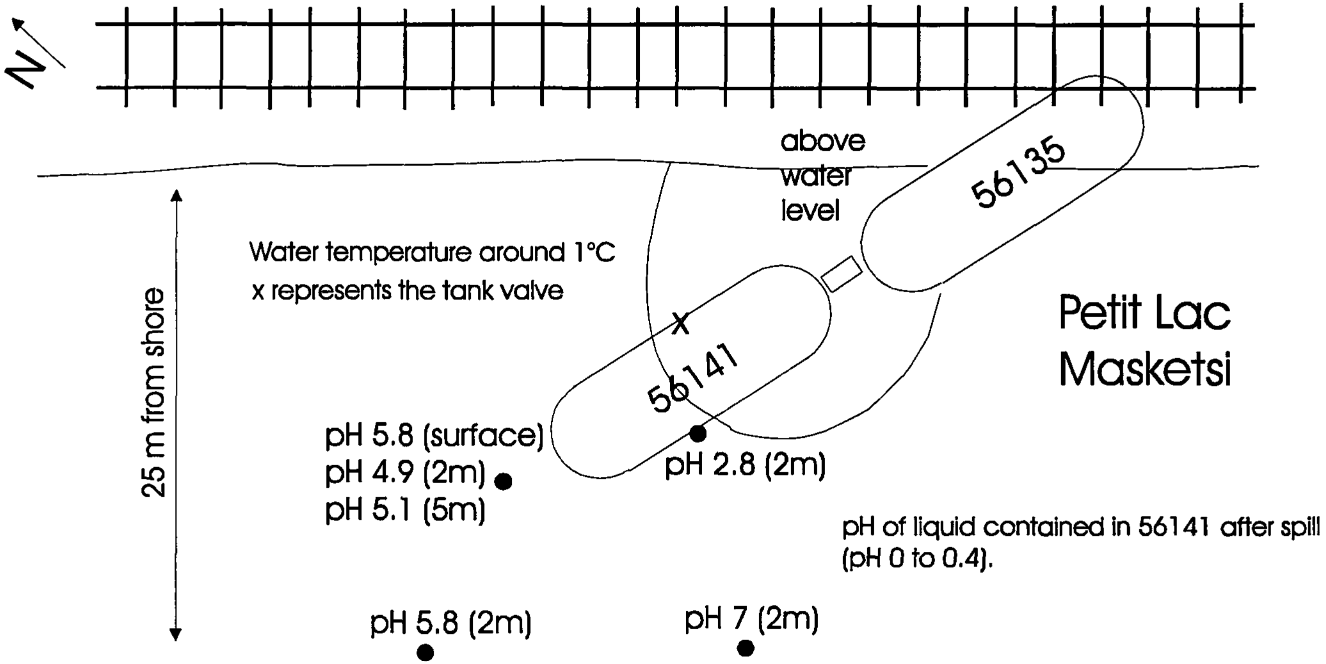
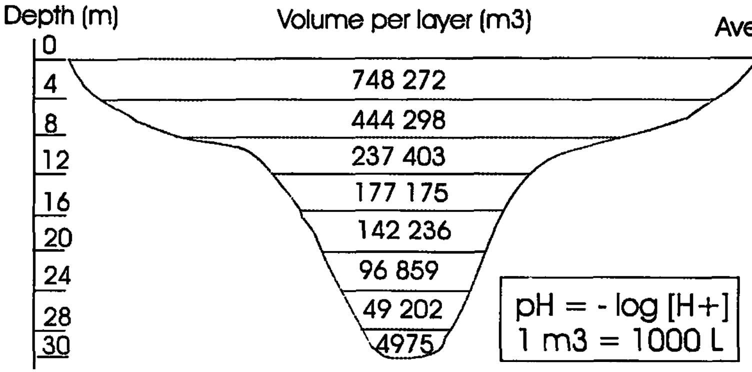


Figure 13 - Sampling around the 56141 tank car after liquid spilled from valve.

Total volume of lake: 1 900 420 m3.



Volume per layer (m3)	Average pH	[H+] in moles/L	moles of [H+]
748 272	6.4	398.107 e-9	298
444 298	6.4	398.107 e-9	177
237 403	3.5	316.228 e-6	75 e3
177 175	2.9	1.259 e-3	223 e3
142 236	2.8	1.585 e-3	225 e3
96 859	2.4	3.981 e-3	386 e3
49 202	2.3	5.012 e-3	247 e3
4975	2.3	5.012 e-3	25 e3

pH = - log [H+]
1 m3 = 1000 L

Total = 1181 e3 moles H+
[H+]=622 e-6 moles/L

$\boxed{\text{pH} = 3.2}$

- To achieve a final pH of 5.5 or 3.162 e-6 mol/L, only 6.006 e3 moles of hydrogen ion can be present. Therefore, 1175 e3 moles of H+ need to be neutralized.

- 1175 e3 moles of $Ca(OH)_2$ correspond to 87 e6 g or 87 000 kg (74 g/mol).

Figure 14 - Calculation of final pH of the lake.

the lake volume was 1.9 x 10^9 L, a final concentration of 0.1648 g/L is obtained, or 0.00168 mol/L. This corresponds to a final pH of 2.8 which is very close the value of 2.7 obtained using the nomogram in Figure 1.

Exchange of 5% of the samples between the ESD mobile laboratory and the MEF laboratory was done to test quality control. The pH aspect of the analysis was emphasized. Table 7 shows the pH results of both laboratories which are in good agreement. The only sample on which conductivity and sulphate analysis were done by both laboratories shows a good correlation between sulphate (25 and 26 g/mL) but some difference is noticed for conductivity results (however, on a 0-100 conductivity scale, the difference is negligible). This exercice demonstrated that the field analytical tools used by both parties were efficient and reliable.

Remediation

Calcium carbonate was used to neutralize of the lake. This material is harmless to the environment as it is found in nature in the form of limestone, marble, calcite and other materials. This compound is practically insoluble in water but soluble in dilute acid.

$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + CO_2$

It was noticed that calcium carbonate sank to the bottom of the lake, probably due to its insolubility in water and the lack of mixing action. To make the neutralizing process more efficient, a pumping system was set-up to pump water from the lake into a basin (1 m^3) where the calcium hydroxide was applied and the neutralized water returned to the lake.

$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2\ H_2O$

Liquid pools found in the soil were first pumped out and collection trenches were dug (1 m deep). Time was allowed to let remaining free liquid accumulate in that trench and the liquid was pumped again. Upon removal of most of the free liquid, sodium bicarbonate was applied and the soil lightly mixed.

$2\ NaHCO_3 + H_2SO_4 \rightarrow Na_2SO_4 + 2\ H_2O + 2CO_2$

The neutralizing substances were selected on the basis of cost and availability. Treatment of water spills should be limited to the use of weak bases such as bicarbonate, sodium carbonate and calcium carbonate. (W. Unterberg et al.)

Although calcium carbonate reacts slower than sodium based agents (poor solubility, see Table 8), it has some advantages for use in neutralizing water spills: it produces carbon dioxide which helps mixing and complete the reaction, calcium and carbonate are naturally present in water and do not add toxics to the water. It has a maximum pH of 9.4 (even if overdosing) and is readily available. Sodium bicarbonate can also be used without a large increase in pH (maximum pH 8.3). Sodium carbonate solutions, however, can bring the pH up to 11.6. The following table lists the solubility of four

Table 7 - Quality control analyses

Date	Sample identification	Source	EC pH	EC conductivity	EC sulphates (mg/L)	MEF pH	MEF cond	MEF sulphates
			Horiba	Horiba	`Hach DR/2000	Hach	Hach	Hach DR/2000
26-Jan	W12	EC	3.74	0.085	25	3.4	0.152	26
27-Jan	27/0910	EC	4	0.25	>75 (dilution 1/50 == 3)	4.1		
27-Jan	Ext ouest apres chaulage #12		3.1	0.305	65			
27-Jan	#20	MEF	2.5	1.72	>75 (dilute 5 in 25 == 72 or 360)	2.3		
	repeat	MEF			dilute 2.5 in 25 (33 or 330)			
28-Jan	#16 (centre lac apres chaulage)		3.32	0.217		3.3		
29-Jan	ouest @ 9'	MEF	3.32	0.219		3.3		
repeat	ouest @ 9'	MEF	3.42	0.305				
29-Jan	pres du deversement @ 8'	MEF	3.91	0.122		4		
repeat	pres du deversement @ 8'	MEF	4.04	0.13				
30-Jan	centre 10	MEF	3.57	0.143		3.6		
repeat		MEF	3.8	0.14				
30-Jan	centre 9	MEF	3.78	0.172		3.6		
repeat		MEF	3.56	0.148				
30-Jan	Ext ouest 2	MEF	4.94	0.053		4.8		
31-Jan	pres deversement 9	MEF	3.81	0.111		4		

neutralizing substances in cold water.

Table 8 - Solubility of neutralizing agents in cold water

Compound	solubility in cold water (g/100 mL)
Na_2CO_3	7.1
$NaHCO_3$	6.9
$CaCO_3$	0.0014
$Ca(OH)_2$	0.185

Laboratory scale test

The ESD laboratory conducted some tests to estimate the amount of sodium bicarbonate required to neutralize soil soaked with acid. A 250 mL sample was used and the following amounts were added, pH values are in brackets: 21.1g (pH 0-1), 24.1g (no pH measured), 21.4g (pH 1-2), 30.2 g (pH 2), 40.6 g (pH 2-3), 39.8 g (pH not measured), 49.9 g (pH 9-10). The reaction is exothermic: bubbles were formed, indicating liberation of carbon dioxide and the volume of soil appeared to increase. After these additions, the soil was quite dry and 200 mL of deionized water was added to ensure the reaction had gone to completeness. The soil became too basic so 250 mL of acidic soil were added. Subsequently, 36.6 g, 10.6g, 100 mL water (pH 1-2), 10.5 g (pH 2), 13.2 g (pH 6-7) and 100 mL water (pH 6-7) were added. Neutralization was complete. The final amounts were 261.4 g of sodium carbonate per 500 mL soil or 520 kg Na_2CO_3/m^3 soil.

The above experiment indicates that Na_2CO_3 only is not sufficient to neutralize the soil, water is required to ensure completion of reaction. Application of neutralizer on soil would be more efficient in a solution form than in powder form. However, melting of the snow should favor complete neutralization.

Conclusion

The analytical equipment contained in the ESD laboratory was efficient and fast in providing answers to the various questions raised by EC Quebec region, the MEF, CN and the consultant. The pH paper, combined with a handheld pH meter, is a useful and reliable screening tool and can provide the appropriate data. The Horiba U-10 probe operated very well at temperatures down to 1.1°C. The multiple tests and instruments used on the samples showed that alternate methods such as conductivity meter, titration and colorimetric reactions can be used and produce reliable analytical results. Measurement of conductivity, sulphate content and titrations were shown to be efficient complementary field tools (at $pH>5$ for sulphate and $pH>1$ for conductivity). However, soil analysis can be a complex process as the soil types vary and the analyte has to be extracted prior to analysis. The nomogram, as published in the EnviroTIPS manuals, used to estimate final concentration of the lake versus volume spilled proved to be a good tool.

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1994 EMERGENCY RESPONSE TO DUMPING OF DDT CANISTERS AT THE BORDER PUMP STATION, RAINY HOLLOW, B.C.

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ABSTRACT

In 1993, a former resident of Haines, Alaska reported to the British Columbia Ministry of Environment, Lands and Parks (BCMELP) that containers of dichlorodiphenyltrichloroethane (DDT) were buried in a dumpsite on the airstrip next to the former Border Pump Station in Rainy Hollow, British Columbia (BC). Preliminary investigations by BCMELP in 1994 confirmed the presence of highly concentrated DDT in one canister located in the Trench. The Province of BC declared the site an Environmental Emergency on September 6, 1994 and thus initiated a full scale emergency response.

Environment Canada retained Golder Associated Ltd. to provide technical assistance for the preliminary environmental assessment and partial remediation of the site. The joint emergency response team faced many challenges in the response that limited the scope of activities. These included the remoteness of the site, the rapidly approaching inclement weather, and the lack of reliable historical data. The results of the investigation along with future work are presented.

INTRODUCTION

The Border Pump Station is located approximately 8 km north of the Canada Customs post at Pleasant Camp, BC in the Tatsheshini-Alsek Wilderness Park and World Heritage site and adjacent to the Klehini River that is upstream of the Chilkat Eagle Preserve. The site is also within the traditional territories of the Champagne and Aishihik First Nations.

The pump station began operation in about 1954 as part of a transborder pipeline facility that transported petroleum products from Haines, Alaska to Fairbanks, Alaska. The pump station ceased operation in the early 1970's and some of the infrastructure was dismantled at that time. Since then, there have been several interim users of the site for mineral exploration and highway construction camps.

In 1993, a former resident of Haines, Alaska reported to BCMELP that containers of DDT were buried in a dumpsite on the airstrip next to the former Border Pump Station in Rainy Hollow, BC. Preliminary investigations by BCMELP in August 1994 confirmed the presence of highly concentrated DDT in one canister located in the Trench. The Province of BC declared the site an Environmental Emergency on September 6, 1994 and thus initiated a full-scale emergency response.

OBJECTIVES

1. To locate and excavate the buried DDT canisters and other potentially hazardous materials, and remove them from the site for treatment at a permitted facility in the United States.

2. To conduct a preliminary site assessment to determine the extent of DDT and hydrocarbon contamination in the soil and groundwater around the lower bench of the Border Pump Station.

OPERATIONAL CONSTRAINTS

The joint emergency response team faced many challenges that limited the scope of response activities. These included the remoteness of the site, the rapidly approaching inclement weather (creating a 15 day window of opportunity), and the lack of reliable historical data. The execution of the field excavation program was also hindered because of uncertainties associated with the contents of the Trench and health and safety concerns.

PRELIMINARY SITE ASSESSMENT

A ***geophysical reconnaissance survey*** was conducted from September 13-17, 1994 on the lower bench area around the former air strip that serviced the Border Pump Station using a combination of electromagnetic, magnetic and ground penetrating radar techniques. This non-intrusive investigation program was used to delineate the limits of the Trench (which is defined as the identified dumpsite used to bury the 40 DDT canisters and other debris) and to identify anomalous zones and hence areas of potential environmental concern at the airstrip. On-site field investigation and plotting of the data enabled the results of the survey to be used as a real time guide for excavation work at the Trench. The survey identified several areas that are inferred to be local refuse dumps where metallic debris exists, a culvert and a utility area near the former water supply pump house.

A ***biological reconnaissance survey*** was conducted on September 22-23, 1994 to assess and characterize the fish habitats and fish species composition in the Klehini River. The concentration of DDT and its metabolites dichlorodiphenyldichloroethylene (DDE) and dichlorodiphenyldichloroethane (DDD) in the fish samples collected for tissue analysis were less than the method detection limit of 0.002 ug/g (ppm) for each isomer.

A ***historical survey*** identified, but did not confirm the presence of, the following principal contaminants of concern (PCOC): chlorinated pesticides (DDT, DDE, DDD, Agent Orange), hydrocarbons (petroleum products, fuels), volatile organic compounds (carbon tetrachloride, degreasers) and metals (as a result of the use of chemicals and products).

PROPERTIES OF SELECT PCOC

The main focus of the 1994 investigations was the potential environmental impacts of DDT at the site. DDT was used in enormous quantities worldwide as a pesticide primarily due to its reasonable cost and effectiveness. Its use was banned in the United States in 1973, after studies linked it to population declines in fish-eating birds. The persistence of DDT and DDE in the environment and their bioaccumulation in the food chain (due to a buildup of fatty tissue of animals) are of particular concern.

DDT and its metabolites are all toxic by ingestion, inhalation and skin absorption. They are normally white crystalline solids at room temperature. The solubility of DDT, DDE and DDD in water at normal temperatures is extremely low at 3.4 ug/L, 40 ug/L and 16 ug/L respectively. The solubility of these substances increases dramatically when mixed with hydrocarbons. DDT is highly adsorbed to organic matter in soils

Agent Orange is a toxic herbicide and defoliant containing primarily 2,4,5-trichlorophenoxy-acetic acid (2,4,5-T) and 2,4-dichlorophenoxyacetic acid (2,4-D). Its use has been restricted. Agent Orange is essentially insoluble in water and soluble in alcohol.

SUB-SURFACE INVESTIGATION

The sub-surface investigation program consisted of 16 test pits and 13 well points installed during the period from September 20-28, 1994. Test pits were chosen as an investigative tool due to the flexibility, mobility and availability of excavation equipment. Test pits would allow sampling of the entire soil cross section from the surface to the water table. Well points were installed to enable sampling of groundwater from the Trench. The presence of boulders and cobbles underlying the airstrip prevented the driving of well points into the ground using drill rigs. Consequently, a backhoe was used to excavate through the soil/boulder zone to the water table, followed by the installation of a well point at the base of the excavation and backfilling of the excavation to hold the plastic casing in place. Please refer to Figure 1 for location of test pits and well points.

Sampling

Priority soil samples were sent to the State of Alaska's Environmental Conservation Laboratory in Juneau and analyzed for DDT by an Environment Canada analyst. All other samples were analyzed at the Environment Canada Laboratory in West Vancouver, B.C. and the Pacific Environmental Science Centre in North Vancouver, B.C.

Analysis

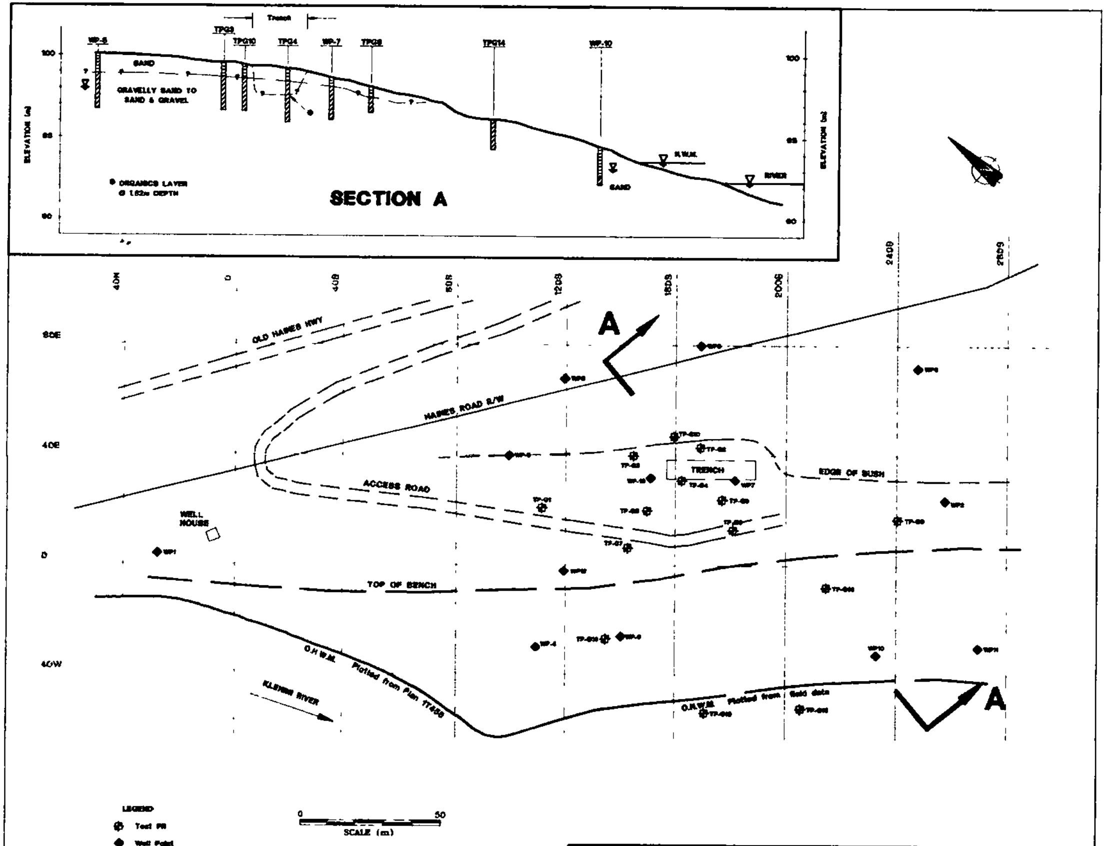
At the State of Alaska Laboratory, a modified Environment Canada method was used to analyze the DDT isomers and metabolites DDD and DDE. At the Environment Canada Laboratories, the EC DDT V-1.0 Method was used. Other chlorinated hydrocarbons, such as PCBs and Agent Orange were analyzed by high resolution gas chromatography with electron capture detector using EC PCB V-3.2 and EPA 8150 Methods respectively.

The concentration of hydrocarbons were determined by InfraRed using the EC O&G V-2.2 Method. The concentration of petroleum hydrocarbons were determined by high resolution gas chromatography with flame ionization detection using EC HCID V-3.3 Method.

The concentration of volatile organic compounds (such as BTEXs) were determined by static headspace high resolution gas chromatography with mass spectrometer using EC VOC V-1.0 and EC BTEX V-1.0 Methods. The VOC and BTEX analyses for soils may have been compromised due to lengthy sample storage times, lack of preservation at the Juneau lab, and in some cases the presence of headspace air volumes in sample jars.

The concentration of polyaromatic hydrocarbons (PAHs) were determined by gas chromatography with mass spectrometer using EC PAH V-1.1 Method.

A metal scan was conducted on select samples using an inductively coupled argon plasma. EC ICP Metals Water V-2.7 and EC ICP Metals Sediment V-3.9 Methods were used for the metal analysis.



TEST PIT & WELL POINT LOCATIONS
BORDER PUMP STATION INVESTIGATION
RAINY HOLLOW, BRITISH COLUMBIA

Golder Associates

Figure 1

REGULATORY CRITERIA

The subject site is located in a B.C. Provincial Park and World Heritage Site where wildlife frequent. The site is adjacent to the Klehini River which is frequented by fish. The potential exists for chum salmon, chinook, coho, Dolly Varden char, cutthroat trout, steelhead, sculpins and white fishes to use the Klehini River for spawning. The population of eagles in the Alaska Chilkat Eagle Preserve located along the Chilkat River, downstream of the Klehini confluence reportedly developed in response to the late fall run of chum salmon that occurs from late September through January. It is also reported that some Alaskans draw water from the Chilkat River.

The following numerical screening criteria were used to assess response and remediation requirements. The relevant criteria are shown on the three tables containing the analytical results.

CCME; *"Interim Canadian Environmental Quality Criteria for Contaminated Sites"*, 1991. This report provides numerical limits for contaminants in soil for various land uses (agriculture, residential/parkland,and commercial/industrial) and in water for various purposes (freshwater aquatic life, irrigation, livestock watering and drinking water).

BC Environment (BCE); *"Draft Part 2 Contaminated Sites Regulation of the Waste Management Amendment Act"*, 1994. This draft document provides similar numerical standards for soils and groundwater based on the different uses.

BC Environment (BCE); *"Criteria for Managing Contaminated Sites in British Columbia (CMCS)"*, Draft 6, June 1989. This document provides numerical criteria for soils and groundwater based on land uses and is in current use in BC for investigating and planning remediation at contaminated sites. This draft document will likely be preceded by the Contaminated Sites Regulation of the Waste Management Act if it becomes law.

RESULTS OF WATER ANALYSIS

The water samples were analyzed for DDT+ (DDT, DDD, & DDE), BTEX, VOC, O&G, HC, PAH and metals. DDT+ was obviously analyzed due to the presence of canisters containing DDT. The analysis for BTEX, VOC, HC, O&G, PAH and metals were conducted on select samples as indicators of the presence of fuel, lubricants, waste oils and crude oil.

Table 1 shows the record and analysis of well point water samples. The CCME or BCE criteria for drinking water and livestock are also noted on this table. These criteria provide an indication of potential impacts on the groundwater resources in this part of the site.

The pH of the groundwater measured in the field ranged from 6.35 to 7.35 and the groundwater temperature ranged from 4.5 to 6.1°C. The field electrical conductivity readings range from 242 to 494 uS/cm over the site, which indicates a relatively low total dissolved solids content and freshwater as would be expected for the groundwater at this site.

The concentration of DDT in groundwater ranged from less than the detection limit of 0.1 ug/L to as high as 6.12 ug/L in WP-13. The latter value exceeds the solubility limit of DDT which suggests the presence of a hydrocarbon carrier for the DDT. None of the groundwater samples exceeded the drinking water criteria of 30 ug/L; however, many exceed the aquatic life criteria of 0.001 ug/L. The concentration of DDT+(DDT, DDE & DDD) was highest in WP-9 at 9.11 ug/L.

The concentration of hydrocarbons in groundwater ranged from less than detection limit (0.2 mg/L) to as high as 33 mg/L. The concentration of total BTEXs ranged from less than the detection limit (1.0 ug/L) to as high as 231 ug/L in WP-7 which is immediately adjacent to the Trench. This highest level is below the drinking water criteria of 331 ug/L; however, the ethylbenzene concentration of 40 ug/L exceeds the drinking water criteria of 2.4 ug/L. The concentration of VOCs were below the various detection limits. The groundwater samples that were analyzed for PAHs were all below the various detection limits.

The groundwater samples were analyzed for many dissolved metals; however, only the analyses of iron and manganese are shown as only these metals were present in concentrations exceeding drinking water criteria.

The concentration of DDT, DDE and DDD in the fish samples collected for tissue analysis were less than the method detection limit of 0.002 ug/g (ppm) for each isomer. Interestingly, the detection limit of 0.002 ug/g is higher than the fresh water aquatic life criteria.

TABLE 1. WELL POINT WATER SAMPLE ANALYSIS

Sample Number	DDT (ug/L)	DDE (ug/L)	DDD (ug/L)	BTEX (ug/L)	VOC (mg/L)	O&G (mg/L)	HC (mg/L)	PAH (ug/L)	Fe (ug/L)	Mn (ug/L)	Water elev.(m)
Drink. water crit.	30	NC	NC	331	50 (TCE)	NC	NC	0.01 (BaP)	300	50	
Livestock crit.	NC	NC	NC	NC	NC	NC	NC	NC	NC	NC	
Det.limit (DL)	0.05	0.05	0.05	1	various	0.2	0.2	various	7	??	
WP-1	0.62	0.17	0.31	<1.0	NA	<DL	<0.2	NA	0	100	98.530
WP-2	<0.05	<0.05	<0.05	<1.0	<DL	<DL	<0.2	NA	900	1800	96.084
WP-3A	<0.05	<0.05	<0.05	<1.0	<DL	<DL	35.1	NA	2600	1400	96.679
WP-3B	<0.05	<0.05	<0.05	<1.0	<DL	<DL	30.6	NA	4800	1400	96.679
WP-3ave	<0.05	<0.05	<0.05	<1.0	<DL	<DL	32.9	NA	3700	1400	96.679
WP-4	<0.05	<0.05	<0.05	<1.0	<DL	<DL	<0.2	NA	NA	NA	94.446
WP-6	<0.05	<0.05	<0.05	NA	NA	<DL	<0.2	NA	NA	NA	96.625
WP-7A	1.93	0.41	1.48	231*	<DL	<DL	13.9	<DL	13200	2100	96.640
WP-7B	1.63	0.37	1.27	213*	<DL	<DL	17.0	<DL	13400	2200	96.640
WP-7ave	1.78	0.39	1.37	222*	<DL	<DL	15.4	<DL	13300	2150	96.640
WP-8	0.09	<0.05	0.06	<1.0	<DL	<DL	<0.2	NA	100	<1	96.844
WP-9	2.16	0.17	6.78	<1.0	<DL	<DL	27.2	<DL	500	2600	93.905
WP-10	2.21	0.22	0.83	<1.0	<DL	<DL	28.4	NA	100	1900	92.540
WP-11	0.43	0.25	0.14	<1.0	<DL	<DL	1.2	<DL	100	100	94.688
WP-12	3.25	0.51	2.09	<1.0	<DL	<DL	<0.2	NA	100	200	96.251
WP-13	6.12	0.52	1.91	<1.0	<DL	<DL	18.7	<DL	4000	1400	96.577

where
NC = no criteria established
NA = not analyzed
NM = not measured
* ethylbenzene is 20 ug/L which exceeds CCME drinking water criteria of 2.4 ug/L
WP-5 = not analyzed since sample bottle was broken
ug/L = ppb

RESULTS OF SOIL ANALYSIS

The soil samples were analyzed for DDT+ (DDT, DDE & DDD), hydrocarbons (HC), BTEX, oil and grease (O&G), volatile organic compounds (VOCs). DDT+ was obviously analyzed due to the presence of canisters containing DDT. The analysis for HC, O&G, BTEX and VOC were conducted on select samples as indicators of the presence of fuel (e.g, gasoline, kerosene), lubricants, waste oils and crude oil. Xylene was specifically analyzed as it was thought to be the hydrocarbon carrier for the DDT. Subsequently, methanol (with small amounts of xylene) was determined to be the hydrocarbon carrier for DDT.

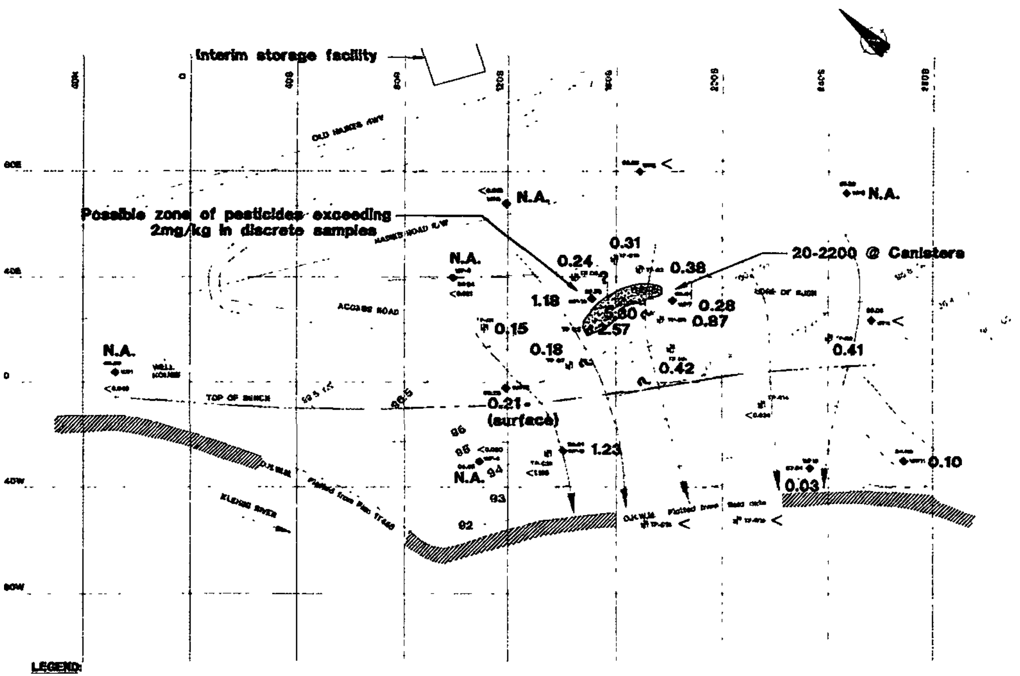
Table 2 shows the record and analysis of test pit soil samples. The concentration of total BTEXs, VOCs, HC and O&G were less than their respective detection limits. The analysis for BTEXs and VOCs may be somewhat compromised due to the lengthy sample storage time and unavoidable head space (as small volume was removed for priority DDT analysis) in sample jars.

The concentration of DDT+ (DDT, DDE & DDD) ranged from less than the detection limit of 0.012 ug/L to as high as 5.30 ppm in TP-G4SA4. The field OVM readings ranged from below the detection limit to as high as 985 ppm in TP-G8SA3. The high OVM readings indicate the presence of hydrocarbons. This would contradict the laboratory analytical results. Figure 2 shows the highest soil

TABLE 2. TEST PIT SOIL SAMPLE ANALYSIS

Sample Number	Depth	OVM (ppm)	Analytical Results (ppm)				
			DDT+	HC	O&G	BTEX	VOC
Res./park crit.			2*	150	1000	13.5	NC
Det.limit (DL)			<0.012**	<5	<0.5	<10	various
TP-G1SA1	0.61-1.10 m		0.15				
TP-G1SA2	2.13-2.44 m						
TP-G2SA1	0.13 - 0.25 m		INC			<10	<50
TP-G2SA2	0.36 - 0.56 m		<0.371			<10	<50
TP-G2SA3	0.61 - 1.22 m		1.339			<10	<50
TP-G2SA4	1.22 - 1.83 m		<0.050			<10	<50
TP-G2SA5	2 44 - 2.74 m		0.38	<5	<0.2	<10	<50
TP-G3SA1	0.30 - 0.61 m		INC			<10	
TP-G3SA2	0.61 - 0.76 m		INC			<10	
TP-G3SA3	0.76 - 0.91 m		<0.014			<10	
TP-G3SA4	1.52 - 1.83 m		<0.015			<10	
TP-G3SA5	2.44 - 2.74 m		0.24	<5	<0.2	<10	<50
TP-G4SA1	0.15 - 0.31 m	20	2.47	<5	<0.2	<10	<50
TP-G4SA2	0.31 - 0.66 m	5.5	0.29				
TP-G4SA3	0.91 - 1.37 m	137	0.33				
TP-G4SA4	1.68 - 1.98 m	665	5.30	<5	<0 2	<10	<50
TP-G4SA5	2.74 - 3.05 m	859	0.59	<5	<0.2	<10	<50
TP-G5SA1	0.15 - 0.25 m	42	0.14				
TP-G5SA2	0.41 - 0.61 m	185	0.70				
TP-G5SA3	0.91 - 1.22 m	142	1.94				
TP-G5SA4	1.83 - 2.13 m	35	2.57	<5	<0.2	<10	<50
TP-G5SA5	2.59 - 2.90 m	108	0.54	<5	<0.2	<10	<50
TP-G6SA1	0 15 - 0.46 m	175	0.15				
TP-G6SA2	0.76 - 1.07 m	807	0.27				
TP-G6SA3	1.22 - 1.52 m	315	0 87				
TP-G6SA4	1.83 - 2 13 m	855	0.72			<10	<50
TP-G6SA5	2.74 - 3.05 m	794	0 43	<5	<0.2	<10	<50
TP-G7SA1	0.15 - 0.30 m	<DL	0.16				
TP-G7SA2	0.61 - 0 91 m	<DL	0 18				
TP-G7SA3	2.13 - 2.44 m	385	0.11	<5	<0.2	<10	<50
TP-G8SA1	0.15 - 0.25 m	258	0.19				
TP-G8SA2	0.30 - 0.61 m	895	0.14				
TP-G8SA3	1 37 - 1.52 m	985	0.42	<5	<0.2	<10	<50
TP-G9SA1	0.15 - 0.25 m	<DL	<0.476				
TP-G9SA2	0.30 - 0.61 m	7.1	<0.023			<10	<50
TP-G9SA3	1.37 - 1.68 m	8.7	0.41	<5	<0 2	<10	<50
TP-G10SA1	0.15 - 0.61 m	<DL	0 19				
TP-G10SA2	0.91 - 1.22 m	5.5	0 11				
TP-G10SA3	2.44 - 2.74 m	13.5	0.31/0.21	<5	<0.2	<10	<50
TP-G11SA1	0.30 - 0.61 m	<DL	INC	INC		<10	<50
TP-G11SA2	1.52 - 1.83 m	<DL	INC	INC		<10	<50
TP-G12SA1	0.61 - 1.22 m	<DL		INC		<10	<50
TP-G12SA2	2.74 - 3.05 m	<DL		INC		<10	<50
TP-G13SA1	0.61 - 0.91 m	<DL	<0 012	INC		<10	<50
TP-G13SA2	1 52 - 1.83 m	<DL	<0 012	INC		<10	
TP-G14SA1	0 61 - 0.91 m	35.7	<0.034	INC		<10	
TP-G14SA2	1.52 - 1.83 m	617	<0.020	INC		<10	
TP-G15SA1	0.30 - 0.61 m	<DL	<0.012	<5	<0.2		<50
TP-G15SA2	0.91 - 1.22 m	<DL	<0.012	<5	<0.2		<50
TP-G16SA1	0.30 - 0.61 m	<DL	<0.012	<5	<0.2		
TP-G16SA2	0.91 - 1.22 m	<DL	<0.012	<5	<0.2		

where INC = analysis is incomplete
DDT+ = sum of DDT, DDE & DDD
* = criteria for total pesticides
**DL for DDT+ (Environment Canada) = 0.012 ppm (0.002 ppm for each of the DDT, DDE & DDD isomers)
DL for DDT+ (State of Alaska) = 0.06 ppm



LEGEND:

▨ Possible area of DDT > 2mg/kg at approx. depth of water table.

⊕ 0.18 Total DDT, DDE and DDD (DDT+) in mg/kg

0 30
SCALE (m)

NOTES:

- Highest concentration shown from test pit samples
- "<" indicates below method detection limit
- "N.A." indicates analysis not available

Golder Associates

DDT CONCENTRATION IN SOILS
BORDER PUMP STATION INVESTIGATION
RAINY HOLLOW, BRITISH COLUMBIA

Figure 2

concentrations of DDT+ (DDT, DDE & DDD) observed in each test pit and well point indicated.

Table 3 shows the record and analysis of well point soil samples. The concentration of total BTEXs and VOCs were less than their respective detection limits. The concentration of HC and O&G ranged from below the detection limit to as high as 1837 ppm in WP7-SA2. The high OVM readings indicate the presence of hydrocarbons. This would contradict the laboratory analytical results.

The concentration of DDT+ (DDT, DDE & DDD) ranged from less than the detection limit of 0.012 ug/L to as high as 1.23 ppm in WP9-SA3. The OVM readings ranged from below detection limit to as high as 869 ppm in WP3-SA3. The presence of Agent Orange was not detected in the samples for which it was analyzed.

PARTIAL REMEDIAL RESPONSE

Excavation

CEDA Reactor Ltd. of Edmonton, Alberta assisted in the emergency response activities with their trained personnel. A site health and safety plan was developed that indicated the level of personal protection (A, B, C or D) that was required for various activities in the Exclusion Zone. Kluhane Construction of Haines Junction, Yukon supplied and operated a backhoe and D4-dozer to support CEDA and remove the more highly contaminated soil and debris from the Trench under the guidance of Environment Canada and British Columbia Environment. Arctic Backhoe Services Ltd. of Whitehorse, Yukon also supplied a track mounted excavator and two dump trucks. Arctic contractors did not work in the Exclusion Zone until after the canisters had been removed and the level of personal protective equipment was down graded to level C.

One crushed canister was discovered on September 5, 1994 and one full canister was discovered on September 6, 1994 during the excavation of a selected portion of the airstrip. The subsequent analysis confirmed that the canisters contained high concentrations of DDT+ in a hydrocarbon carrier. The soils excavated during that activity were stockpiled next to the Trench. The soils were also analyzed and contained concentrations of DDT+ ranging from 0.92 to 23 mg/kg.

Twenty eight canisters were discovered on September 18, 1994 and an additional ten canisters were discovered on September 19, 1994. All forty canisters were placed in overpack drums as they were removed from the Trench. The other hazardous wastes (e.g., transformer oil, possible PCB contaminated material, soil highly contaminated with DDT) encountered during this activity were also packaged appropriately.

TABLE 3. WELL POINT SOIL SAMPLE ANALYSIS

Sample Number	Depth	OVM (ppm)	Analytical Results (ppm)				
			DDT+	HC	O&G	BTEX	VOC
Res./park crit.			2*	150	1000	13.5	NC
Det.limit (DL)			<0.012	<5	<0.5	<10	various
WP1-SA1	0.61 - 0.91 m	<DL	<0.034				
WP1-SA2	2.29 - 2.59 m	<DL	<0.043				
WP1-SA3	2.90 - 3.20 m	<DL	<0.029	<5		<10	<50
WP2-SA1	0.46 - 0.76 m	<DL	<0.012	<5	<0.2	<10	<50
WP2-SA3	0.91 - 1.22 m	<DL	<0.012	<5	<0.2	<10	<50
WP2-SA3	1.80 - 2.13 m	<DL	<0.012	<5	<0.2	<10	<50
WP3-SA1	0.46 - 0.76 m	86.9	<0.012	<5	<0.2	<10	<50
WP3-SA2	1.22 - 1.52 m	383	<0.012	<5	<0.2	<10	<50
WP3-SA3	2.29 - 2.59 m	869	<0.012	431	436	<10	<50
WP3-SA4	3.20 - 3.51 m	730	<0.012	147	150	<10	<50
WP4-SA1	0.05 - 0.20 m	8.7	<0.020	INC		<10	<50
WP4-SA2	0.61 - 0.91 m	2.3	<0.014	INC		<10	<50
WP4-SA3	1.68 - 1.98 m	<DL	<0.015	INC		<10	<50
WP5-SA1	0.20 - 0.41 m	<DL	< 0.015	INC		<10	<50
WP5-SA2	0.61 - 0.91 m	<DL	< 0.015	INC		<10	<50
WP5-SA3	1.22 - 1.68 m	2.3	<0.013	INC		<10	<50
WP5-SA4	2.29 - 2.74 m	8.7	<0.014	INC		<10	<50
WP5-SA5	3.05 - 3.35 m	346	<0.012	INC		<10	<50
WP5-SA5	3.05 - 3.35 m	346	INC	INC		<10	<50
WP6-SA1	0.15 - 0.25 m	<DL	INC	INC		<10	<50
WP6-SA2	0.61 - 1.22 m	2.3	INC	INC		<10	<50
WP6-SA3	1.52 - 1.83 m	<DL	INC	INC		<10	<50
WP6-SA4	2.13 - 2.44 m	<DL	INC	INC		<10	<50
WP7-SA2	1.07 - 1.37 m	762	<0.012	1837	1837	<10	
WP7-SA3	2.13 - 2.44 m	709	0.28	300	300	<10	
WP8-SA1	0.15 - 0.30 m	<DL	<0.020			<10	<50
WP8-SA2	0.91 - 1.22 m	<DL	<0.014			<10	<50
WP8-SA3	2.13 - 2.44 m	<DL	<0.021			<10	<50
WP8-SA4	3.35 - 3.66 m	<DL	<0.012			<10	<50
WP9-SA1	0.08 - 0.15 m	24.6	<0.012	<5	<0.2	<10	<50
WP9-SA2	0.30 - 0.61 m	53.7	<0.012	<5	<0.2	<10	<50
WP9-SA3	1.06 - 1.52 m	859	1.23	387	387	<10	<50
WP10-SA1	0.08 - 0.25 m	75.5	<0.012	16	16	<10	<50
WP10-SA2	0.30 - 0.76 m	85.1	0.03	<5	7	<10	<50
WP10-SA3	1.07 - 1.52 m	210	<0.012	107	175	<10	<50
WP10-SA4	1.72 - 183 m	7.1	<0.012	<5	<0.2	<10	<50
WP10-SA5	1.98 - 2.29 m	210	<0.012	<5	37	<10	<50
WP11-SA1	0.30 - 0.91 m	<DL	0.06	8	8	<10	<50
WP11-SA2	1.52 - 1.83 m	<DL	0.02	5	8	<10	<50
WP11-SA3	2.74 - 3.05 m	<DL	0.10	16	16	<10	<50
WP12-SA1	0.15 - 0.56 m	<DL	0.212	7	10	<10	<50
WP12-SA2	0.69 - 0.91 m	18.2	<0.012	<5	<0.2	<10	<50
WP12-SA3	1.22 - 1.83 m	<DL	<0.012	<5	<0.2	<10	<50
WP12-SA4	2.74 - 3.05 m	2.3	<0.012	6	6	<10	<50
WP12-SA5	3.96 - 4.27 m	<DL	0.014	<5	<0.2	<10	<50
WP13-SA1	0.05 - 0.20 m	116.9	1.183	1334	1395	<10	<50
WP13-SA2	0.41 - 0.60 m	126.4	<0.012	<5	<0.2	<10	<50
WP13-SA3	0.90 - 1.22 m	115.7	<0.012	<5	<0.2	<10	<50
WP13-SA4	1.80 - 2.44 m	361	0.01	74	74	<10	<50
WP13-SA5	3.20 - 3.35 m	298	0.061	118	118	<10	<50

where INC = analysis is incomplete
DDT+ = sum of DDT, DDE & DDD
* = criteria for total pesticides
**DL for DDT+ (Environment Canada) = 0.012 ppm (0.002 ppm for each of DDT, DDE & DDD isomers)
DL for DDT+ (State of Alaska) = 0.06 ppm

All hazardous wastes identified in Table 4 were shipped, according to regulation, for disposal to the United States after approval was obtained from the U.S. EPA, EC and BCMELP. The hazardous wastes were shipped, by Philip Environmental Services Ltd., to a facility operated by Burlington Environmental Limited of Aragonite, Utah (U.S.) where they were to be incinerated.

Other wastes including metals, tires, construction debris and so forth were sampled for the PCOC and found to be non-contaminated. These wastes were placed in a shipping container (approximately 30' x 8' x 8') and subsequently disposed of in an approved sanitary landfill.

A polyethylene membrane (e.g., an Arctic 30 liner) was placed in the excavated Trench and was backfilled with surface materials, including soils ranging in DDT+ concentration from 0.22 to 0.62 mg/kg. A reinforced polyethylene membrane line (e.g., RPE15) cover was placed over the backfilled materials to prevent further infiltration. A snow fence was installed to inhibit wildlife and park visitors from walking through the area.

TABLE 4. SUMMARY OF HAZARDOUS WASTES SHIPPED
TO U.S. FACILITY FOR DISPOSAL

Type of Hazardous Waste	Number of drums
DDT Lab Packs	14
DDT Washwater	6
DDT Drummed Solids	2
DDT Contaminated Soil	2
DDT Contaminated Drums (empty)	10
PCB Contaminated Material	1
Transformer Oil	1 pail
Unknown Solids (potentially contaminated)	2
Canisters of DDT (5 US gallons)	Number of canisters
Full When Recovered	33
Partially Empty (damaged when buried)	5
Partially empty (damaged during recovery)	2
Total number of canisters recovered	40

Temporary Storage Facility

A temporary storage facility was constructed on the upper bench about 30 m east of the old Haines Highway. The location was selected in an area which was relatively flat, free of boulders, and sufficiently wide to permit all of the soils to be managed in one facility. The location of the area is also above the flood plain for the Klehini River. The northern portion of the pad is underlain by a polyethylene liner of 30 millimetre thickness which was the only material immediately available. The southern portion of the pad was later underlain by a reinforced polyethylene liner (e.g., an Arctic 30 liner).

After removal of the debris from the stockpiles, approximately 550 m^3 of silty sand and some gravel were hauled by truck from the Trench area to the Temporary Storage Facility and end-dumped at the edge of the pad.
The concentration of DDT and its metabolites in the temporary storage facility varied from 4.8 to 35.8 mg/kg which exceeds the BCE criteria for total pesticides of 2 mg/kg for park or residential land uses. Berms were constructed to prevent surface water from running onto the pad area. Two 24' x 80' RPE15 covers were laid on top of the pile so that the edges were covered, leaving a two-foot gap along the centreline of the pile. A 40' x 80' RPE15 cover was placed on top to provide a double layer over the majority of the materials. The Temporary Storage Facility was subsequently enclosed within a chain linked fence, and the tarps tied down to the fence posts. The fence gate was locked and signs posted at the site to notify park visitors of site conditions.

CONCLUSIONS

The objectives of the emergency response activities were met as the buried DDT canisters were located and removed from the site; and a preliminary assessment of the extent of DDT and hydrocarbon contamination on the site was conducted.

Forty canisters containing pesticides and the more highly contaminated soil (in the immediate vicinity of the canisters) were removed from the Trench between September 6-24, 1994. The canisters and highly contaminated soil were transported off-site for disposal at a permitted facility in the USA.

The remaining contaminated soils and debris (approximately 550 m^3) in the Trench were excavated and stockpiled at the Temporary Storage Facility located on the Upper Bench of the Border Pump Station.

The groundwater samples analyzed for DDT and its metabolites were below the CCME or BCE criteria for drinking water. The Klehini River water samples and fish tissue samples analyzed were also below the method detection limit for DDT and hydrocarbons.

RECOMMENDATIONS

Supplementary information (e.g., handling and use of chemicals, location of waste storage and disposal) on the history of the site should be obtained from all available sources (e.g., Canadian and American government records, former workers and residents).

Options for the treatment and disposal of the remaining contaminated soils and debris (approximately 550 m^3) should be evaluated. The most feasible option should be selected and implemented.

Potential exposure pathways for contaminants around the Trench should be assessed.

A detailed environmental site assessment should be conducted on the rest of the Border Pump Station site which may result in further site remediation.

ACKNOWLEDGEMENTS

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THE DIVEX EXPLOSIVE SITE
Columbia, South Carolina

by
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INTRODUCTION

On September 6, 1993, Mr. Jack Sutherland, owner of the Divex Corporation, was working alone at his manufacturing facility outside the city of Columbia, SC. Mr. Sutherland was synthesizing a batch of lead styphnate, an explosive initiating compound in a plastic drum. While he was working with this drum, the drum exploded killing Mr. Sutherland.

The initial response to the incident was provided by the Richland County Emergency Management Services(RCEMS) and the South Carolina Department of Health and Environmental Control (SCDHEC). A week after the explosion, an employee of Divex working with SCDHEC and an attorney who was the bankruptcy attorney for Divex, injured his foot in an another explosion at the site. Divex had applied for bankruptcy in the Summer of 1993.

The site is comprised of several locations; a laboratory located in a commercial/residential area near downtown Columbia, the main facility where the initial explosion occurred which is ten miles north of Columbia in a rural/ residential area, and a warehouse located near the Richland County Landfill.

On October 22, 1993, the Emergency Response and Removal Branch of EPA Region IV was notified of the conditions at the laboratory and the main facility by Senator Strom Thurmonds's office through the RCEMS. The RCEMS personnel believed that the measures being used to address the hazards at the laboratory and at the main facility by the bankruptcy attorney and ex employees of the company were inadequate. Also, on October 22, 1993, EPA Region IV learned that the power to both the laboratory and the main facility were going to be shut off. This posed an extreme human health hazard, since 300 vials of 98 - 99 % nitroglycerin were located in a refrigerator, along with other shock, friction and heat-sensitive materials stored at the laboratory site. Also, there was little information known about the materials that were stored at the main facility. An EPA Region IV On-Scene Coordinator (OSC) was dispatched to the incident to assess and manage the various hazards at the main facility and laboratory, since the local and state authorities did not have resources to handle a complex site like Divex.

THE THREAT

The Divex Corporation explosive site possessed an enormous threat to response personnel and the local population. It was determined that the blast radius from the explosive material stored in the laboratory was approximately one quarter of a mile and could have killed, injured, and/or exposed several hundreds to thousands of persons working or living near the laboratory. The laboratory also contained several hundred containers of poison, corrosive, flammable, and other hazardous substances.

The main facility contained tens of thousands of pounds of highly sensitive military ordnance(i.e., personal mines, rockets, initiators fuses, and artillery shells), and high explosives (i.e., PETN, OCTOL, RDX,) which were stored in 23 magazines and trailers. The estimated blast radius from the detonation of this material would be approximately eight miles and would kill or injured thousands of people. The following hazardous material were also stored at the main site facility with the explosives: gas cylinders such as diborane pentaborane, Chlorine trifloride, HCl, and phosgene, low level radioactive material, and drums of flammable,and poisons metals and batches of metal azides and styphnates. None of the drums, reaction vessels, and/or drums were labeled appropriately. The only person who new what was in each drum or trailer was Mr. Sutherland.

HIGHLIGHTS OF THE RESPONSE

The Region IV OSC immediately activated the Regional Response Team (RRT) to obtain support from other Federal agencies, including the Bureau of Alcohol, Tobacco and Firearms (ATF) and Department of Defense (DOD). The first phase of the response occurred at the laboratory facility where an assessment and a removal of highly unstable explosives was conducted by EPA using ATF, and EPA's Emergency Response Cleanup Contractor (ERCS), State, and local officials. All explosive materials from the laboratory were shipped via bomb trailers and exploded at a remote site near Richland County landfill.

In order for EPA to obtain the expertise in disposing and handling the various explosives devices and other materials associated with this response, the OSC developed

Interagency Agreements (IAG's). The IAG's were with the following agencies and for the following purposes: the U.S. Army Corps of Engineers (USACOE) Savannah District for temporary relocations of 16 families who lived near the sites, the ATF Explosives Technology Branch ETB for dedicated resources and expertise in explosives, the U.S. Coast Guard Gulf Strike Team for site safety and preliminary assessment, and the USACOE Huntsville division for packaging and removal of the tens of thousands of pounds of military ordnance and explosives found at the main facility.

Significant removal actions that occurred at this site are highlighted below:

- USACOE Huntsville conducted a detail inventory and repackaging of military ordnance and explosives which were sent to a munitions plant for disposal.
- The ERCS contractor conducted a cleanup and lab packing activities at the warehouse facility.
- Possible shock-sensitive materials chemicals and explosive compounds were removed from the warehouse by the Richland County Bomb Squad, ATF, and ERCS contractor and shipped to the main facility.
- The ERCS contractor performed a known container consolidation and treatment operation at the main facility.
- ATF, Explosive Ordnance Disposal group from Fort Jackson removed and detonated military ordnance and explosives items at Fort Jackson. This included a Dragon anti-tank missile warhead and its components, proximity fuzes, gator mines, and other explosive materials unstable for on-site detonations or transportation to an army ammunition plant for disposal.
- EPA, ERT and ERCS while conducting a hazard characterization of containers in main building were explosion occurred. Small "pops" from unreacted crystals of shock-sensitive materials occurred.
- Large chunks of shock-sensitive material detonated during the remote removal of unknown drums from the main building. The blast was heard 15 miles away. There were no injuries or secondary fires due to the explosion.

- ATF, ERT and the OSC collect wipe samples from the main building, after it was washed with copious amounts of water, to determine which areas may be safe to enter in order to remove containers of hazardous materials that could not be safely burned or detonated. These drums were removed using a pulley system after fire fighting foam was placed on the floor of the main building to decrease friction.

- ATF, with other agency support conducted 45 on-site detonations/enhance burns.

- Explosive waste water and residue was treated on site.

- A flask containing a five pound of barium styphnate crystals was detonated on-site using a wood structured filled with high density foam to control the explosive force.

- Because of explosive residue left in the main building, the main building was burned remotely by ATF.

- Six 300 pounds cylinders of pentaborane are neutralized on site using an alcohol/base hydrolysis reaction. During initial treatment small fires occurred. The process for treatment was changed by keeping cylinders and liquid lines filled with nitrogen. A person working with the cylinders is exposed to pentaborane fumes. Due to the quick actions of the emergency medical personnel for Richland County which have been station at the site during the removal work, the person made a full recovery.

- Other cylinders of hazardous materials were treated on site using specialized equipment and a containment structure.

CONCLUSIONS

The most important lesson learned was cooperation and teaming. No one group or agency was capable of addressing all the different hazards associated with this site. Only through numerous Federal IAGs, several contractors and sub-contractors, and local officials from Richland County, could this site be properly cleaned up without a major release or explosion.

Environment Canada's Role in the Canadian Coast Guard Training Exercise
Corner Brook, Newfoundland
June, 1994

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Summary

During June 1994 a multi-agency marine training exercise took place in Corner Brook, Newfoundland. The Canadian Coast Guard (CCG) Emergency Response Groups from Newfoundland and Maritime Region were the primary organizers. Additional agencies included the Emergencies Science Division, Newfoundland Regional office and Maritime Regional office, all components of Environment Canada and local police and fire departments. The principle objective of the training exercise was to evaluate the ability of the various agencies and emergency response groups from different regions to work together. A significant effort was made by the organizers to impose as many life-like conditions as possible on the training program. These included staging the exercises on board a working ship and public waterfront, setting up a simulated communication line with the captain of the vessel and inviting the local press to report the exercise.

The exercise was held over a three day period. The first and final day were table-top planning and de-briefing sessions respectively while the hands-on training took place throughout the middle day. On the first day (Day 1) the chemical emergency scenario was established. A container vessel, one day outside of port, was caught in a storm and reported possible damage and loss of cargo. The captain of the vessel had contacted port authorities as a precautionary measure, informed them of the uncertain status of the ship's cargo and provided the United Nations chemical identification numbers for all hazardous chemicals listed on the ships manifest. As in the case of a real spill the response personnel were told to set about preparing to respond to a worst case multiple chemical spill situation. Throughout the day work included obtaining additional information, contacting necessary agencies, and testing equipment. On the second day, as per the scenario, the vessel arrived in port. Further reports from the vessel confirmed that some cargo was lost

overboard and there remained a strong possibility of a chemical spill on board the vessel. All response activities were transferred to and carried out port-side. Activities included perimeter and exterior inspections of the ship, personnel in fully encapsulated suits carrying out onboard inspection and an additional response to deal with some cargo which had washed up on the beach. The final day (Day 3) was a debriefing session. The organizers of the exercise had evaluated the performance of all groups and presented their critique. As well, additional training took place to show response personnel how best to maintain records for the purposes of recovering costs from the freight company.

Standard operating procedures have been established by the Federal Government outlining the roles of the various government agencies during emergency response situations. For ship-source marine spills Transport Canada (CCG) is the lead agency and Environment Canada would act as a resource agency. Thus during this exercise the actual donning of protective equipment and site entry actives were carried out by the two CCG teams. Environment Canada's role was to provide technical support to the CCG response teams. Environment Canada's regional offices act as the department's primary contact with the lead government agency. Nevertheless, the scientific staff at the Environmental Technology Centre (ETC) have acquired a significant amount of expertise in this field and are often requested to provide technical, analytical and on-site assistance. During this case ETC-Emergencies Science Division (ESD) staff were on-site to assist the Coast Guard. The following is a list of the tasks carried out by Environment Canada:

- inform and communicate with various government agencies which may be of assistance during the spill. Examples being Canutec (Transport Canada, Ottawa), Atmospheric Environment Services regional weather offices (Environment Canada, St. John's), the National Environmental Emergencies Centre (Environment Canada, Ottawa), the Emergencies Science Division (Environment Canada, Ottawa);
- identification of the chemical name of the compounds from the United Nations numbers;
- obtaining information on the health and safety and environmental concerns related to the chemicals;
- obtain information on the suitability of the CCG protective clothing against the hazards associated with the chemicals. This information had to be summarized and presented to the CCG team leaders;
- assist CCG staff with the set up and evaluation of their person-portable instrumentation;
- evaluate the person-potable analytical instrumentation available on-site and select the most appropriate equipment for entry into the site. Provide a review of the operation of the instrumentation to the site entry team.

The training exercise was an overall success. Many benefits and experience were gained by the participants, not the least of which was an opportunity to work with various public and private agencies.

GUIDELINES FOR THE SAFE MANAGEMENT OF MERCURY SPILLS IN QUEBEC HOSPITALS

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Abstract. In Quebec, medical instruments containing mercury (Hg) are still widely used in hospitals. These are mostly thermometers and sphygmomanometers. Mercury present in these instruments does not in itself constitute a risk of contamination since this metal is contained within a closed system. However, breakage, inadequate maintenance and disposal of such instruments can expose workers and the public to this toxic substance. Only 35% of hospitals recently surveyed have recovery procedures in case of spillage, and most mercury spills are apparently not reported. This paper presents guidelines for the safe management of mercury spills in Quebec hospitals.

1. Introduction

In Quebec, an important quantity of medical instruments containing metallic mercury (Hg) are used in hospitals. These are mostly thermometers and sphygmomanometers. Even if new types of equipment are available, instruments containing Hg are still widely used (Guerrier et al., 1994).

Hg present in medical instruments does not in itself constitute a risk of contamination since Hg is contained within a closed system. However, because metallic Hg is in liquid form at room temperature, it vaporizes when spilled or left in the open and has a tendency to scatter into small droplets when spilled (Lauwerys, 1990). Breakage, disposal or maintenance of an instrument can expose workers and the public to this toxic substance (McNerney, 1988). Futhermore, inadequate management of these Hg wastes can lead to the release of this metal into the environment.

The Centre de toxicologie du Québec (CTQ) has been involved several times in recent years after spills occurred in hospitals and has developed an expertise in Hg recovery procedures (Guillot, 1993).

The Quebec Environmental Health Committe (CSE) cooperates with the CTQ to provide hospitals with guidelines for the safe management of Hg spills.

2. The Present Situation in Quebec

A sphygmomanometer contains between 18 and 30 cc of Hg (between 250 and 400 g). Usually, in a hospital, there is one sphygmomanometer per two beds, as well as one instrument in each examination and operating room. A thermometer normally contains less than 10 g of Hg, depending on its size (normally between 2 and 5 g). There is normally one thermometer for each patient, plus a certain number in circulation.

A recent study, the MER-MED (MERcury in MEDical instruments) (Guerrier, Coté, Paul, 1994) project, has pointed out that 80% of the institutions surveyed use Hg sphygmomanometers and 45% use Hg thermometers. The study also revealed that only 35% of the 28 surveyed hospitals have recovery procedures in case of spillage.

The study also indicated that there are no official guidelines in the Quebec hospital network for recovery, handling and disposal of Hg. The existence of some kind of procedure in one particular hospital is often the result of the initiative of one person in the hospital.

3. Recommended Actions

Until Hg has totally disappeared from hospitals, different courses of actions can be considered for hospitals to reduce the risks of exposure to Hg and contamination of the environment:

- **Inform all hospital personnel about the risks and health problems associated with the handling and the inappropriate disposal of Hg;**
- **Assure the adequacy of disposal methods of Hg: dispose of the Hg recovered from the spill in accordance with all federal, provincial and local hazardous waste disposal regulations and stop sending Hg to medical waste incinerator;**

- **Inform all hospital personnel about procedures for the safe handling of Hg and for the safe management of Hg spills (CSE, CTQ, 1994; Terrene Institute, 1995):**

Prevention

- Hg should be only used or handled in uncarpeted, well-ventilated areas.
- A working area should be reserved for Hg uses only.
- All Hg-containing equipment should be cleaned and calibrated according to the manufacturer's recommended handling procedures.
- Traffic should be restricted in the area.
- Smoking, eating and drinking should be prohibited in the area.

Preparedness

- Workers should remove all watches and other jewelry - especially gold jewelry, since Hg readily combines with gold.
- A Hg vacuum sweeper and spill cleanup kit should be easily accessible.
- Simulation exercises of Hg spills should be carried out.

Response

- Consult experts.
- Evacuation should be considered.
- Contaminated clothes, especially shoes, should be left in the room.
- Heating of the room should be turned off.
- The room should be ventilated.
- For large spills, Hg droplets should be collected with a Hg vacuum sweeper.
- Workers should wear a Hg vapor respirator and protective clothing: gloves, disposable gowns and shoe coverings. Hg droplets cling to clothing, especially knitted fabrics, and to shoe soles - so that workers can easily take this hazard home with them (homes of employees of a thermometer factory were found to have high levels of Hg in the air).
- For smaller spills, Hg droplets can be aspirated with a disposable plastic syringe.
- Adhesive tape strips can also be used to collect Hg droplets.
- Hg droplets can be coated with a chemical that can also be used to react with the Hg to form an amalgam. HgX or sulfur compounds will eliminate Hg vaporization and decontaminate the surfaces affected by the spill.
- Notify the relevant public health department.

Monitoring

- In some cases, even if spilled Hg seems completely recovered, there are often small residual quantities left, particularly if the recovery procedures are not totally efficient. It is therefore important to emphasize that the area where the spill has occured must be monitored. Very often, after a Hg spill has occured, monitoring indicates that other areas have been contaminated because of previous spills, especially if Hg had not been a serious concern before. Hg testing in employee physical examinations should be also considered.

In order to estimate the number of medical instruments containing Hg used and stored in hospitals as well as to facilitate the follow-up of the reduction of the use of this toxic metal, hospitals should:

- **Keep an inventory of all instruments containing Hg (used and stored);**
- **Keep an inventory of the quantities of Hg stored.**

In Quebec, the CSE and the CTQ intend to jointly publish a brochure that would provide hospitals with guidelines to handle and dispose of Hg safely. Similarly, in the USA, the Terrene Institute, of Washington D.C., has been mandated by the U.S. Environmental Protection Agency to produce a brochure that will introduce hospital personnel to the dangers of Hg in the environment, to alternatives for Hg in the health care setting, and to the proper management of used Hg or Hg spills.

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Standard Operating Procedures for Environment Canada Emergency Response Officers

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Abstract

Environment Canada has established Standard Operating Procedures (SOPs) for their Emergency Response Officers so that they can respond to environmental emergencies with a uniform and professional approach. The SOPs cover a wide range of issues due to the complexity of spill response.

Procedures for responding to spills include, but are not limited to: conducting a preliminary assessment of the spills; determining action level; determining lead government agency responsibility; assessing and addressing response and protection needs; accessing sources of assistance; ensuring appropriate information is documented and distributed to concerned groups; dealing with the media; obtaining legal evidence and acquiring legal support; arranging finances; conducting post-incident activities; and using and obtaining approval for implementing certain response technologies.

Introduction

Environment Canada (EC) has several environmental emergency response centres for federal response located throughout the country. Provincial government centres are also located in each province. There are five main EC regional offices (Atlantic, Quebec, Ontario, Prairie & Northern and Pacific & Yukon), several district offices and a headquarters office (Ottawa-Hull). The National Environmental Emergencies Centre (NEEC) receives information on significant spills and other events from the regional and district offices and disseminates to concerned senior management within EC and other national and international interests. Similarly, NEEC relays any pertinent information to the appropriate regional or district office. Table 1 shows the Environment Canada addresses and 24-hour environmental emergency telephone reporting numbers in each region and headquarters.

Preliminary Assessment of Spills

When an EC Emergency Response Officer (ERO) is informed of a spill, the ERO must pose a number of questions to the spill reporter in order to determine if any action needs to be taken as a result of the report. A few examples of such questions include, but are not limited to: "Who is responding and do they need assistance?", "What is your name and telephone number?", "Have you called anyone else to report this incident?", "What substance and how much of it was spilled?", "Where did the substance spill?", "Is the spill still in progress?", "What time did the spill occur and how long did it last?", Where did the spill come from?", "Are there any conspicuous sources nearby?", "What is the type and cause of the accident?", "Are there any casualties or fatalities and how are they being cared for?", "Is there a need for evacuation of area due to human health concerns?", "Is there anyone else at the scene of the incident?", "Are there any environmental concerns?", "Is there a fire?".

Table 1. Contact Numbers for Reporting Environmental Emergencies (24-hours/7-days basis)

Environment Canada Mailing Address	Response Contact	Emergency Contact Number	
		Provincial	Federal
Atlantic Region	Maritimes (PEI, NS, NB)	1-800-565-1633	1-800-565-1633
45 Alderney Drive	Newfoundland/Labrador	1-800-563-2444	1-800-563-2444
Dartmouth, NS			
B2Y 2N6			
Quebec Region	Province of Quebec		1-514-283-2333
1179 de Bleury Street	Eastern Region	1-418-643-4595	
Montreal, QB	Western Region	1-514-873-3454	
H3B 3H9			
Ontario Region	Ontario		1-416-346-1971
25 St. Clair Avenue East	Provincial Spills	1-800-268-6060	
Toronto, ON	Action Centre	1-416-325-3000	
M4T 1M2			
Prairie & Northern Region	Manitoba	1-204-944-4888	1-204-981-7111
Twin Atria #2	Saskatchewan	1-800-667-7525	1-306-536-9991
210-4999-98th Avenue	Alberta	1-800-222-6514	1-403-499-2432
Edmonton, AB	Northwest Territories	1-403-920-8130	1-403-920-8130
T6B 2X3			
Pacific & Yukon Region	British Columbia	1-800-663-3456	1-604-666-6100
224 West Esplanade	Yukon Territories	1-403-667-7244	1-403-667-7244
North Vancouver, BC			
V7M 3H7			
National Environmental Emergencies Centre			1-819-997-3742
351 St. Joseph Blvd.			
Hull, QB			
K1A OH3			

Criteria for Determining Action Level

Each spill reported must be assessed and assigned an EC incident level (0 to 3) which represents the importance of the incident. Examples of different incident levels are indicated below. The EC criteria for judging the severity of an incident may include: possibility of a pollutant crossing an international or provincial boundary; danger to human life; potential health hazard; quantity and toxicity of material released or spilled; damage to property or natural resources; ability of local responders to deal with the incident; the uncertainty of the nature and magnitude of the incident; and media interest.

Level O:	An auto mechanic spilled 20 litres of motor oil on his or her property. He or she cleaned up the spill with rags and disposed of them appropriately.
Level 1:	Due to faulty tank measuring gauges, an oil tank was overfilled by about 90 litres which were consequently released onto the ground. A contractor was hired to clean up the spill. EC is providing spill cleanup and debris management advice.
Level 2:	A pipeline broke releasing 300 pound of ammonia (anhydrous) to the atmosphere. The plant (120 people) was evacuated. The company's emergency response team cleaned up the spill. EC is monitoring the situation.
Level 3:	A train, carrying toxic and flammable substances, derailed in an environmentally sensitive region. At the present time, five of ten cars train cars are damaged. Some of these damaged cars are releasing unidentified liquids and vapours. The media has become extremely interested in the situation. The public fears that this may be another Oakville, Manitoba incident. EC is on-scene and providing advice as necessary.

Lead Agency

Environment Canada is the lead federal agency responsible for ensuring adequate Canadian response to: marine-based mystery spills (except in the Great Lakes where Canadian Coast Guard fills this role); spills of deleterious substance into waters frequented by fish (violation of the Pollution Provisions of the Fisheries Act); spills of substances regulated under the Canadian Environmental Protection Act; spills originating from an EC facility or land; spills impacting on interprovincial boundaries or on the international inland boundary; and any spill not assigned to any other agency or level of government and where the environment is not otherwise adequately protected. EC is responsible for ensuring the polluter takes appropriate action to contain, cleanup and generally mitigate the effects of a spill. If a polluter is unknown, unwilling or unable to undertake a cleanup in an area of federal jurisdiction, then EC may take control of the incident. The decision to take over the cleanup is made in consultation with the ERO, Regional Environmental Emergency Coordinator (REEC), Regional Director General (RDG) and the Chief of NEEC.

As a lead government agency, EC can respond to a spill in one or more of the following ways: contact the polluter if known, and obtain as much information about the spill as possible and give verbal/written recommendations detailing response and cleanup actions; contact the appropriate local representative and ask if they would make an initial assessment of the incident; dispatch an ERO to the scene of the spill to investigate; ensure other implicated federal departments are notified and informed; ensure United States agencies are informed if the incident threatens or impacts borders; monitor the incident; or merely maintain a record of the incident.

Each federal facility or land is responsible for managing their own spills; however, EC becomes the lead federal environmental agency for such spills.

Assessing and Addressing Response and Protection Needs

The role of EROs during spill situations is usually to observe, investigate and report. Commensurate with expertise and jurisdictional authority, advice (such as containment and cleanup) and directions (as per statutory authority) may be given. EROs may take physical action if it's clearly an EC mandate to do so, a provincial agency requests them to do so, the potential to the environment is great, and the risks are minimal.

When responding to a spill, trained and equipped EROs should only enter the site with a trained and equipped "buddy". If an ERO is unsure about an activity or condition which places them or anyone else at risk, the ERO should not proceed until they have consulted with their supervisor or a person in charge and their concerns have been addressed. The health and safety of the ERO and response team are of paramount concern.

Accessing Sources of Assistance

Most spills do not require a significant amount of resources and can be managed regionally. For larger spills, where there are not enough administrative or technical resources available in the regional EC office to manage the spill, the REEC may access members of the Regional Environmental Emergencies Team (REET) or EC staff from other regions or headquarters. The NEEC is kept informed of such needs for briefing purposes.

The REET is a group of experts in the field of environmental emergencies who represent various federal and provincial government departments as well as private sector agencies, academia and local individuals. The REET provides consolidated technical and scientific advice to industry, government and other agencies in environmental emergency spill preparedness, planning and response.

The Environmental Technology Centre (ETC) of EC focuses on the development of technology and technical knowledge associated with response to and cleanup of pollution emergencies and measurement of air pollution from or near emission sources. Consequently, ETC provides most of the departmental technical advice, central laboratory, and on-site specialized support during response to pollution emergencies of federal interest. ETC also provides advice on post-emergency site assessment and remediation.

Additional sources of assistance include other federal and provincial departments, spill response coops and contractors and corporate response teams. Examples of such federal and provincial departments include the Department of Fisheries and Oceans (DFO), Emergency Preparedness Canada (EPC), Canadian Transport Emergency Centre (CANUTEC), and provincial ministries responsible for environment and transportation. Examples of such corporate response teams include Chlorine Emergency Plan (CHLOREP), Sulfur Dioxide Mutual Assistance Response Team (SMART), and Transportation Emergency Assistance Plan (TEAP).

EROs and other qualified EC staff are sometimes loaned to other agencies to provide assistance and expertise during international incidents (e.g, Gulf War, Exxon Valdez).

Documentation and Distribution of Information

Within EC, a computerized communication network, the National Environmental Emergencies System, interlinks all regions and several district offices with NEEC. The regional and district staff of EC provide their expertise on environmental emergency preparedness and response, as required, and complete log books for all events and pollution incident reports (PIRs) for significant spill events. The PIRs are transmitted electronically to NEEC which is responsible for disseminating information to concerned senior management within EC and national and international interests. The PIRs are also transmitted to other agencies within the region and district.

Briefing Notes and Question & Answer Sheets are often required. These are internal documents intended for the personal use of Ministers and other senior department officials. Briefing Notes usually cover the issue, current status, options/considerations, recommendations, next steps and background. Questions

& Answer Sheets usually address questions that the reader may be required to respond to from interested parties. The ERO is responsible for distributing the appropriate information in the region, while NEEC is responsible for distributing the appropriate information within headquarters and back to the region as appropriate.

Dealing with the media

Most EROs are trained and authorized to deal with the media regarding spill incidents. However, the ERO confines statements to facts that are not in dispute, such as: identification of the location, name of installation or vessel involved; time of the accident; type of substance spilled; and actions being taken to combat the spill. The ERO doesn't speculate about any aspect of the situation in order to avoid legal repercussions. The regional communications unit may assist the ERO for larger spill incidents.

Legal evidence and support

The ERO must ensure that any legal evidence taken is appropriately sampled, handled, analyzed and documented so that it will be admissible in court if so required. The ERO can seek legal assistance through Environment Canada's Legal Service Unit.

Finances

The ERO usually has full financial authority to commit appropriate response and cleanup expenditures of up to $5000. If response action is necessary and expected expenditures will exceed $5000, then the ERO must contact the REEC and request approval for additional funds and expenditures. These costs may be recovered by the REEC through their RDG from Corporate Finance and NEEC, provided prior approvals in writing have been requested and received by the Region. If funds cannot easily be found within EC nationally, Corporate Finance will then prepare and send a written request for funds to Treasury Board.

In the event the polluter is identified after a cleanup is initiated, appropriate actions will be taken to recover or transfer these costs depending on the status of the cleanup operation. If EC is acting on behalf of another agency, then EC can invoice the agency directly for recovery of funds.

The ERO should consult with their regional operations and financial managers for more specific financial authorization.

Post-incident activities

Significant and/or high profile incidents may require post-incident activities which may include, but are not limited to: completing spill investigation and other legal/regulatory actions; continuous or periodic monitoring of the site; recovery of response and cleanup costs; post-mortem reviews; preparation of "lessons learned" report; environmental damage claims; assessment of the capabilities and limitations of the technology development in the area of emergency response; and psychological counselling of stressed or traumatized employees.

Countermeasure Guidelines

Environment Canada has established guidelines for the use of and approval process for dispersants and in-situ burning during emergency spill situations. EC is also experienced in the applicability of other countermeasure technologies. Examples include, but are not limited to, the incineration of oil-contaminated debris; the advanced oxidation and steam stripping of organic-contaminated water; and the suitability of sorbents, booms and skimmers. It is essential that the environmental advantages and disadvantages that may result from the application of a countermeasure technology be carefully scrutinized to ensure that a net environmental benefit will be achieved.

Conclusion

Standard Operating Procedures were established for EC EROs in order to provide them with a uniform and professional approach to emergency response. New and less experienced responders can use them as one of many aids in their training while Senior Management may use them to become familiar with the practices of their responders. The SOPs cover a wide range of issues due to the complexity of spill response. It must be emphasized that the SOPs provide a framework of basic procedures that the ERO can follow but the final actions taken by the ERO are dictated by the nature of the event and their relevant experience.

For additional information on Environment Canada's Standard Operating Procedures for Emergency Response Officers, please contact the Senior Operations and Response Officer (819-953-6674).

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INTERNATIONAL INITIATIVES BY THE EMERGENCIES ENGINEERING DIVISION OF ENVIRONMENT CANADA

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ABSTRACT

The Emergencies Engineering Division (EED) of the Environmental Technology Centre (ETC) is currently conducting a number of international initiatives related to the remediation of abandoned missile sites and associated facilities in states of the former Soviet Union. These activities are primarily funded by Foreign Affairs and International Trade Canada with additional funds coming from EED, private sector companies and the local ethnic community. Negotiations with Latvia began in the summer of 1992 and the project was approved in May 1994. Negotiations with Ukraine began in February 1994 and the project was approved in March 1995. The background, objectives and phases of the Latvian and Ukrainian projects currently being conducted are presented.

LATVIAN PROJECT

Background

In the summer of 1992, the Dean of Civil Engineering from Riga Technical University in Latvia was visiting the Ottawa-Canadian Latvian community and expressed an interest in arranging for a guest lecturer at his University on the remediation of spill sites including contaminated soil and groundwater. Consequently, the Chief of EED was invited to conduct lectures on these subjects. The Bureau of Assistance for Central and Eastern Europe (BACEE) at Foreign Affairs and International Trade Canada (FAITC) agreed to partially cover the costs of this trip.

Subsequently, two representatives from Environment Canada attended several meetings with representatives of Riga Technical University, the Latvian Ministry of Environmental Protection and Regional Development, the World Bank, the Canadian embassy in Riga and the BACEE to discuss a potential joint project related to spill cleanup and the remediation of former missile sites and related facilities. An administrative agreement was prepared between FAITC and EED to address the financial contributions and related provisions of the project. The project was approved by FAITC in May 1994 and commenced in June 1994.

Objectives

The objectives of the Latvian Project agreement are: to develop and deliver training programs in order to transfer Canadian environmental assessment and remediation technology to Latvian engineers; to carry out an environmental assessment, spill cleanup and remediation demonstration project at two former defence missile sites near Tasi and Barta in the Liepaja district of Latvia; and to help establish the Chemical Technology Faculty at the Riga Technical University as the leading centre for spill site and other environmental remediation techniques and technology in Latvia.

Phases

The project will take place in three phases over a three-year period.

During ***Phase I*** (1994-95), two engineering professors and two recent engineering graduates were selected for training and arrived in Canada on June 22, 1994 . During their stay, the four visiting engineers obtained formal and informal training at Environment Canada and Gartner Lee International Inc. (GLII). The formal training included: Workplace Hazardous Materials Information System (WHMIS), laboratory safety, personal protective equipment, on-site analysis of pollutants, occupational health and safety and laboratory analysis. The informal training resulted from conducting research and development work and assisting in site assessment and remediation activities. Arrangements are currently being made for acquiring and delivering a mobile laboratory consisting of a gas chromatograph, atomic absorption spectrophotometer, chemicals, gases, glassware, computers and other relevant equipment. The lab will be mounted on an appropriate truck and trailer for site assessment activities in Phase II of the project.

During ***Phase II*** (1995-96), an additional two professors and two recent graduates from Riga Technical University will be selected for formal and informal training in Canada as indicated above. A Canadian team of engineers from GLII and EED, and the recently trained Latvian engineers (from Phase I) will visit the site of the demonstration project in August 1995. The Latvian engineers will be shown how to conduct and document site assessment activities. The Canadian team will return to Canada after a period of three weeks while the Latvian engineers will continue to conduct site assessment activities over a period of six months. Additional Latvian engineers will be trained on-site. Arrangements will be made for acquiring and delivering remediation equipment for Phase III of the project.

During ***Phase III*** (1996-97), a Canadian team of engineers from GLII and EED, and the recently trained Latvian engineers (from Phase II) will visit the site of the demonstration project. The Latvian engineers will be shown how to conduct and document spill cleanup and remediation activities. The Canadian team will return to Canada after a period of one month while the Latvian engineers will continue to conduct spill cleanup and remediation activities over a period of one year. Additional Latvian engineers will be trained on-site.

UKRAINIAN PROJECT

Background

In April 1994, Canada pledged $15 million toward nuclear dismantling in Ukraine so that Ukraine can accede to the Nuclear Non-Proliferation Treaty (NPT) as a non-nuclear-weapon state. A portion of the funding was allocated to support environmental assessment, spill cleanup and remediation activities. As a result of the Latvian project, FAITC requested that EED prepare a similar project for Ukraine.

Consequently, representatives from EED, GLII and Fenco MacLaren Inc. (FMI), went to Kiev, Ukraine in the Spring of 1994 to negotiate a similar but larger scale project with the Ukrainian Ministry of Defence. A protocol was signed establishing the responsibilities and reporting relationships between Ukrainian and Canadian officials and identifying specific activities that need to be carried out in order to successfully implement the project. The scope and budget for this project was approved by FAITC in March 1995 and will commence in June 1995.

Objectives

The objectives of the Ukrainian Project agreement are: to develop and deliver training programs in order to transfer Canadian environmental assessment and remediation technology to Ukrainian engineers and scientists; to carry out an environmental assessment, spill cleanup and remediation demonstration project at two former intercontinental ballistic missile sites in Ukraine.

Phases

The project will take place in three phases over a three-year period.

During ***Phase I*** (1995-96), nine specialists (scientists, engineers) from the Ukrainian Ministry of Defence (MOD), Ministry of Environment (MOE) and Academy of Science were selected for training and will arrive in Canada on June 1, 1995 . During their stay, the nine specialists will obtain formal and informal training at Environment Canada, GLII and FMI. The formal training will include: Workplace Hazardous Materials Information System (WHMIS), laboratory safety, personal protective equipment, on-site analysis of pollutants, occupational health and safety and laboratory analysis. The informal training will result from conducting research and development work and assisting in site assessment and remediation activities. A project office, with full time local support staff and one permanently attached Canadian expert, will be set up in Kiev in July 1995. An initial site reconnaissance in Ukraine will take place in September 1995.

Arrangements will be made for acquiring and delivering a mobile laboratory consisting of a gas chromatograph, atomic absorption spectrophotometer, chemicals, gases, glassware, computers, and other relevant equipment. The lab will be mounted on an appropriate truck and trailer for site assessment activities in Phase II of the project.

During ***Phase II*** (1996-97), nine to fifteen specialists (scientists, engineers) from the Ukrainian MOD, MOE and Academy of Science will be selected for formal and informal training in Canada. A Canadian team of engineers from FMI, GLII and EED, and the recently trained Ukrainian scientists (from Phase I) will visit the site of the demonstration project in July 1996. The Ukrainian specialists will be shown how to conduct and document site assessment activities. The Canadian team will return to Canada after a period of three weeks while the Ukrainian specialists will continue to conduct site assessment activities over a period of six months. Additional Ukrainian specialists will be trained on-site. Arrangements will be made for acquiring and delivering remediation equipment for Phase III of the project.

During ***Phase III*** (1997-98), a Canadian team of engineers from FMI, GLL and EED, and the recently trained Ukrainian speciailists (from Phase II) will visit the site of the demonstration project. The Ukrainian specialists will be shown how to conduct and document spill cleanup and remediation activities. The Canadian team will return to Canada after a period of one month while the Ukrainian specialists will continue to conduct spill cleanup and remediation activities over a period of one year. Additional Ukrainian specialists will be trained on-site.

CONCLUSION

Once the projects are complete, the Latvian and Ukrainian personnel will continue to assess and cleanup the bases using Canadian methods. There are potential commercial interests for Canadian environmental expertise and technology based on the personnel's exposure to Canadian experts.

Similar negotiations have started with other eastern european countries.