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DE L'ENVIRONNEMENT

PROCEEDINGS OF THE ELEVENTH  
TECHNICAL SEMINAR ON  
CHEMICAL SPILLS

COMPTE RENDU: 11<sup>e</sup> COLLOQUE  
TECHNIQUE SUR LES DÉVERSEMENTS  
DE PRODUITS CHIMIQUES

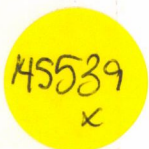


JUNE 6 AND 7, 1994  
VANCOUVER, BRITISH COLUMBIA

LES 6 ET 7 JUIN, 1994  
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## PROCEEDINGS

## COMPTES RENDUS

Eleventh Technical Seminar  
on Chemical Spills

Onzième colloque  
technique sur les  
déversements de produits  
chimiques

June 6 and 7, 1994  
Coast Plaza Hotel  
Vancouver, British Columbia

6 et 7 juin, 1994  
Hôtel Coast Plaza  
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Seminar sponsored by

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**THE REDUCTION OF CHLORINATED METHANES  
AND 1,2-DICHLOROETHANE USING ZINC METAL**

by

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**1.0 ABSTRACT**

It was found that carbon tetrachloride (CTET) and chloroform (CHL) were susceptible to reduction by zinc metal under acidic conditions at STP, but that methylene chloride (DCM) and 1,2-dichloroethane (1,2-DCEA) were not. The experimentally observed pseudo first order rate constants for the reductions of CTET and CHL were found to be  $1.3 \text{ min}^{-1}$  and  $0.1 \text{ min}^{-1}$  respectively.

Byproducts from the reduction of CTET were found to be DCM, hydrogen gas,  $\text{Zn}^{2+}(\text{aq})$ ,  $\text{Cl}^{-}(\text{aq})$ , and  $\text{SO}_4^{2-}(\text{aq})$  ions. CHL was the intermediate for the conversion of CTET to DCM. Thus, a stepwise dechlorination/protonation redox mechanism was proposed.

The Gibb's free energy values of formation and for the reaction with zinc were evaluated according to the proposed mechanism. These values showed that the reaction was thermodynamically more favourable for the tri- and tetra-chloromethanes than the other chloromethanes and the chloroethanes.

It was found that the  $\text{Zn}^{2+}(\text{aq})$  contaminated effluent which resulted from the process was treatable to below discharge requirements, ( $<5 \text{ ppm}$ ) by precipitation with hydroxide ion at a pH of 8, followed by filtration.

**2.0 INTRODUCTION**

The Emergencies Engineering Division (EED) of Environment Canada's Environmental Technology Centre (ETC) in Ottawa performs ongoing testing of site remediation technologies. One of the many technologies tested are the advanced oxidation processes (AOP's). These processes have proven to be very effective for the oxidations of many of the priority pollutants.

It has been shown that chlorinated compounds such as CTET are resistant to degradation by ultraviolet enhanced oxidation processes. Also it has been found that the addition of hydrogen peroxide is an interference to direct photolysis of chloromethanes as it slows the degradation rate up to eleven times, as is the case for CTET.<sup>1</sup>

For organic compounds that are highly oxidized by chlorine it is clear that a reducing process, such as the use of zero valence metals may be more suitable. Tests performed previously have shown that some transition metals such as iron have the ability to degrade compounds like CTET.<sup>2,3,4,5</sup>

The object of this report was to investigate further the effectiveness and potential applicability of zinc metal as a reducing agent for the hydrogenation of chlorinated compounds.

### 3.0 EXPERIMENTAL

A mixture of commercial grade solvents including CTET, CHL, and DCM was prepared by dissolving the fore mentioned solvents in two litres of deionized water. This mixture was then recirculated through a bed of five hundred grams of 100 mesh zinc metal at a flow rate of one litre per minute. See Figure #1.

The pH was adjusted to a value of three using a ten percent solution of sulphuric acid. After the pH had stabilized, the time zero sample was acquired. Samples were then acquired at regular intervals and each was analyzed immediately after being taken by purge and trap gas chromatography. A Varian ALS 2016 autosampler, and a Varian 3400 gas chromatograph were used to perform the analyses. The compounds were detected by an electron capture detector and a flame ionization detector simultaneously.

Peak areas for the compounds were normalized with respect to time zero and graphed against time to obtain the experimental rate constants. Residence time values were calculated using the rate constant and standard pseudo first order rate theory.

In a similar manner to that outlined above, other tests were performed on solutions contaminated with only carbon tetrachloride, only methylene chloride, and only 1,2-dichloroethane. These tests were conducted in order to determine byproduct information and the time rate of

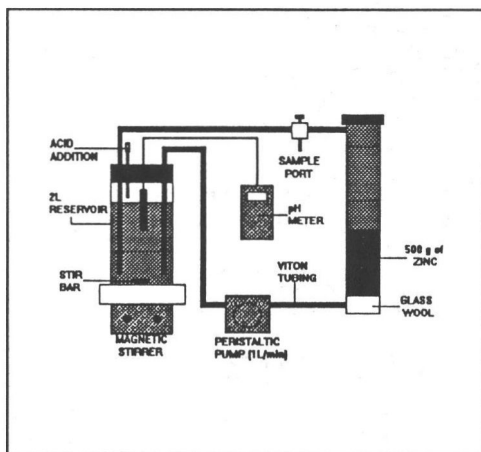


Figure #1: Apparatus Used in Zinc Metal Tests.

change of the pH in the case of the CTET solution, and to investigate the effect that the zinc metal had on DCM alone and 1,2-DCEA alone in solution. Tests on the contaminants were also performed using soluble zinc sulphate in place of the zinc metal to determine what if any effect was attributable to the  $Zn^{2+}$  ion.

The removal of the aqueous  $Zn^{2+}$  ion by precipitation as zinc hydroxide was investigated by adding sodium hydroxide to the reaction solution after the reaction time had elapsed. The pH was altered to between seven and nine to allow the precipitation of  $Zn(OH)_2$ . The precipitate was then gravity filtered through Whatman #4 filter paper.

Samples collected prior to, and after the precipitation were analyzed by atomic adsorption spectroscopy. The efficiency of the precipitation was calculated to determine if the discharge requirement for zinc could be achieved.

#### **4.0 RESULTS/DISCUSSION**

When a mixture of carbon tetrachloride, chloroform, and methylene chloride in deionized water was recirculated through a bed of zinc metal it was found that there was a rapid reduction in the carbon tetrachloride and chloroform concentrations. No significant reduction of methylene chloride concentrations were observed. See GRAPH #1.

When solutions containing only carbon tetrachloride were recirculated an almost complete conversion of carbon tetrachloride to chloroform was observed. This was followed by the formation of methylene chloride from the chloroform. See GRAPHS #2(a)-2(c). This led to the proposed mechanism as outlined later in this report.

The degradation of carbon tetrachloride observed a pseudo first order scheme and was treated as such to evaluate an observed rate constant of  $1.3 \text{ min}^{-1}$ . The residence time curve was then evaluated over the concentration range that was known to be approximately linear. See GRAPHS #2(d), 3, & 4.

During the degradation of carbon tetrachloride the pH was observed to increase at a rate of 0.22 pH units per minute. Therefore to maintain a pH of three, a ten percent sulphuric acid solution had to be added at a rate of about one millilitre per minute. See GRAPHS #5(a) & 5(b).

The tests performed on acidic and neutral solutions containing only 1,2-dichloroethane showed that the zinc metal had no significant effect. See GRAPH #6(a). The concentration of the 1,2-dichloroethane did not change appreciably over the one hour reaction time. Similar results were obtained for runs performed on methylene chloride alone. See GRAPH # 6(b).

When 2.5 L of carbon tetrachloride and 1,2-

dichloroethane solutions were treated with 80 mg of  $\text{ZnSO}_4$ , no appreciable reductions in the contaminant concentrations were observed. For both compounds this reduction amounted to about 10 % in one hour. See GRAPHS #7 & #8. This amount of reduction was likely attributable to degassing of the solution by diffusion or stripping of the volatiles by the evolved hydrogen gas.

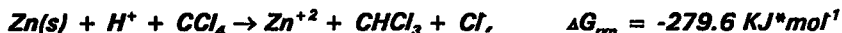
Effluent solutions that contained dissolved  $\text{Zn}^{2+}$  at a concentration of approximately 500 ppm were treated with NaOH solution until the pH was around 8. The  $\text{Zn}^{2+}$  ion was observed to precipitate as the hydroxide  $\text{Zn}(\text{OH})_2$ . After gravity filtration the filtrate was determined to contain less than 5 ppm Zn. This corresponded to a precipitation efficiency of 99% and achieved the discharge requirement of less than 5 ppm.

The free energies of formation for the compounds showed that CTET and CHL did not conform to the trend observed for the chloroethanes. See GRAPH #9(a). It was found that the formational stability of CTET and CHL deflected toward less energetically favourable states, while the trend observed for the chloroethanes was a continuous increase in the formational stability. A possible explanation for this was the steric interference that would be experienced by the chlorine ligands in CTET and CHL.

The free energies for the reactions of CTET and CHL with the zinc metal showed that these two compounds reacted somewhat more spontaneously than any of the others. One possible explanation the mechanism was seen to stop at methylene chloride involved the consideration of the ligand field stabilization energy caused by chlorine ligand.

If the mechanism involved a free radical intermediate (e.g.  $\text{CCl}_3\cdot$ ) then it was conceivable that the formation of the  $\text{CH}_2\text{Cl}\cdot$  was unfavourable due to a large activation barrier that resulted when not enough field stabilization energy was supplied by the single remaining chlorine ligand to support a free electron.<sup>6</sup>

#### PROPOSED MECHANISM





## **5.0 CONCLUSIONS**

In conclusion the use of zinc metal as a reducing agent for the dechlorination of CTET and CHL was effective. Unfortunately, it was found that DCM and 1,2-DCEA were not susceptible to the process.

Hydrogen gas, DCM,  $Zn^{2+}$ , and acidic solutions were found to be byproducts of the reductions of CTET and CHL with zinc metal, thus further processing of the effluent was necessary for discharge requirements to be met.

Adjusting the effluent pH to 8 through the addition of sodium hydroxide both neutralized the acidity and caused the precipitation of zinc hydroxide which was then filtered. The filtrate met the discharge requirement for pH, and for less than 5 ppm zinc.

The DCM, however remained in the water. To remove it further processing by existing technologies was found to be necessary. Alternatives could include the photolysis, photo-oxidation, or air stripping followed by flash photolysis of the DCM contaminated effluent.

The evolution of large amounts of hydrogen gas from the reaction was of concern as mixtures of hydrogen and air are explosive. Reclamation or combustion of this gas would be desirable in the event that the use of zinc metal were to be implemented. More alkaline pH's would result in less hydrogen gas evolution, however the reaction rates would likely be somewhat reduced as the mechanism seems to be dependant on the pH.<sup>7</sup>

The use of zinc metal as a dechlorinating agent for the reduction of CTET and CHL was found not to be an effective in-situ treatment method due to the apparent incomplete dechlorination. The data would seem to indicate that at best only the more highly oxidized species would be affected, although the conversion of CTET to DCM in itself is desirable as DCM is somewhat less toxic than CTET, the water on the effluent side of a zinc wall landfill barrier would still be contaminated with dangerous compounds.

CTET has been found to photolyze about three times faster than DCM in Solarchem's Rayox<sup>®</sup> reactor with none of the same by products that were observed in the reductions by zinc. When treated with a combination of UV and hydrogen peroxide, the rate of DCM destruction was found to be slowed to a much lesser degree (3.2 times) than the CTET degradation (11.4 times). Therefore, when the matrix is complex it would seem to be favourable to perform partial dechlorinations as this would result in species that are more susceptible to oxidation by UV generated hydroxyl radical.

One interesting possibility is the use of zero valent metal canisters as a pre-treatment to the pump and treat methods of AOP's. When the groundwater matrix is complex the partial dechlorination of the fully chlorinated compounds would be desirable if the intention

is to perform UV photolysis in conjunction with an oxidant like hydrogen peroxide.

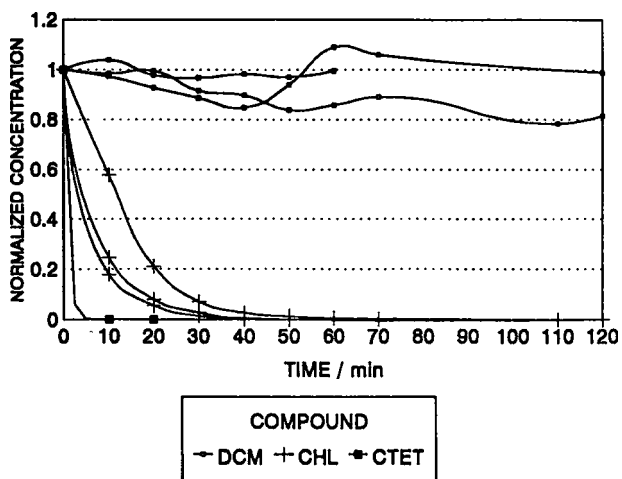
Another interesting application could be the treatment of pure streams of highly halogenated materials including CFC's. Preliminary study of 1,1,2-trichlorotrifluoroethane show that these types of compounds (those including fluorine) are susceptible to zero valence metal enhanced reductions in the aqueous phase.

Other work being conducted presently is the classification of the intermediates produced from the reduction of perchloroethylene (PCE). Work to follow will involve compounds that have been shown to be susceptible to similar reductions by iron.

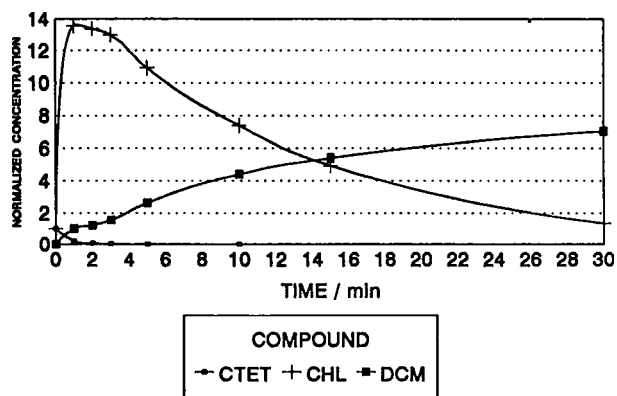
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- 1) Argue, S., 'The Advanced Oxidation of Chloromethanes Using Solarchem's Rayox<sup>®</sup> Technology', In House Report, 1993.
- 2) Gillham, R.W., et al., 'Metal-Enhanced Degradation of Halogenated Aliphatic Compounds', 1992.
- 3) Gillham, R.W., et al., 'Metal Catalyses Abiotic Degradation of Halogenated Organic Compounds', 1992.
- 4) O'Hannesin, S.F., et al., 'A Permeable Reaction Wall for In-Situ Degradation of Halogenated Organic Compounds', 1992.
- 5) Gillham, R.W., et al., 'Metal Enhanced Abiotic Degradation of Halogenated Aliphatics: Laboratory and Field Trials', 1993.
- 6) Personal consultation with Dr. J. Wright, Professor of Chemistry, Carleton University.
- 7) See references 2-5.

GRAPH #1: NORMALIZED CONCENTRATION VERSUS TIME CURVES FOR A MIXTURE OF CHLOROMETHANES IN WATER AT A pH OF 3 CONTACTING ZINC METAL

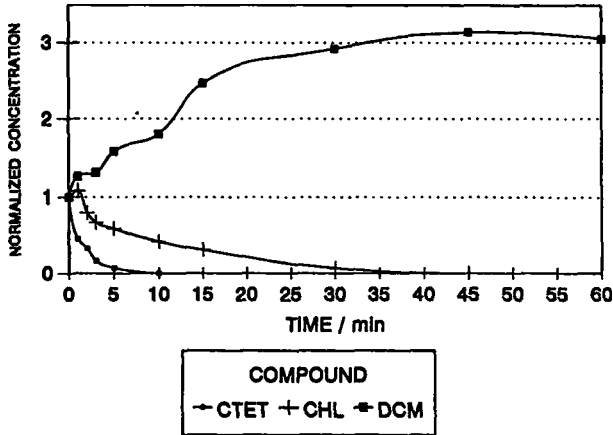


GRAPH #2(a): NORMALIZED CONCENTRATION VERSUS TIME FOR CARBON TET IN WATER AT A pH OF 3 CONTACTING ZINC METAL SHOWING THE FORMATION AND DEGRADATION OF BYPRODUCTS

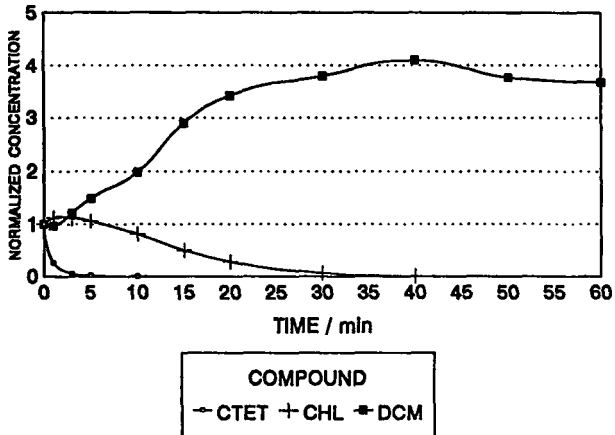


- \* INITIAL CONCENTRATION OF CTET WAS 1.38 ppm
- \* MAXIMUM CONCENTRATION OF CHL FORMED WAS 1.18 ppm
- \* MAXIMUM CONCENTRATION OF DCM FORMED WAS 0.90 ppm

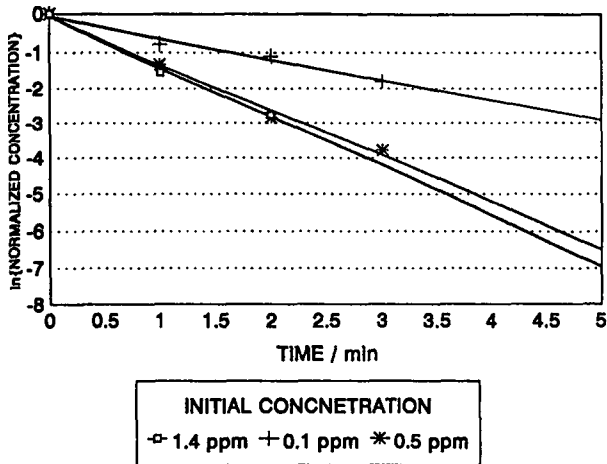
GRAPH #2(b): NORMALIZED CONCENTRATION VERSUS TIME FOR CARBON TET  
IN WATER AT A pH OF 3 CONTACTING ZINC METAL SHOWING THE  
FORMATION AND DEGRADATION OF BYPRODUCTS



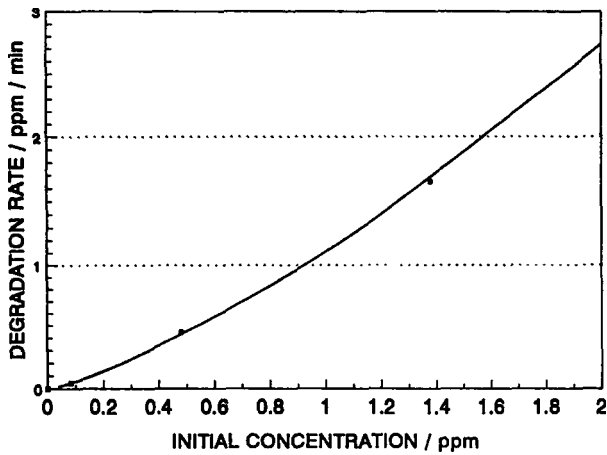
GRAPH #2(c): NORMALIZED CONCENTRATION OF CARBON TET  
IN WATER AT A pH OF 3 CONTACTING ZINC METAL SHOWING THE  
FORMATION AND DEGRADATION OF BYPRODUCTS



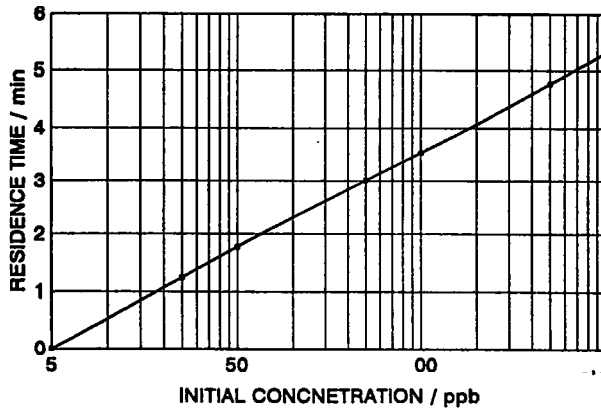
GRAPH #2(d): NATURAL LOGARITHM OF THE NORMALIZED CARBON TET CONCENTRATION VERSUS TIME AS A FUNCTION OF INITIAL CONCENTRATION



GRAPH #3: RATE OF CARBON TET DEGRADATION IN WATER AT A pH OF 3 CONTACTING ZINC METAL VERSUS THE INITIAL CONCENTRATION OF CARBON TET

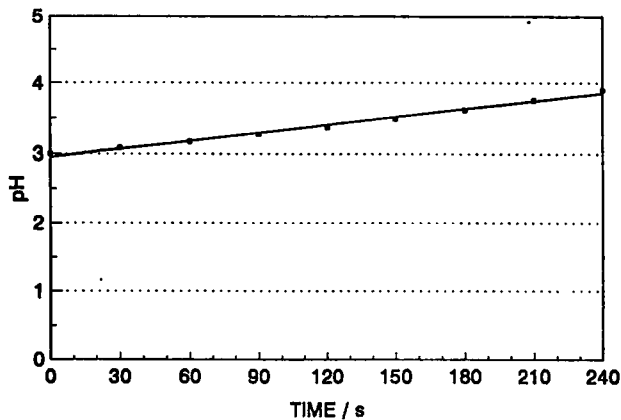


**GRAPH #4: PREDICTED RESIDENCE TIMES FOR THE DEGRADATION OF CARBON TET IN WATER AT pH 3 CONTACTING ZINC METAL**



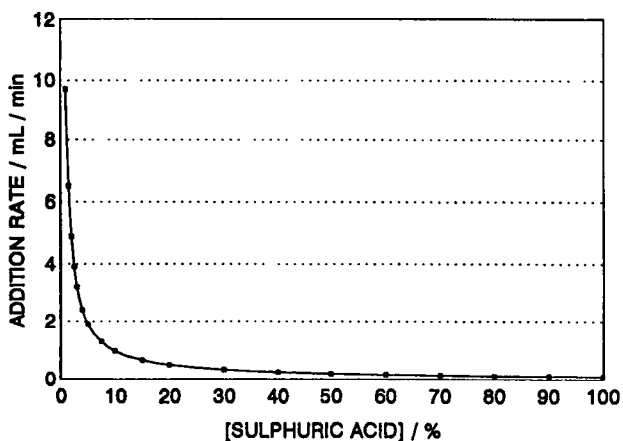
\* BASED ON A DISCHARGE LIMIT OF 5 ppb AND THE RATE CONSTANT OF 1.3/min EVALUATED FROM GRAPH #3

**GRAPH #5(a): pH VERSUS TIME DURING THE DECOMPOSITION OF CARBON TET IN WATER CONTACTING ZINC METAL**

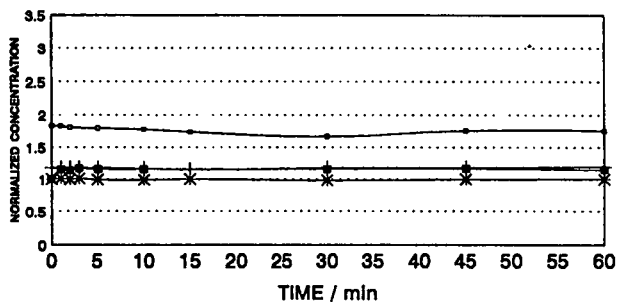


\* RATE  $\approx$  0.22 (pH UNITS/min)

**GRAPH #5(b): ADDITION RATE OF SULPHURIC ACID VERSUS THE CONCENTRATION OF THE SULPHURIC ACID**



**GRAPH #6(a): NORMALIZED CONCENTRATION OF 1,2-DICHLOROETHANE VERSUS TIME AS A FUNCTION OF VARIOUS PARAMETERS**



RUN #

—○— CONTROL    + RUN 1    \* RUN 2    ■ RUN 3

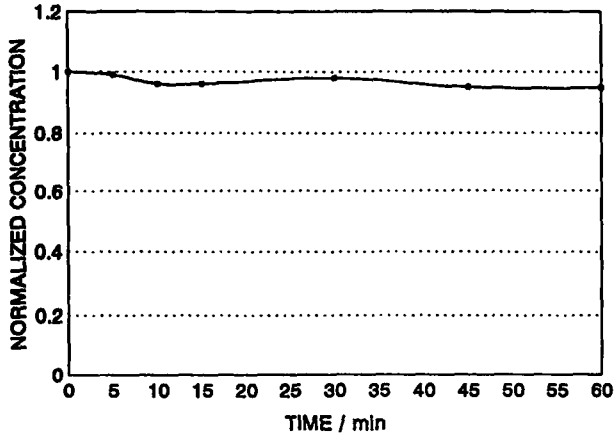
RUN 1: 5g OF ZINC; pH 3

RUN 2: 5g OF ZINC; pH 7

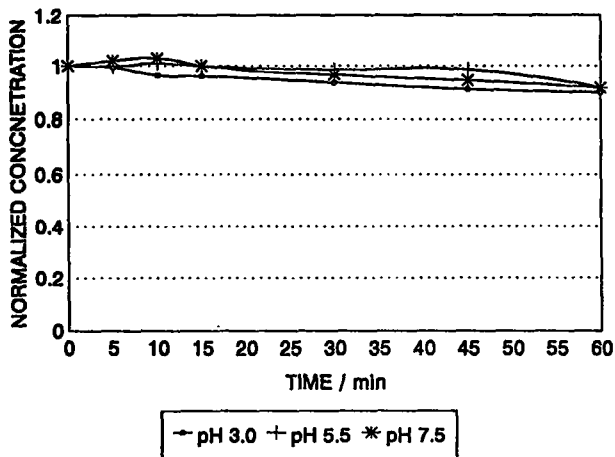
RUN 3: 500g OF ZINC; pH 3



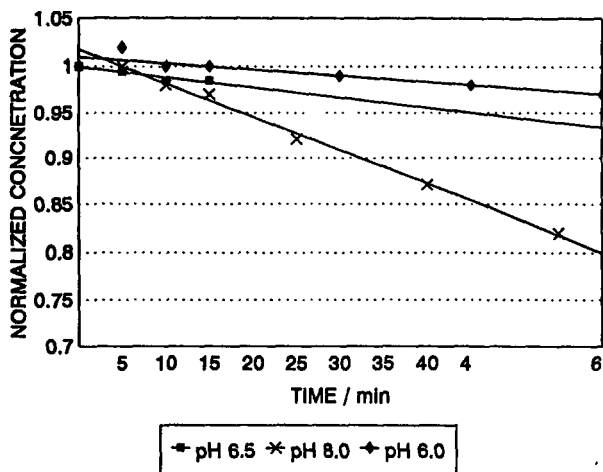
GRAPH #6(b): NORMALIZED CONCENTRATION OF DCM IN WATER  
AT pH 3 CONTACTING ZINC METAL VERSUS TIME



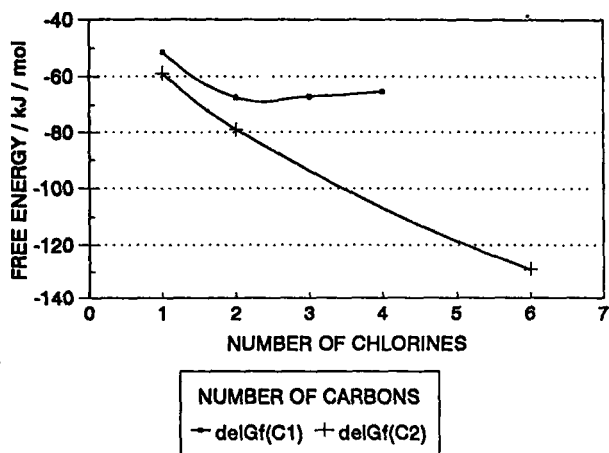
GRAPH #7: NORMALIZED CONCENTRATION OF CARBON TET IN WATER  
CONTAINING 30 ppm ZnSO<sub>4</sub> VERSUS TIME AS A FUNCTION OF pH



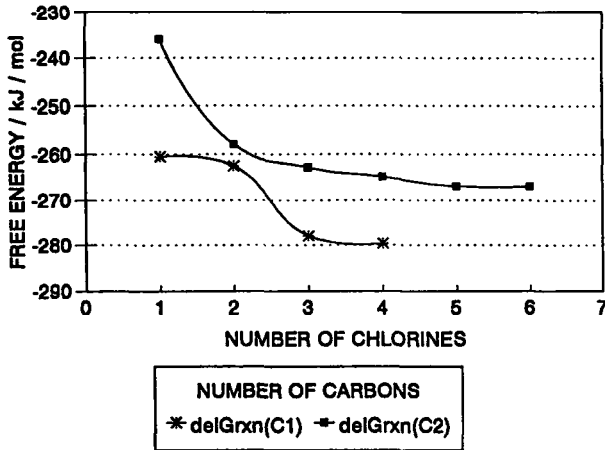
GRAPH #8: NORMALIZED CONCENTRATION OF 1,2-DICHLOROETHANE IN WATER CONTAINING 80 ppm  $\text{ZnSO}_4$  VERSUS TIME AS A FUNCTION OF pH



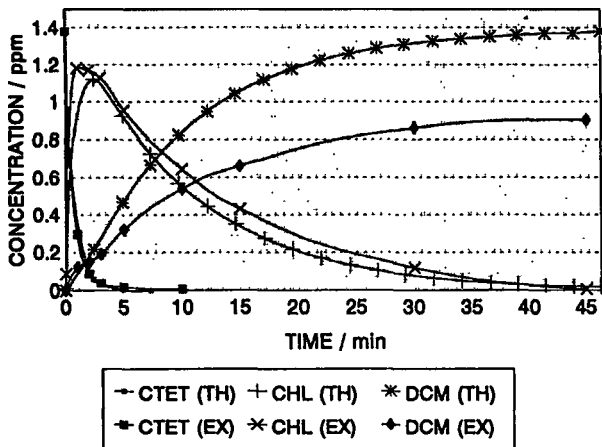
GRAPH #9(a): FREE ENERGY OF FORMATION FOR THE INDICATED CHLORINATED COMPOUND



**GRAPH #9(b): FREE ENERGY OF THE REACTION FOR THE INDICATED CHLORINATED COMPOUND WITH ZINC METAL**



**GRAPH #10: THEORETICAL (RUNGE-KUTTA) AND EXPERIMENTAL CONCENTRATION VERSUS TIME CURVES**



## **ARSENIC REMOVAL BY POLYMERIC BINDING AND MEMBRANE SEPARATION**

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### **SUMMARY**

Previous researchers have demonstrated the efficiency of polymeric binding/membrane separation process to separate metal ions from contaminated water. This paper summarizes studies using this hybrid method involving selective polymeric binding by water soluble polymers and ultrafiltration separations. The latest application of this process for the treatment of arsenic contaminated groundwater is discussed. The results reported provide evidence that the PEI is more suitable for industrial use than DADMAC for the separation of arsenic from groundwater. Bench-scale tests demonstrated the industrial potential of this new system to obtain an arsenic removal efficiency exceeding 99.9%. The investigation was performed using a closed loop experimental set-up using 0.1 or 0.3 ppm of arsenic and 1,000 ppm of PEI in the circulation loop. The results from the work show that this new process represents a viable solution to reduce the arsenic contamination in aqueous solutions.

### **INTRODUCTION**

The contamination of water with arsenic is a serious environmental issue. An extensive literature search [Balint-Ambro, 1974] [Gecker et al, 1986][Shen, 1973] [Bellack, 1971] [Ferguson and Gavis, 1972] [Grigir'ev and Puskarev, 1986] [Gulledge and O'Connor, 1973] [La Peintre, 1954] [Patterson, 1975] [Sripach et al, 1970] reveals that the following three main techniques are currently employed for the extraction of arsenic from aqueous solution: ion exchange, adsorption, and precipitation. Several other methods such as filtration and sedimentation have also been investigated, but have not been considered for additional studies due to various limitations [Clifford and Chieh-Chieh, 1991]. Studies have shown that the three methods previously mentioned will efficiently remove arsenic from contaminated solutions; however, none of them will reach the discharge limit of 25 ppb imposed by the Canadian government [Canadian Council of Ministers of the Environment, 1991]. Currently ferric chloride,  $\text{FeCl}_3$ , is widely used in industry as a reagent to precipitate arsenic from water, but this method normally does not sufficiently reduce the arsenic content to comply with environmental discharge limits.

The development of a hybrid method using polymeric binding and membrane separation was investigated for the treatment of aqueous solutions having low concentrations of arsenic. The results from this research demonstrated that the removal of arsenic from contaminated groundwater is affected by various factors [Legault et al, 1993] 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. Each of these factor affects the retention of arsenic to different extents. Tests were performed using two different polymers, poly-dially dimethyl ammonium chloride (DADMAC) and poly-ethylenamine (PEI) which were selected based on their commercial availability and their physico-chemical properties [Mangravite, 1983]. Based on previous results, further tests were performed to determine which polymer was the most promising for a continuous system, and to determine the efficiency of an industrial application using a closed loop membrane process for the separation of arsenic from contaminated water.

## ANALYSIS FOR ARSENIC SOLUTIONS

The analysis of arsenic was achieved using an atomic absorption equipment, model 3100, manufactured by Perkin Elmer (Norwalk, U.S.A.). This equipment was combined with a mercury/hybrid 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 hybrid generator. The generator reduces interference when analyzing arsenic which is caused by arsenic's wavelength being similar to that of visible light. The atomic absorption system was used manually. The reagent used was 1.5 % HCl and the pressure of gas used was 40 psi. An initial solution of 0.1 ug of As/ml was used to calibrate the equipment.

## EXPERIMENTAL

Synthetic groundwater was produced for two series of experiments by preparing solutions containing a total NaCl concentration of 1,000 ppm. A 1,000 ppm pentavalent arsenic solution ( $\text{Na}_2\text{HAsO}_4$ ) was used to make the spiked solutions. 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 both trials, all samples were refrigerated until they were analyzed. All tests were performed using standard ultrafiltration equipment. Bioken polyethersulphone membranes with a molecular cut-off of 10,000 Daltons were employed. The retention of arsenic on the high pressure side (feed side) of the membrane ( $R_{As}$ ) was used to characterize the efficiency of arsenic removal [Volchek et al, 1992] using the equation (1):

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

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

respectively.

#### Experimental 1

The first study investigated the effect of the polymer concentration on the retention of arsenic. Two Amicon (Beverly, U.S.A.) stirred cells (cell A and B) each having a volume of 50 ml were used in parallel for these experiments. An initial spiked solution of 200 ml was made containing 0.3 ppm of arsenic, 1,000 ppm NaCl and a fixed concentration of 1 ppm, 1,000 ppm or 5,000 ppm of either polymer. Each solution was then separated in four equal volumes for four replicate tests. The system pressure was kept constant at 40 psi. Prior to the testing, the pH of the solution was adjusted to 7.0 with a solution of either 1 % NaOH or 1.5 % HCl. Samples of the permeate and the concentrate streams were taken for the first series of experiments twenty minutes after steady state was reached.

#### Experimental 2

The second series of experiments was designed to represent a continuous industrial process. The hybrid system used a recirculation loop and contained two initial solutions. The first one contained 0.1 or 0.3 ppm of arsenic and 1,000 ppm of NaCl. This first solution was added to the recirculation loop at a flowrate equal to the rate of collection of the permeate. The second solution was also composed of a fixed initial arsenic concentration of either 0.1 or 0.3 ppm, 1,000 ppm of PEI, and 1,000 ppm NaCl. This second solution was recirculated within the membrane system at a constant pressure of 40 psi. No pH adjustments were made to either solution 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

#### Results 1

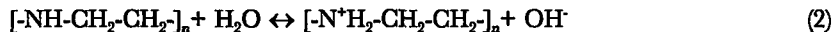
In the first series of tests, the effect of the polymer concentration was investigated. The results obtained as well as the standard deviation for each stirred cell are reported in Table 1.

**TABLE 1 Arsenic Retention and Standard Deviation of Measurements for DADMAC and PEI at Various Concentrations.**

POLYMER	POLYMER CONC. (ppm)	R <sub>As</sub> (%) Cell A	R <sub>As</sub> (%) Cell B	R <sub>As</sub> (%) Average
DADMAC	1	23.68±5.20	13.75± 2.42	23.87± 8.90
	1,000	25.65±0.40	22.13± 5.03	29.08± 7.51
	5,000	47.39±6.68	36.54±18.08	46.80±13.94
PEI	1	14.82±3.28	6.06 ± 3.85	10.44± 5.84
	1,000	47.00±5.42	92.46 ± 4.23	69.75±26.33
	5,000	74.45±5.59	99.99±0.00	82.97±15.27

The standard deviation was strongly influenced by the utilisation of different samples of Bioken membrane. The results show that the standard deviation for a specific cell is generally less than 7 % rather than the standard deviation for a fixed quantity of polymer increased to 26 %. This phenomenon can be explained by the variation of pore size of different membrane samples.

The results show that a low DADMAC concentration i.e., 1 ppm, results in an arsenic retention of  $23.87 \pm 8.90$  % which is superior to  $10.44 \pm 5.84$  % obtained for the PEI at similar concentration. The low percentage indicates the competitive aspect existing in the system between the chlorine and arsenic anions. However, when the concentration of polymer is increased to 1,000 ppm, the arsenic removal reached  $69.75 \pm 26.33$  using PEI which was more efficient than the DADMAC which yielded only  $29.18 \pm 7.51$  % arsenic retention. This is consistent with the observation made in previous work [Legault et al, 1993] which reported that by using PEI, the arsenic removal can be increased by simply using a higher polymer concentration. Using 5,000 ppm initial polymer concentration, the PEI still remains more efficient than the DADMAC with  $82.97 \pm 15.27$  % and  $46.80 \pm 13.94$  % arsenic retention respectively. The data can be explained by the following equilibrium equation of the polymer in solution:



Once the equilibrium is reached, the number of charged polymer molecules stays constant. However, when the polymer concentration is increased, the production of cations is favoured, increasing the sites available for the binding between the arsenic and the polymer. Therefore, it was found that the retention of arsenic from contaminated groundwater can be increased significantly by increasing the polymer concentration when using PEI. In general, the water soluble polymer PEI was found to be a more suitable polymeric agent than the DADMAC.



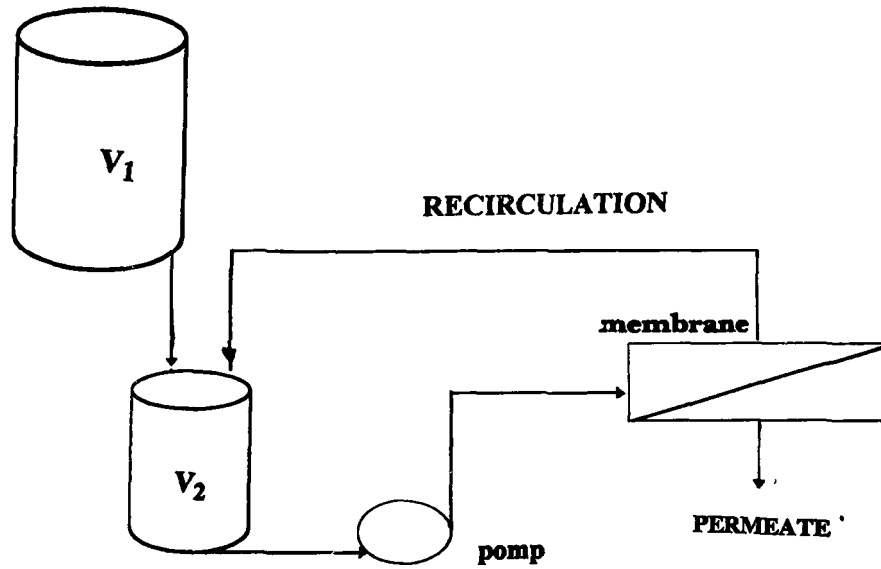


Figure 1 Plates and frame continuous system.

## Results 2

The second series of tests performed involved the application of the hybrid method in a continuous process. The continuous process is a closed loop system designed to represent an industrial process as Figure 1 demonstrates. The system has two initial solutions, one referred to as  $V_1$  having 6 litres or 3.5 litres of synthetic water, and the other referred to as  $V_2$  having 300 ml containing the water and the polymer. Both tests involved a fixed concentration of arsenic and NaCl and 1,000 ppm PEI. The quantity of polymer was determined by an economic evaluation of the process. The first test was performed using a concentration of 0.1 ppm of arsenic, and the second one using a concentration of 0.3 ppm. The results of the tests are reported in Figure 2 as B1000 #1 and B1000#2 respectively. The graph shows the  $V_p/V_c$  as a function of the retention of arsenic (%), where  $V_p$  is the volume of permeate collected and  $V_c$  is the dead volume of the experimental system. Based on the data obtained from this study, the system has been proven to be very efficient with a 96.0 % retention for the first test and >99.9 % for the second one.

During the first trial, the arsenic 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 0.0325 ppm to 0.0050 ppm of arsenic during the treatment, resulting in an increase in the arsenic retention of 24.3 %. During the second trial, 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. This observation could possibly be explained by the formation of a polymeric gel at the surface of the membrane. From the results obtained, it was noticed that a higher removal was achieved using higher initial arsenic concentration. The literature cited 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.

## CONCLUSIONS

The results obtained during the present investigation indicate that:

1. Selective polymeric binding followed by ultrafiltration is an effective method to treat contaminated groundwater with arsenic.
2. PEI is a suitable water soluble polymer for the removal of arsenic from groundwater.
3. The continuous process is promising for industrial application.
4. Low concentrations of arsenic can be achieved while respecting the discharge limit set by Canadian government using this new hybrid technique.

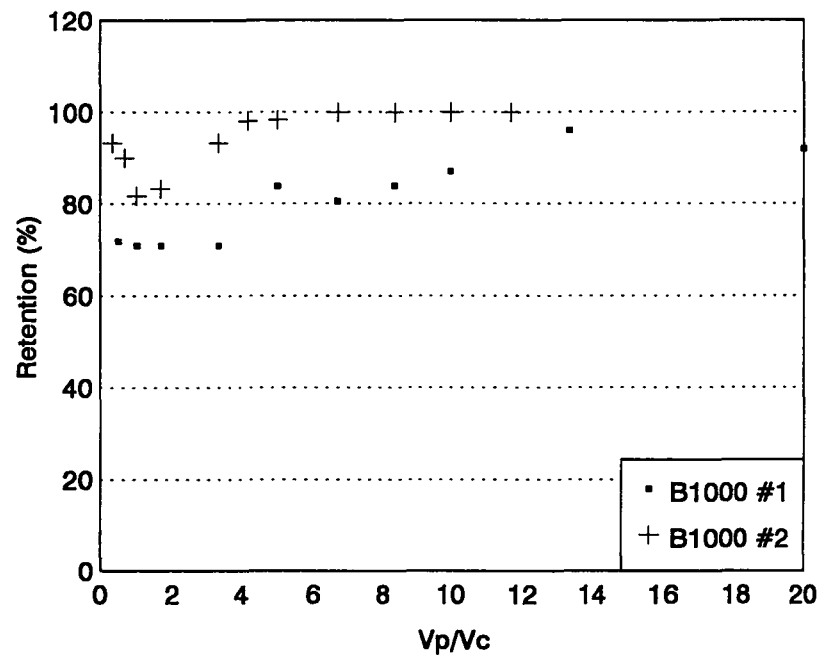


Figure 2 Arsenic retention using the closed loop continuous system with 1,000 PEI.

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## REMOVAL OF LEAD FROM CONTAMINATED SOIL

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### ABSTRACT

A treatability study was performed to investigate the effectiveness and applicability of soil washing for remediation of a lead contaminated soil sample. A mineralogical analysis of the soil revealed that the majority of the contamination existed in the fine fraction. The soil was treated using conventional soil washing to extract concentrated contaminated fines. Acid leaching and combined chelation was successfully applied to reduce the lead levels of the fines to below the sanitary limits. Three chelants: EDTA, catechol and pyrogallol were evaluated and their regeneration was investigated. The rinse water was treated via reagent precipitation. A process train was proposed for treatment of the soil.

### INTRODUCTION

Lead is one of the major heavy metal contaminants that finds its way into soil, water, and due to the extensive organic chemistry of lead, into the food chain and poses serious health hazard to humans and other animals.

Emergencies Engineering Division of Environment Canada (EED) has been involved in an ongoing research on the removal of heavy metals from contaminated soil fines. The present paper is based on a treatability study that was performed for one of EED's clients, which serves as a pilot study for a two year research project underway at EED. This study presents recommendations and cost estimates, and demonstrates that soil washing based treatment technologies can be competitive and probably more effective than some alternative options. The soil used for the experiments was obtained from a site that had been used for lead reclamation operations from old car batteries and was also used as a battery parts dump site.

In the treatment of heavy metal contaminated soil, the metal contaminants should either be fixed in a non-leachable form or removed from the soil by physical and chemical methods. The authors believe that the safer and more practical method is the removal of the heavy metals from the soil. In this study, acid leaching enhanced by chelation was applied.

Three chelating agents were tested: ethylenediaminetetraacetic acid (EDTA), pyrogallol, and catechol. EDTA has extensive commercial and analytical applications and is also known by many different commercial names such as Veresene, Calsol, and chelaton. It is a white anhydrous crystalline solid with a minimum solubility of 0.5 g/L at 20°C [1]. EDTA molecule has six possible coordination positions; two from the amine groups and four from the carboxylic acid groups. Pyrogallol and catechol are benzene alcohols. Pyrogallol forms a white odourless crystal and has a solubility of 588.23 g/L of water, and solubility of catechol is 434.78 g/L of water [2].

## **OBJECTIVES**

The objectives of this study were to:

- evaluate the feasibility of soil washing and leaching for the removal of lead from a contaminated soil,
- determine feasibility of regeneration of the chelating agent with the best performance,
- propose a process train suitable for the treatment of the contaminated soil, and
- compare related costs with a solidification/stabilization approach.

## **EXPERIMENTAL PROCEDURES**

### **Sampling Procedure and Soil Preparation**

The soil sample was initially air dried and well mixed. Agglomerated portions of the sample were crushed to ensure that a true representation of the size distribution could be achieved. In order to achieve representative sampling, the soil was first uniformly spread on a tray. Small grab samples were then taken from different positions, so that all the surface area of the tray was sampled.

### **Dry and Wet Classification**

#### **Dry classification**

A representative sample of the test soil was taken and placed in a setup of sieves. Ceramic mill balls were placed inside each sieve in order to provide an attrition and scrubbing action to enhance separation of fines from larger particles in the matrix. The sieves were put in a shaker for half hour and the separated fractions were weighed and analyzed.



### **Wet classification**

The procedure for wet classification was similar to that of dry classification. After the fractions were separated, each one was washed into the next smaller fraction with deionized water. The final products of the separations were then dried in an oven at 20°C over night, weighed and analyzed.

### **Visual Inspection**

The samples were spread uniformly on a tray so that all the surface area of the tray could be examined. A stereo microscope was used to examine the fractions smaller than 4 mm. Random samples were taken from the tray and thoroughly examined under the microscope at different magnifications.

### **Metal Speciation**

A sample of the test soil was sent to Canada Centre for Mineral and Energy Technology's (CANMET) Mineral Sciences Laboratories for a complete mineralogical analysis in order to determine the speciation of the metals present in the soil. Lead was the primary contaminant of concern.

### **Soil Washing/Leaching Tests**

For the purpose of soil washing/acid leaching tests, 25 g samples of each of the desired fractions were contacted with leaching reagent in a ratio of 1:8 in 500 mL beakers. The slurries were mixed using a multiple stirrer at 200 rpm and 20°C, for two hours. The slurry was then filtered using a vacuum filter and rinsed with 200 mL of the leaching reagent. The pH was held constant. Both the filter cake and the filtrate were analyzed for metals. All tests were carried out in duplicates and triplicates in order to assure the reliability of the results.

During the second set of experiments (leaching/chelation), three different chelating agents were used and the leaching solutions were prepared so that the molar concentration of the chelant was 5 times higher than that of lead. The pH was varied for different runs (from 0.5 to 6). At specific time intervals, 5 mL aliquots of sample were taken for analysis.

### **Metal Analysis**

The soil samples were incinerated using a muffle furnace for four hours and then pulverized to 200 mesh (74  $\mu\text{m}$ ) particle size. 0.5 g of the prepared sample was then digested in a digestion tube. An aqua regia (1:3 v/v of 70% nitric acid/37% hydrochloric acid) digestion procedure was used to determine the metals in the soil. The metal content was then determined by atomic absorption spectrophotometry (AA) (direct flame aspiration, air/acetylene flame). AA was also used for analysis of wastewater samples.

## SOIL CHARACTERIZATION

### Particle Size Distribution

The soil was dried and crushed in order to break up the dried soil agglomerates to prevent a biased and incorrect size distribution. The soil was then mixed to obtain a homogeneous sample. All plastic battery casing fragments were removed. Random samples of the homogenized soil were taken and classified into five size fractions of +11.2 mm (Fraction A), -11.2 +4<sup>1</sup> mm (Fraction B), -4 +1 mm (Fraction C), -1 +0.106 mm (Fraction D), and -0.106 mm (Fraction E), using wet and dry classification methods. Figures 1 and 2 present the size distribution of different size fractions of the test soil.

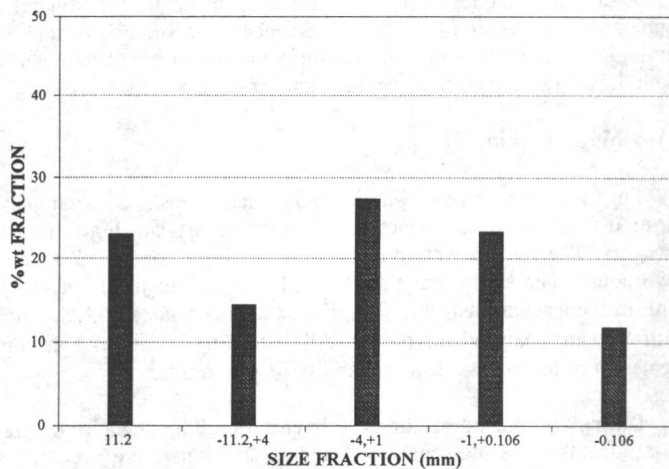


Figure 1. Particle size distribution in the soil matrix after dry classification.

<sup>1</sup> The negative sign preceding the number indicates a particle size smaller than that number and plus sign indicates a particle size larger than that number. -11.2 +4 means a size smaller than 11.2 mm and larger than 4 mm.

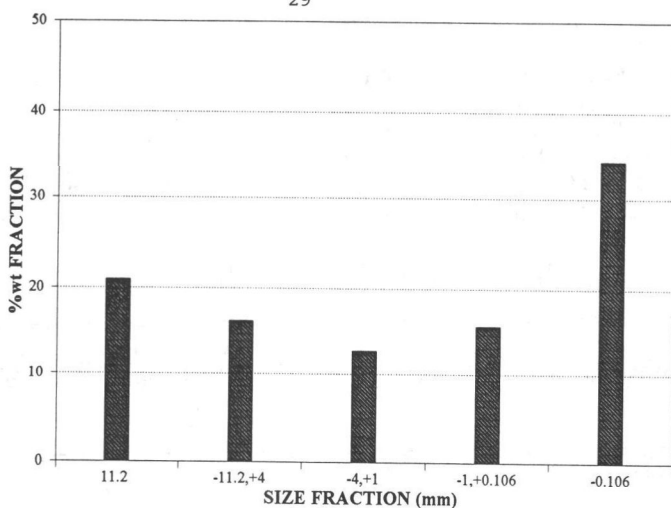


Figure 2. Particle size distribution in the soil matrix after wet classification.

The above figures illustrate that by applying wet classification the fines which are attached to the surface of larger soil particles will be separated, thus providing an accurate picture of the size distribution in the soil matrix. Normally the majority of the metal contamination is present in the finer fraction. By application of wet classification alone a 38% reduction in the volume of the contaminated soil was accomplished.

### Visual Description

The test soil was inspected visually for the presence of any battery parts and other metal contamination. The soil was wet and muddy and the only visual contamination detectable was plastic fragments of battery casings, several centimetres in size. No large metal fragments were observed.

After classification of the soil into five size fractions, and separation of plastic casing fragments, each of the fractions were inspected visually. Fractions A and B contained no visual contamination of any kind. Fractions C, D, and E were inspected under stereo microscope. Inspection of fraction C showed presence of metallic fragments of the size range of the fraction. The metallic fragments were not very abundant but enough to raise concern and cause high lead readings in the metal analysis. Fraction C also contained a substantial amount of organic matter in the form of leaf and bark fragments and small stems in addition to plastic battery casing fragments and tar particles of the same size range of the fraction. No metal fragments were detectable in fraction D but a substantial amount of organic matter (fine plant residues and humus) was observed which may contain lead complexed with organic acids such as humic acid. No metallic lead or battery casing fragments were observed in fraction E.

### Heavy Metal Content and Soil Condition

The soil was analyzed for carbonate content, pH, and lead. Table 1 presents the results of the analysis. The results indicate that the soil lead concentration exceeded both residential and industrial limits set by the Canadian Council of Ministers of the Environment (CCME).

Table 1. Results of the analysis of the test soil.

Parameter	Detected Levels	CCME Criteria for Residential Area	CCME Criteria for Commercial/Industrial Area
Moisture (%)	15	-	-
pH	7.5	6-8	6-8
Carbonate (ppm)	46	-	-
Pb (ppm)	6300 - 8800	500	1000

### Lead Distribution

The concentration of lead was determined in each fraction generated in dry and wet classification. Table 2 presents the lead concentration in each of the fractions after wet classification. When a range of concentrations is given, it indicates the lowest and highest readings that were obtained from the analysis of any given sample. Figures 3 and 4 show the lead distribution (% lead content) in each soil fraction.

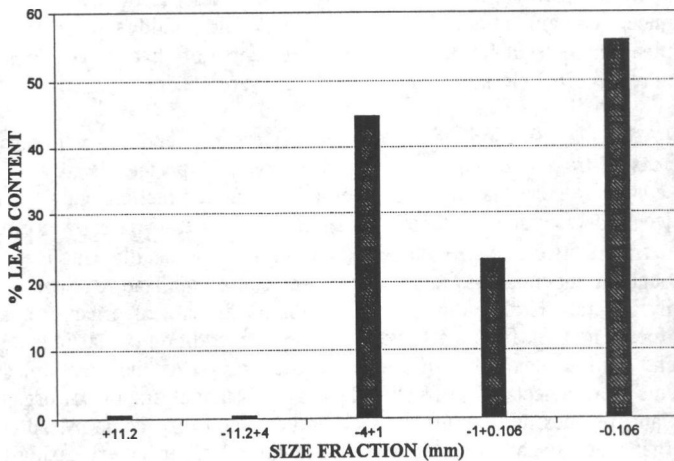


Figure 3. Distribution of lead in the soil after dry classification.

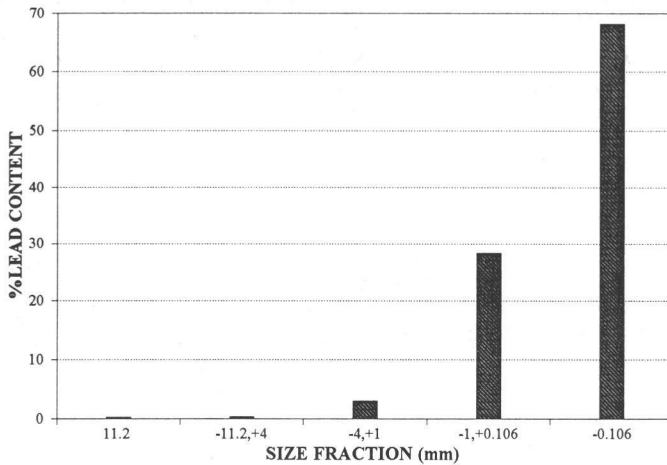


Figure 4. Distribution of lead in the soil after wet classification.

Figures 3 and 4 clearly indicate that washing the soil can concentrate the contamination into fine fraction and reduce the volume of contaminated soil. Each of the fractions resulting from dry and wet classification were analyzed for metal content. Table 2 shows the metal concentrations in the soil.

Table 2. Lead concentrations in the soil after wet classification.

Soil Fraction	[Pb] (ppm)
A	30 - 180
B	60 - 340
C	250 - 11890
D	5350 - 7100
E	5900 -6620

### Metal Speciation

A mineralogical study was carried out on the soil in order to determine the metal speciation and different metal carriers in the soil. The study was carried out at CANMET's Mineral Sciences Laboratories in Ottawa. The soil sample sent to CANMET was dried and screened into three fractions: +4.76 mm, -4.76 +1.19

mm, and -1.19 mm. Fractions of larger than 1.19 mm were not of interest for the mineralogical study because they consisted of rock fragments. The study was performed on the -1.19 mm fraction and showed that 90-95% of the lead in that soil fraction was present as lead carbonate. According to the mineralogical study lead was present as: lead carbonate, lead oxide, metallic lead, lead sulphate, lead phosphate, lead sulphide, and minor amounts in goethite and in carbonaceous matter.

## **TREATABILITY TESTS**

After classifying the test soil into five size fractions, soil washing tests were performed on fractions C, D, and E (-4+1 mm, -1+0.106 mm, and -0.106 mm respectively). Due to heterogeneity of the test soil, the effectiveness of each test was evaluated based on each individual sample tested.

### **Soil Washing/Leaching Tests**

Soil washing experiments were carried out in order to determine the effectiveness of acid leaching and a combination of acid leaching and chelation. The soil washing tests were applied after the soil was subjected to different mechanical treatments.

### **Wet Classification/Soil Washing**

As a result of wet classification, fractions A and B were clean with lead concentration well below CCME criteria. Fractions C, D, and E were used for the soil washing/leaching tests. It was not expected that soil washing/leaching would be effective for treatment of fraction C because of the presence of lead fragments; however, fraction C was also included in the tests in order to determine if there were any potential for soil washing/leaching. Several sets of experiments were performed using 0.1 M hydrochloric acid (HCl), 0.1 M HCl and saturated EDTA solution at pH 1.0, 0.1 M nitric acid (HNO<sub>3</sub>) and 1 M acetic acid (CH<sub>3</sub>COOH). Table 3 presents the results of the experiments. Results demonstrate that leaching is not a successful method for the removal of metal fragments.

Table 3. Results of soil washing/leaching tests.

Wash With 0.1 M HCl	Fraction	Initial [Pb](ppm)	Final [Pb](ppm)	% Removal
	C	5150	260	95
	D	7100	4400	17
	E	6240	470	93
Wash With 0.1 M HCL/ EDTA	Fraction	Initial [Pb] (ppm)	Final [Pb] (ppm)	% Removal
	C	700	270	61
	D	8750	2420	72
	E	6930	450	91
Wash With 0.1 M HNO <sub>3</sub>	Fraction	Initial [Pb] (ppm)	Final [Pb] (ppm)	% Removal
	C	3750	3750	0
	D	6490	1060	84
	E	6490	590	91
Wash With 1 M Acetic Acid	Fraction	Initial [Pb] (ppm)	Final [Pb] (ppm)	% Removal
	C	4890	1990	60
	D	6190	3150	49
	E	5490	1920	65

Fraction D consisted mostly of sand and therefore had high levels of silicates. Lead can readily replace potassium in its silicates [3]. It is possible that a substantial amount of lead in fraction D was in form of silicates which are stable and do not leach unless extremely strong acidic conditions are present (such as in presence of aqua regia). If this was the case, fraction D could be considered clean after the acid wash and would be safe to be returned to the site.

The results of soil characterization and soil washing tests indicate that due to the diversity in form and speciation of lead present, no single treatment method would be sufficient for treatment of the site. Soil washing can however be an effective part of a process train for the treatment of a substantial part of the soil.

### Mechanical Treatment of Fraction C

For removal of lead fragments from fraction C, a gravity separation was used. A jig was constructed and used for the separation of metallic lead fragments. The Jig successfully separated almost all of the lead fragments. Visual inspection of the fraction after the mechanical separation under stereo microscope, did not show any lead fragments. The lead concentration of the treated sample dropped from 12,000 ppm to 180 ppm.

### Leaching and Chelation Tests

For the experiments of this part of the study were limited to soil samples from fraction E. Combination of acid leaching and chelation was compared with acid leaching alone at different pH, with the change in the metal concentration of soil being monitored over a 24 hr period. The leaching tests without the presence of the chelating agents were carried out to establish a bench mark for comparison. Figure 5 illustrates the results of acid leaching using hydrochloric acid at a pH range of 0.5 to 3.0.

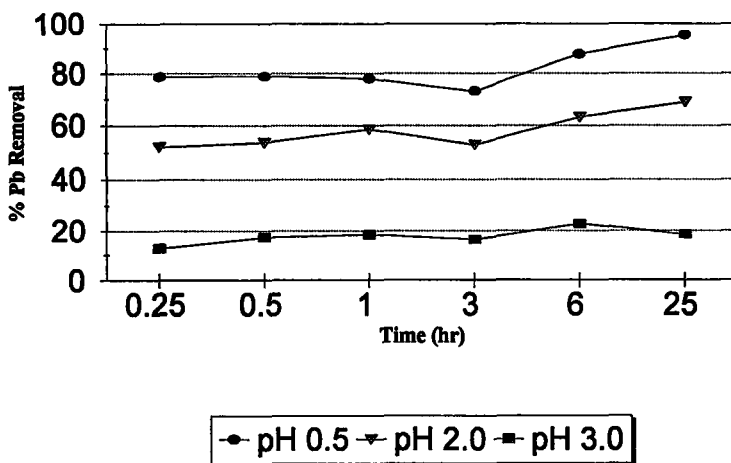


Figure 5. Removal of lead from the fines (-0.106 mm) with HCl at different pH after 24 hours contact.

### Acid/EDTA leaching

EDTA was added to the leaching solution in a 5:1 EDTA/Pb molar ratio. Lead removal was evaluated at pH range of 1 to 6. Figure 6 illustrates the results. As the results indicate, most of the lead was removed within the first four hours of the experiment. This indicates that most of the leachable lead was removed during



the experiment and the remaining lead species were in a non-leachable and stable form. The chelating agent present in the solution promotes the leaching process by removing lead from the vicinity of the soil particles and maintaining a large concentration gradient which is the driving force for the solubilization and mobilization of lead. A comparison of Figure 6 with Figure 5 clearly shows that when EDTA is present the same removal levels can be achieved at higher pH's compared to when there is only acid present. pH 4 was the most suitable choice among the pH's evaluated.

In all cases, the final lead concentration of the soil after 24 hours of treatment was below the limits set by CCME for industrial parklands ( 1000 ppm ). This indicates that EDTA can be used in the leaching solution at higher pH for the removal of lead from contaminated soils. The following important facts can be pointed out:

- leaching at higher pH will require less acid and may reduce the overall cost of the leaching process,
- at a higher pH leachability of naturally occurring metals in soil, such as iron, will decrease which can help in preserving the chemical integrity of the soil, and
- the removal of lead will increase.

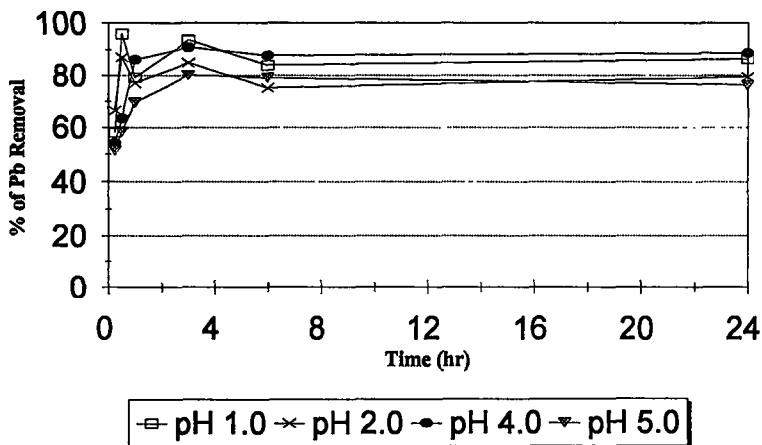


Figure 6. Removal of lead from the fines (-0.106 mm) with HCl and EDTA (5:1 molar ratio EDTA:Pb) at different pH after 24 hours of contact.

### Acid/Catechol leaching

Figure 7 illustrates the results of acid leaching tests in the presence of catechol. As illustrated in Figure 7, lead removal was not as high as that of the case for HCl alone or HCl/EDTA for a given pH. The best removal obtained was approximately 60% at pH 1 whereas at higher pH's the removals did not exceed 20%. Based on the results addition of catechol to the leaching solution does not appear to enhance the leaching process.

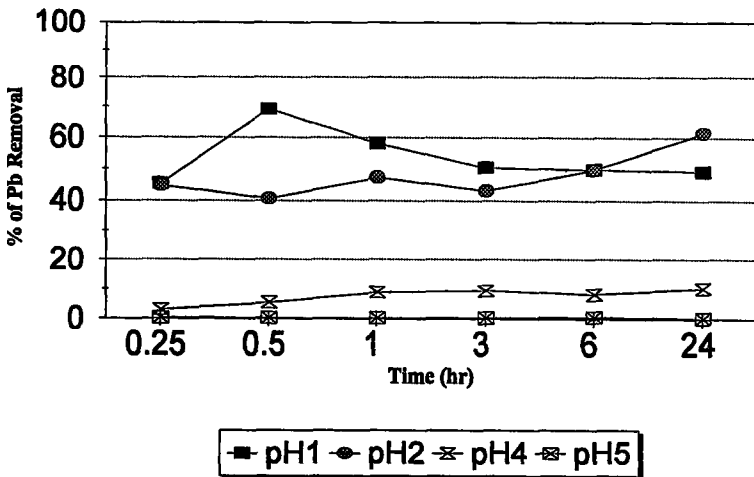


Figure 7. Removal of lead from the fines (-0.106 mm) with HCl and catechol at different pH after 24 hours contact.

### Acid/Pyrogallol Leaching

Figure 8 illustrates the results of leaching tests using pyrogallol as chelating agent. The Figure shows that lead removals were lower than all other cases mentioned before at any given pH. Pyrogallol is therefore the least effective chelating agent, for Lead removal, among the three chelating agents tested.

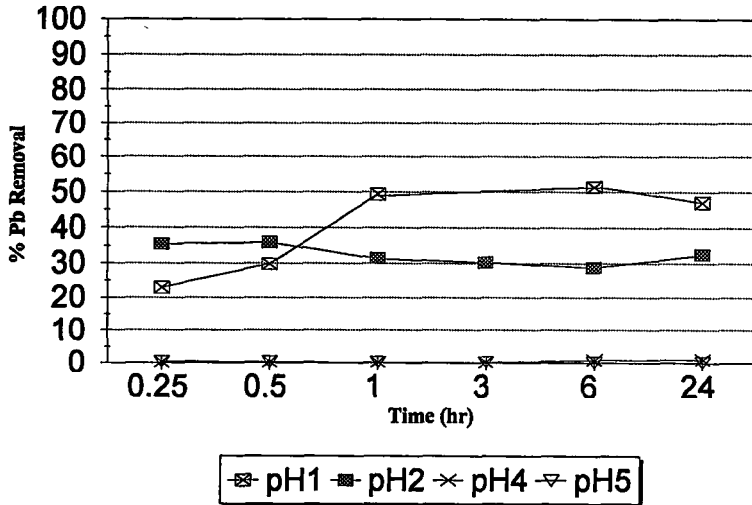


Figure 8. Removal of lead from the fines (-0.106 mm) with Hydrochloric acid and pyrogallol at different pH's after 24 hours contact.

### Chelant Regeneration

A leachate generated during HCl/EDTA leaching tests, was acidified to pH 1. At low pH chelating bonds between EDTA molecules and lead are broken and solubility of EDTA decreases. This results in crystallization and precipitation of EDTA which can be separated from the rest of the solution. 56% of the initial EDTA was recovered in this way. The low recovery of EDTA can partly be attributed to losses of EDTA during the filtration and rinsing processes. In addition EDTA is partly soluble at low pH and this would determine the maximum yield of the regeneration process. The authors believe that the regeneration conditions can be optimized and the recovery yield can be increased.

Membrane separation (nanofiltration) was also investigated as a possible method for separation of EDTA from lead; however, the rejections of lead and EDTA were very close, due to comparable size of EDTA molecule and a hydrated lead ion, and the tests were terminated.

## WASTEWATER TREATMENT

Table 4 demonstrates the metal concentration in two different wastewater streams generated in the treatment process: rinse water after soil washing and leachate.

Table 4. Metal concentrations in rinse water

Metal	Concentration in Leachate (Fraction A&B) (ppm)	Concentration in Rinse Water (Fraction D&E) (ppm)	Discharge Limits For Municipal Sewer (ppm) <sup>2</sup>
Pb	71 - 582	0.2 - 0.8	5
Cu	0.5 - 4	0 - 0.2	3
Zn	0.4 - 8	0 - 0.1	3
Ni	2.8 - 10	0 - 0.3	3
Cd	0.1 - 0.3	0	1

Table 4 shows that the rinse water generated in soil washing process can be discharged without treatment. On the other hand the concentration of the metals in the leachate all except cadmium exceeded the discharge limits.

Sodium sulphate can be successfully used to remove the lead from the leachate because lead sulphate has very low solubility. The acid leaching effluent of some of the tests were retained and mixed in order to make up a typical effluent. The initial lead concentration of the effluent was 222 ppm. The effluent was treated with sodium sulphate using a 1 M sodium sulphate solution. 96 % of the lead in the effluent was removed and the effluent had a final concentration of 14 ppm. After treatment of the effluent with sodium sulphate, the pH of the final discharge water was adjusted to 7 by addition of a sodium hydroxide. The pH adjustment resulted in further decrease in the lead concentration yielding a lead concentration of 11 ppm. This waste stream can be combined with rinse water stream from the wet classification process and be discharged or recycled and reused in the wet classification stage.

There are other methods such as reverse osmosis, nanofiltration, polymer binding and ultrafiltration, and adsorption and microfiltration which has been applied successfully by EED for removal of metals from contaminated water and wastewater. The contaminated wastewater may also be treated with sulphuric acid

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<sup>2</sup> The municipality of Metropolitan Toronto bylaw No. 153-89 to regulate the discharge of sewage and land drainage in the Metropolitan area; adopted by council on November 9, 1989.

followed by neutralization with lime which may be less expensive to use than sodium sulphate.

### SUGGESTED PROCESS TRAIN

Figure 9 illustrates the suggested process train for the remediation of the site.

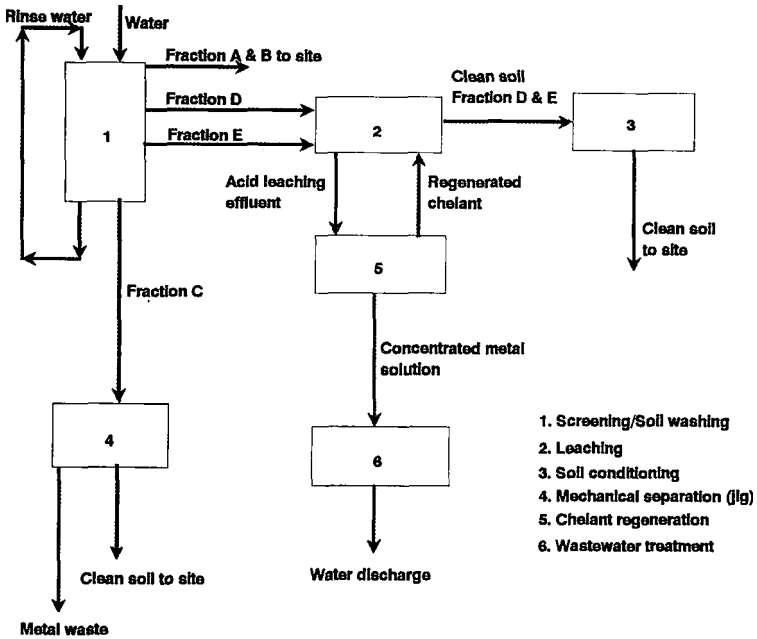


Figure 9. Proposed process train for removal of lead from the contaminated soil.

## **AVAILABLE OPTIONS AND RELATIVE COSTS**

The options available for treatment of the site under investigation may include: excavation and off-site disposal at a cost of \$150-240 per tonne, on-site soil washing at a cost of \$60-110 per tonne, on-site solidification at a cost of \$110-220 per tonne, in-situ vitrification at a cost of \$280-380 per tonne and in-situ solidification at a cost of \$110-190 per tonne [4]. The total amount of soil that required treatment was approximately 13,000 tonnes. Three treatment scenarios were considered as follows for the purpose of cost comparison:

### **Option I. Solidification of the Entire Soil**

If on-site solidification is selected as a method of treatment, a total of \$1,400,000 to \$2,900,000 would be the cost of the application of this technique to the whole 13,000 tonnes of soil.

### **Option II. Mechanical Separation and Solidification**

The initial separation of fractions A and B from the remainder of soil would reduce the treatment volume considerably (38% in the test sample). This would result in a cost reduction from Option I down to \$900,000 - \$1,800,000. The additional costs of wet classification would be added to this amount. Total costs should still be much less than Option I since wet classification is a much less expensive technique than solidification.

### **Option III. Mechanical Separation and Acid Leaching**

The total cost of treatment would be a sum of the costs of mechanical separation, leaching, and wastewater treatment. If soil conditioning is required, its cost must be added as well. Fractions D and E which will be treated by acid leaching represent approximately 50% of the entire soil. The cost of leaching alone would therefore be approximately \$400,000 - \$700,000. Cost data for wastewater treatment was not available; therefore the total cost for this treatment scenario could not be estimated. It is known, however, that reagent precipitation is among the most inexpensive techniques for water treatment. It may be cautiously assumed that the total cost in Option III may be even lower than that in Options I and II.

It should be stressed that the above numbers are a result of a rough approximation and may serve only for an approximate comparison of the three treatment scenarios.

## CONCLUSIONS

- A combination of mechanical separation and Soil washing/leaching was successful in removing lead from the contaminated soil sample.
- Mechanical separation (sol washing) resulted in substantial reduction in the volume of the contaminated soil.
- Application of a jig effectively removed metallic lead fragments from the -1 +0.106 mm soil fraction.
- Acid/chelant leaching effectively reduced the lead concentration to below the CCME criteria.
- EDTA was the most effective chelating agent among the chelating agents evaluated and its addition to the leaching solution resulted in better lead removals.
- EDTA was regenerated by acidification of leaching effluent to pH 1 and filtration of precipitated crystals, and lead was removed via chemical precipitation.
- A cost estimation indicated that soil washing/leaching is competitive with remediation alternatives such as solidification/stabilization.

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## **STUDY OF THE MAP™ ENHANCED SOLVENT EXTRACTION PROCESS FOR THE REMOVAL OF ORGANIC CONTAMINANTS FROM SOIL**

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### **ABSTRACT**

The Microwave-Assisted Process (MAP™), patented by Environment Canada, is a novel method which uses microwave energy to enhance the solvent extraction of soluble products from a wide range of materials. The Environmental Technology Centre is currently investigating the applicability of the MAP™ to enhance the solvent extraction remediation of soils contaminated with organic compounds. To date, numerous lab-scale tests have been performed providing encouraging results. A pilot-scale evaluation is scheduled to begin shortly using a recently constructed microwave unit. The objectives of the project are the optimization of operating parameters, the evaluation of extraction efficiencies obtained for various contaminant-soil systems and a cost estimate analysis for a full-scale commercial operation based on the pilot-scale results. In order to maintain the credibility of the test results, all soils being investigated are obtained from actual contaminated sites rather than being prepared in laboratory.

### **INTRODUCTION**

The Environment Technology Centre (ETC) is currently investigating the use of microwave energy to enhance the extraction of organic contaminants from soil using solvents. This method is based on the patented Microwave-Assisted Process (MAP™) developed by one of ETC's research scientists. Environment Canada holds the intellectual property rights for this technology in various jurisdictions.

MAP™ was originally developed for the extraction of aromas and flavours from plant material. The results from this work have been very promising, with a purer product being obtained in a fraction of the time required by other extraction methods such as steam distillation. Other environmental applications of the technology are being validated by the Emergencies Science Division - concentrating on the analysis of contaminated soil and the extraction of collected contaminants from filter media used in air monitoring equipment. [1-4]

The results from the MAP™ applications described above as well as from the preliminary laboratory-scale experiments using contaminated soils are encouraging. The process is expected to overcome some of the major limitations of current solvent extraction remediation technologies, such as the

requirement for long extraction times and large volumes of solvent, while increasing the extraction efficiency.

## **PROCESS DESCRIPTION**

The ETC will be studying the applicability of MAP™ to the extraction of organic contaminants from soil using a pilot-scale process. The main components of the process are a 6 kW microwave generator and a process cavity capable of treating 4 GPM of slurry. These units were constructed by Progressive Recovery Inc. (PRI) of Dupon Illinois, according to specifications developed by ETC and PRI. Design details of the equipment can be found in Figure 1.

A schematic of the proposed complete pilot-scale solvent extraction process is shown in Figure 2. Initially, the soil is screened to a particle diameter size of 4 mm or less. Previous studies have revealed that particles greater than this cutoff size often have negligible contamination or, if contaminated, can be more suitably treated with other methods. The screened soil and chosen solvent are then mixed in an auger pump, which transfers the slurry through a spiral configuration of Teflon™ tubes which are transparent to microwaves. As the slurry runs through these tubes, it is irradiated with microwaves. The microwave are directed to the slurry through a waveguide at a frequency of 2450 MHz from a specialized power generator. It is in this step that the microwave is used to enhance the transport of the contaminants from the soil to the solvent (see below). The slurry is then sent through a centrifuge and filter apparatus to separate the soil from the solvent. The soil is dried to remove any additional solvent and the contaminants are separated from the solvent through distillation.

The solvents to be used in this investigation will be either fully or partially transparent to microwave irradiation, which allows selective and localized heating of the moisture and contaminant in the soil, without excessive heating of the complete mixture. The increased temperature and pressure causes the contaminants to migrate from the soil to the surrounding, relatively cold solvent which traps and dissolves the contaminants. The transparency of the solvent can be determined by the dielectric properties of the solvent. As an example, hexane and dichloromethane have low dielectric constants whereas water has a relatively high dielectric constant. It must be noted, however, that while free water has a high dielectric constant, water that is bound within the soil exhibits a low dielectric constant. Residual free water present within the soil is therefore the important source of thermal energy provided to the solvent/soil mixture when subjected to microwave, whereas bound water will be relatively transparent to microwave. [1,3]

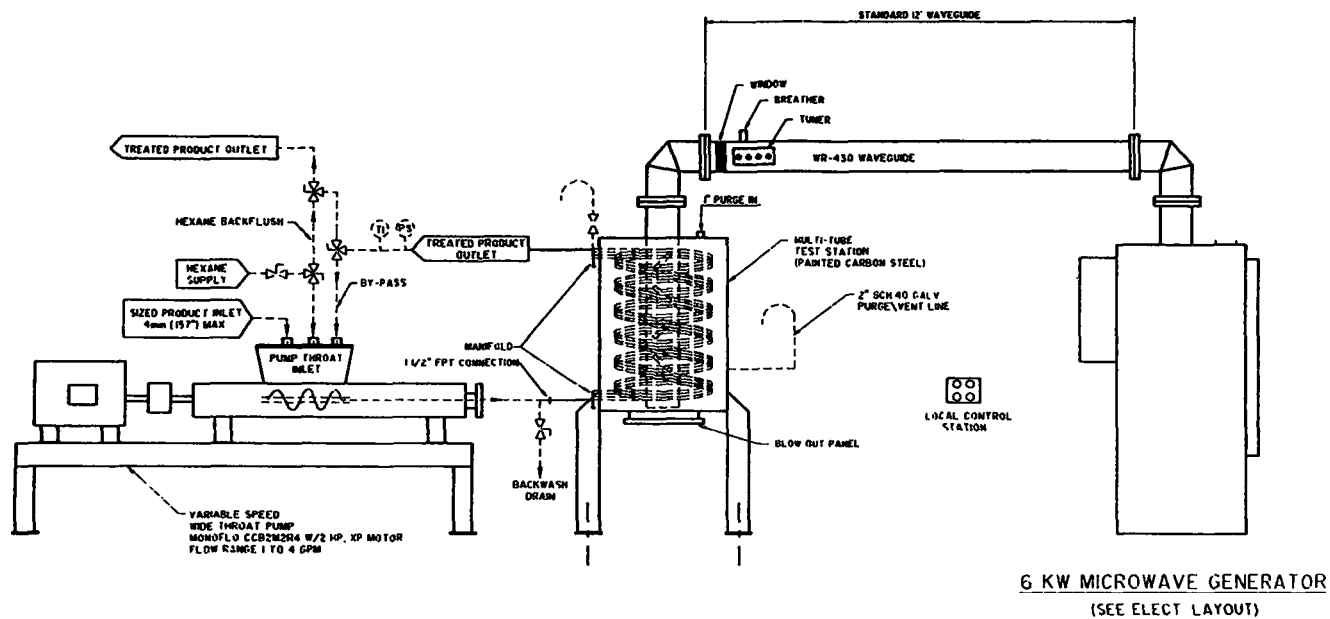


Figure 1 - Pilot-Scale Microwave Process Unit

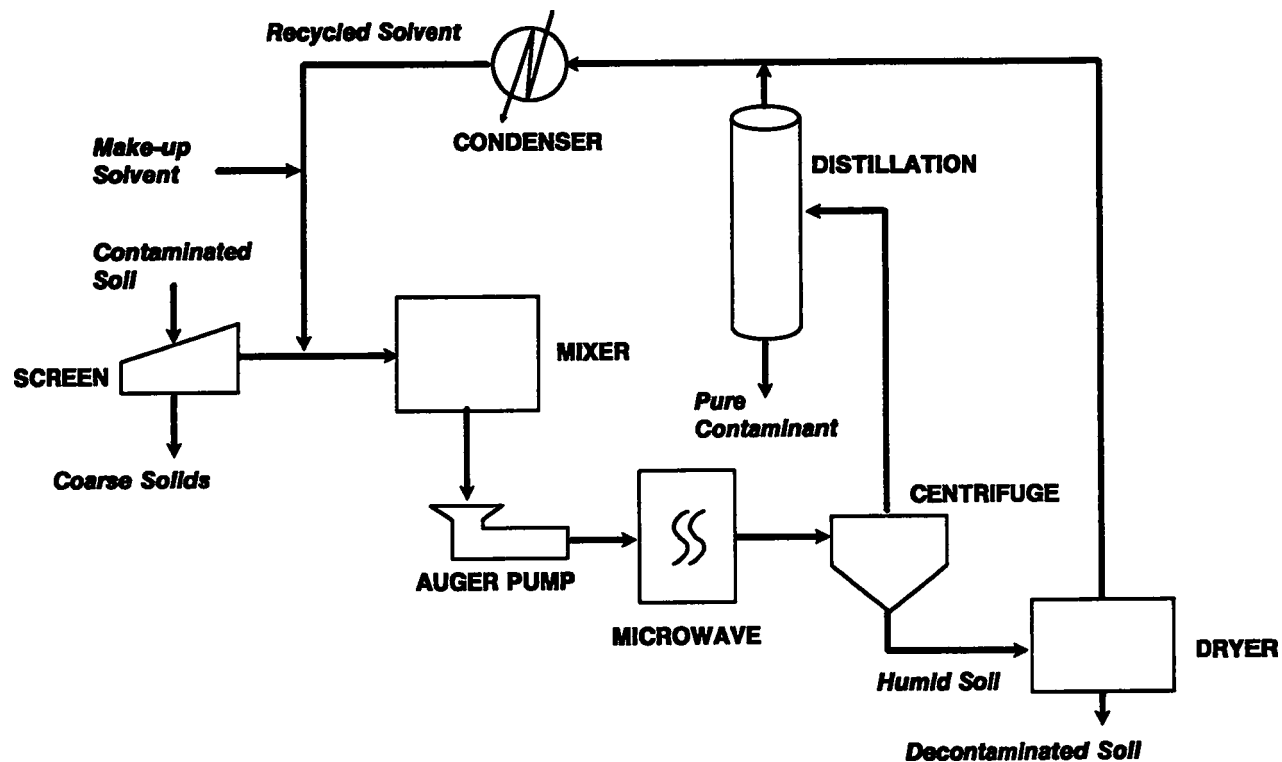


Figure 2 Solvent Extraction Process Enhanced with MAP™

## **PROJECT OBJECTIVES**

The pilot scale microwave process unit is expected to be operational by mid-June 1994. At that time, ETC will conduct preliminary tests to become familiar with the operation of each aspect of the unit. The microwave unit has been designed to operate on a continuous basis and offers the possibility of on-line process controls which were not available for the lab-scale work. In order to fully understand the effectiveness of the MAP™ process, ETC will study and optimize the following parameters: residence time, microwave exposure level, solvent to soil ratio, humidity level and recirculation or multiple passes.

Ideally, all work will be performed using soils obtained from various contaminated sites across Canada. Doing so will add to the validity of the results as the use of synthetically contaminated soils do not fully simulate soils obtained from actual sites.

Following the pilot-scale evaluation, a field-scale MAP™ unit will be designed and constructed. Its conception and operation would be based on the pilot-scale unit, taking into consideration any required modifications arising from the results of the work performed at the smaller scales. An organization capable of commercializing the technology would then be granted a licence to use and/or manufacture the technology for the treatment of contaminated soil.

Assistance would be given to the licensed organization in terms of training on the field-scale unit and selection of operating parameters. Furthermore, when the field-scale unit is to be used on site, ETC could perform tests using their pilot-scale unit to optimize the process parameters for the particular type of soil.

## **PRELIMINARY LAB-SCALE TESTING**

Prior to evaluating the MAP™ enhanced solvent extraction process at the pilot-scale, several laboratory-scale tests were performed. The main objectives of these experiments were to gain an understanding of the general effect of all parameters involved in the MAP™ process and prepare a general test plan for preliminary testing of the pilot-scale unit, taking into consideration the functional differences between the batch mode microwave oven and the continuous spiral configuration of the pilot-scale unit.

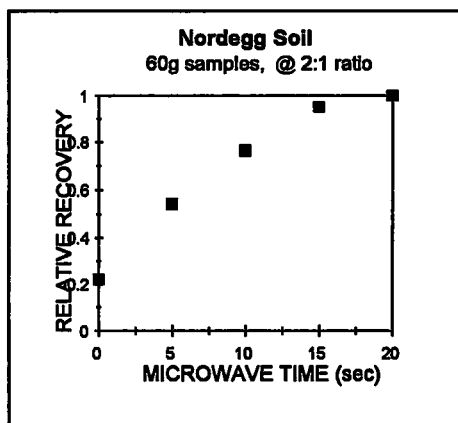
A series of tests were performed based on simple factorial designs to evaluate the relative interactions between parameters and the individual influences of the parameters on the process. The parameters of interest were the solvent to soil ratio, the microwave exposure time and the humidity level in the soil. Equipment and materials used in the lab-scale experiments were as follows:

<b>Microwave oven:</b>	SANYO model #EM-573TWS Household Microwave Oven Microwave frequency: 2450 MHz Power consumption: 1450 W Max power output: 700 W
<b>Solvent:</b>	Hexane (distilled in glass, 95% n-Hexane)
<b>Soils:</b>	Nordegg site - Gulf Strachan Refinery Strachan, Alberta Contamination: 5000 ppm diesel Type: sandy loam, high clay content

An example of one of the laboratory experiments conducted is a series of tests using a simple matrix designed to single out one of the process parameters and clearly identify its influence on the system. Triplicate tests were performed to insure reproducibility. The parameter chosen for investigation in these test was the microwave exposure time. The influence of exposure time on the process had been observed in previous tests but the conclusions lacked definition and accuracy.

### Results

Figure 3 clearly shows the influence of the microwave exposure time on the recovery of a solvent extraction system. The relative recovery scale represents the efficiency of the hexane solvent to extract the hydrocarbon contaminants from the soil during one extraction stage with a total contact time of 1 minute. In this case, 15



**Figure 3**

seconds of microwave irradiation during the 1 minute contact time was sufficient to quadruple the recovery of diesel type contaminants from the Nordegg soil.

### ESTIMATED PROCESS COSTS

A detailed cost estimate of the solvent extraction process enhanced with the MAP™ was performed. [5] A summary of the cost breakdown for the process is shown in Table 1. The analysis was based on the pilot unit designed by PRI operating at the following conditions:

Capacity:	900 L/h (maximum operation)
Operating time:	220 day/yr, 16 h/day
Solvent type:	Hexane (~95% n-Hexane)
Solvent cost:	0.47 \$/L (Caledon 93/01/01)
Soil type:	Natural topsoil (Greely Sand and Gravel)
Solvent to soil ratio:	1:1 by weight
Operating temperature:	25 °C

**Table 1 - Summary of cost analysis**

Item	Cost (\$/tonne)
Capital depreciation	47
Power requirements	12
Solvent replenishment	36
Total	95

The following four main assumptions were used for the cost estimate:

1. Equipment life is estimated at 10 yrs and capital costs are depreciated over the 10 yr period using a straight line method.
2. Process operates as a full time remediation technology (i.e. 220 days/yr).
3. The process requires only one extraction stage to decontaminate the soil.
4. The microwave energy required to decontaminate the soil is equal to the amount needed to heat the moisture in the soil to its boiling point. This can be considered a worst case scenario.

This initial operating cost estimate performed on the proposed MAP™ soil treatment system includes initial soil handling, solvent extraction, microwave energy and solvent recovery. Not included are the costs associated with the disposal of the collected contaminant and mobilization of equipment and personnel. The operating cost for MAP™ is low when compared with other *ex-situ* treatment technologies where the contaminant is recovered, such as low temperature thermal desorption (without an afterburner) and conventional solvent extraction. These technologies have operating cost ranges of \$100-\$200/tonne and \$145-\$155/tonne (all in Canadian dollars), respectively [6]. More definite operating costs for the MAP™ unit will be determined using the pilot-scale unit.

## **SUMMARY**

ETC is about to embark in an in-depth pilot-scale study of the MAP™ process as applied to the remediation of soils contaminated with organic compounds. Preliminary lab-scale tests have been conducted in order to anticipate any problems related to the process and to help design the structure of the pilot-scale studies. While testing continues, ETC will be actively promoting the technology in order to attain the eventual goal of commercialization. One of the key selling points is the expected low process cost of remediation when compared to other ex-situ technologies.

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## APPLICATION OF THERMAL PHASE SEPARATION IN TREATMENT OF HYDROCARBON CONTAMINATED SOIL

by

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*Many soil Thermal Treatment processes face the uncertainty of obtaining operating permits, specifically if the contaminated soil due to chemical spills are located in a heavily populated area. The Thermal Phase Separation (TPS) process can provide an alternative soil treatment. Soil contaminated with high molecular weight hydrocarbon and chlorinated compounds can easily be treated using this type of process. Soil is indirectly heated to increase the vapour pressure, this process then cools the gaseous contaminants and condenses them into a liquid form. The liquid containing the contaminants may be recycled depending on its constituents. The attractive feature of this process over conventional Thermal Desorption or high temperature incineration with a direct heating process is that TPS minimizes Products of Incomplete Combustion (PIC) formation which allows for ease of siting and regulatory approval.*

### INTRODUCTION

There are a number of sites in Canada that are contaminated with compounds such as PolyAromatic Hydrocarbons (PAHs), creosotes, chlorophenols, (PCPs) and Polychlorinated Biphenyls (PCBs).

Many of these sites were used for wood preserving and sawmilling operations or other manufacturing activities.

Contamination at these sites was generally caused by accidental spills, leaks, disposal of residuals from the manufacturing and chemical application processes or simply as a result of poor operating practices.

Several remediation techniques have been developed to treat hydrocarbon contaminated soils, all of which may be considered as a viable alternate to the traditional methods of incineration or landfilling. Some of the most widely used mobile or in-situ technologies are:

- Low Temperature Thermal Desorption
- Solvent Extraction
- Bioremediation
- Stabilization/Fixation
- Thermal Phase Separation

Thermal Phase Separation (TPS) is considered as a reliable, cost effective solution for the remediation of complex hydrocarbon contaminated soils.

## **TECHNOLOGY CONCEPT**

Thermal Phase Separation (TPS) utilizes indirect heating as the principal process to separate water and hydrocarbon contaminants from soils, sludges and other host materials. The gaseous water and hydrocarbon contaminants are condensed into a liquid form. The condensate is then separated into organic and water fractions.

The process uses the vaporization and condensation features of compounds under treatment to volatilize and subsequently recover them using the condensation process (Figures 1, 2).

The indirect heat application in the process is designed to drive off hydrocarbons with boiling points as high as 660°C. High boiling points PAHs such as pyrene and chrysene as well as chlorinated compounds such as PCB and PCPs can be recovered using this technology.

## **PROCESS DESCRIPTION**

### **Feed Handling**

Feedstock soil, previously screened to remove rock cobbles, is deposited in a feed hopper by a small front-end loader, from which it is moved away by a horizontal conveyor belt. This belt discharges the material into a clay lump breaker which in turn discharges the fragmented soil onto an inclined conveyor for delivery to the extraction chamber. During the movement of the soil up the 17.5 degree incline, an indication weigh scale provides both an instantaneous feed rate and totalized feed amount.

### **Extraction Chamber/Thermal Unit**

The soil is discharged from the inclined conveyor to a small hopper, shaped to direct the material to two rotary paddle airlock valves (Figure 3). Upon passing through the airlock, the soil drops into the extraction chamber. Two parallel screw augers, each 12.2 m long, move the material through the heat treating zones.

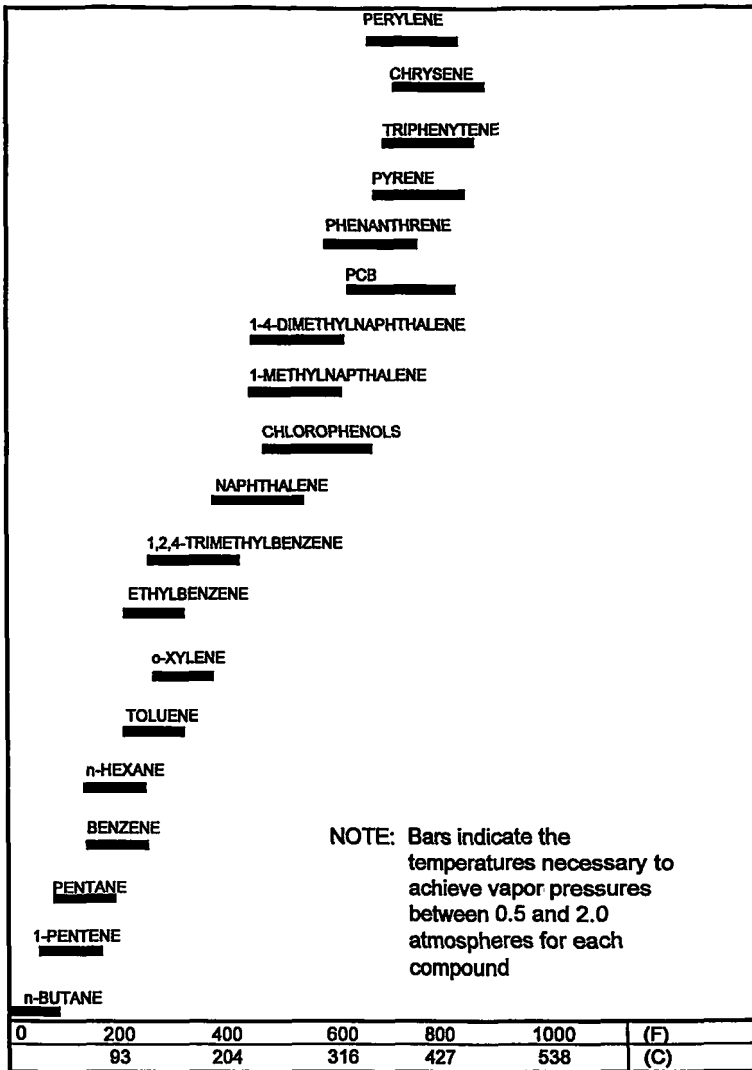


Figure 1: Vaporization Temperature of Hydrocarbon Constituents



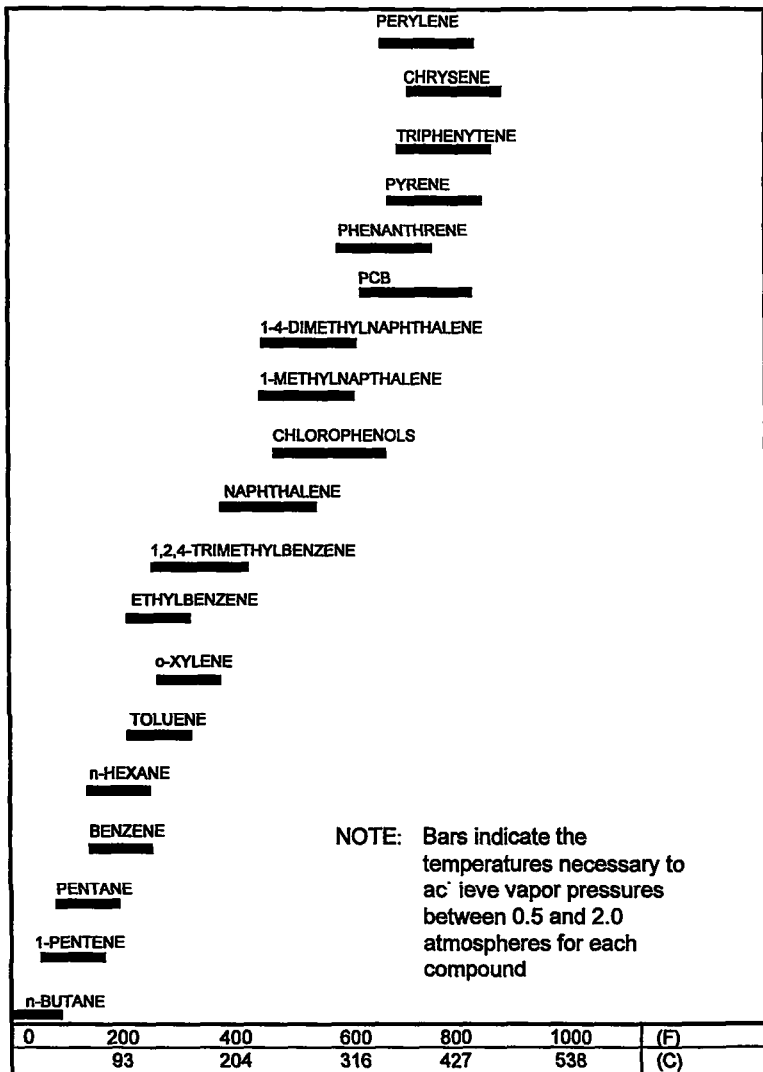


Figure 2: Condensation Temperature of Hydrocarbon Constituents



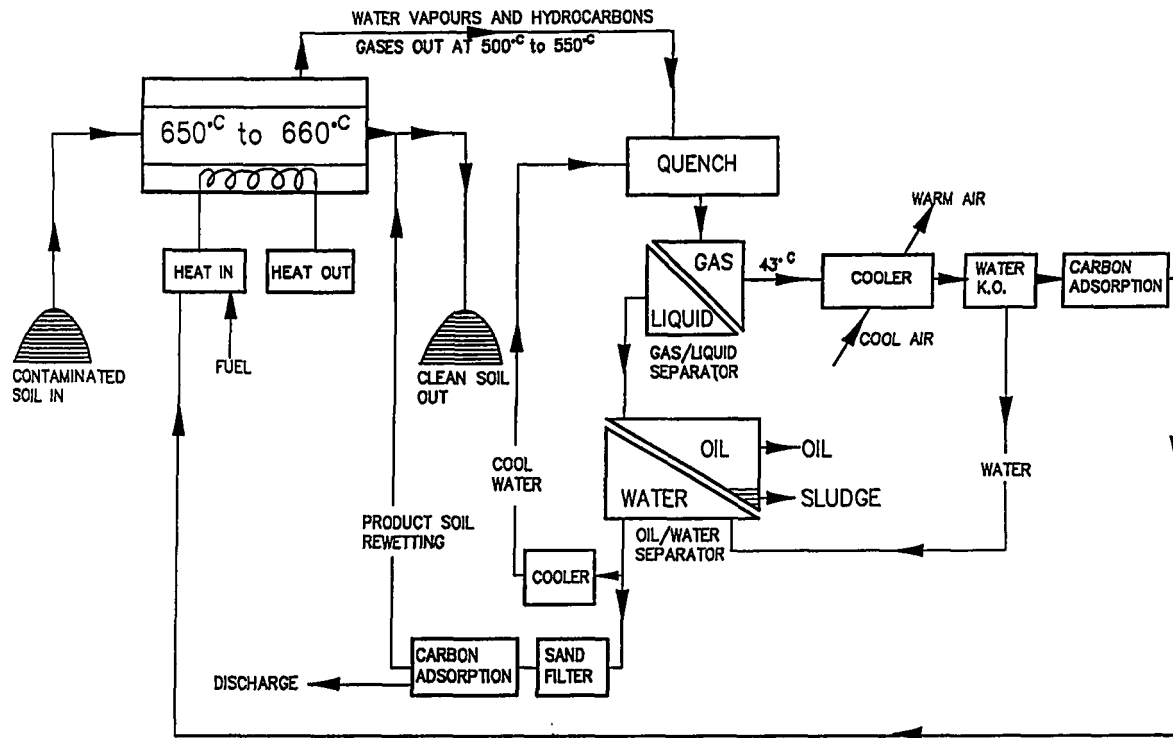


Figure 3: Thermal Phase Separator Flow Diagram



The extraction chamber remains physically separated from the combustion system by an alloy steel plate. The firebox derives its heat by combusting propane in a series of burners along the entire length of the extraction chamber so as to achieve even heat distribution. Heat is transferred from the combustion firebox to the soil via conduction through the steel plate. Modulation of the heaters is performed so that the soil temperature is elevated to a maximum of 660°C to vaporize hydrocarbons and moisture in the soil.

A draft inducer is utilized to maintain a slight vacuum in the firebox combustion chamber. The draft inducer utilizes an ambient air blower and eductor situated downstream of the stack sampling ports to provide the vacuum.

### **Treated Soil Handling**

The two extraction chamber augers direct the product soil to a discharge auger. The hot processed soil exits the discharge auger through a heat resistant paddle wheel airlock valve, which in turn directs the treated material to a pug mill. Water is sprayed into the pug mill, to achieve cooling of the soil and to prevent fugitive dust emissions. Any particulate originating in the rewetting process is removed in a small scrubber. The remaining vapour stream is further treated in the condensing system.

The cooled, wetted product is discharged to a belt takeaway conveyor and collected in a pile for eventual removal by a front-end loader.

### **Gas Treatment**

The water vapour and gaseous hydrocarbons originating in the extraction or separation chamber are subjected to three sequential treatment stages:

**Firstly**, the gas steam is cooled to approximately 45°C via direct contact water sprays in a quench chamber.

**Secondly**, the gas stream is cooled to a temperature only a few degrees above ambient, by a fin fan cooler. The resulting water content in the saturated gas stream is between one and five percent.

**Thirdly**, the relatively dry gas stream of non-condensable gases is subjected to final polishing in a mist eliminator (for fine aerosol removal) and a carbon adsorption bed. A positive displacement induced draft fan ensures movement of gaseous products through the system, from the extraction chamber to the condensing components. The discharge from the carbon adsorption bed, consisting of non-condensable gases (including traces of non-chlorinated, light, straight chain hydrocarbons such as methane and ethane), is directed to the combustion air inlet of the first propane fuel gas heater of the thermal unit's firebox.

## Emissions

Since the system is essentially a closed loop system and mass flow is relatively low, the following flue gas parameters are typical:

Compound	Concentration (mg/Rm <sup>3</sup> )	Mass Flow (kg/hr)
Particulates	37.5	0.21
HCl	<0.4	<0.002
SO <sub>2</sub>	2.3	0.013
NO <sub>x</sub>	200	1.11
CO	25	0.14
THC (as CH <sub>4</sub> )	5	0.028
PCP	<0.35	<1.95
Total PAHs	<1.23	<6.84

## Water/Condensate Treatment

A relatively large amount of water is recirculated through the quench to achieve cooling of the gas stream. This volume of recirculated water, together with products condensed from the gas phase are routed through a sludge settling chamber and a three phase oil/water/solids separator (Figure 3). Hydrocarbon liquids and sludges are drawn off for analysis, storage and possible reuse. The temperature of the remaining water is decreased in a fin fan cooler prior to recirculation back to the quench chamber. A slipstream of this waterflow is removed to ensure adequate level control and is treated by sand filtration and carbon adsorption prior to reuse for wetting/cooling of the treated product soil. Should the contaminated soil feedstock contain less than ten percent moisture, zero discharge of liquid effluent occurs. If greater than ten percent, a net production of water occurs.

## Other System Highlights

- The system is mounted on three trailers and is easily mobilized/demobilized
- A utility/control trailer allows for remote operator control and safety
- The TPS has a built-in water treatment system
- Up to 7.5-15.0 tonnes per hour of soil can be processed

## **RESULTS**

Based on commercial field application, TPS has provided excellent removal efficiencies for various hydrocarbons and chlorinated organics.

In March of 1993 the TPS process was used in a demonstration project. Different soil types with varying degrees of contamination were used as feed stock.

### **Soil Type 1**

In order to determine TPS effectiveness in treating various soil with different proportions of clay and sand, a very high content clay soil (up to 40%) was selected for this test.

High clay content soil was screened and preconditioned before treatment. Individual PAH compounds in the treated soil consistently met or exceeded BC Level C cleanup criteria. More than 45% of individual PAHs met BC Level B cleanup criteria (Table 1). The total PAH concentration in the feed stock was 1887.5 ppm. The treated soil from this feed stock resulted in 66.30 ppm of total PAHs representing 99.96% removal efficiency.

### **Soil Type 2**

This soil was typified by high PAH and PCP contamination with a sandy/clay texture. Individual PAH compound concentrations in the clean soil were well below BC Level C cleanup criteria.

The total PAHs also met Level C criteria with a 99.98% removal efficiency (Table 2).

The results for the chlorophenols were averaged from three batches of the feed stock during this demonstration test. The first two batches produced well below Level C results for chlorophenols in the clean soil, however, due to mechanical failure which resulted in lower temperatures in the heating chamber, the optimum removal efficiency for chlorophenols was not achieved. This batch was treated later with optimized operating conditions which resulted in chlorophenol compliance with BC Level C for chlorophenols.

### **Process Optimization**

Thermal Phase Separation technology or any similar soil thermal treatment process requires proper soil conditioning and soil preparation before treatment. Several factors must be taken into consideration prior to starting any projects:

- soil moisture content
- concentration of each contaminant



**INCOMING WASTE TYPE:**

High clay content soil with low PCP contamination

PARAMETER	BC LEVEL		INPUT CONC.	OUTPUT CONC.	% REMOVAL
	B	C			
NAPHTHALENE	50	50	23	0.63	97.26
ACENAPHTHYLENE	10	100	9.5	0.06	99.37
ACENAPHTHENE	10	100	160	0.48	99.70
FLOURENE	10	100	140	1.5	98.93
PHENANTHRENE	5	50	320	16	95.00
ANTHRACENE	10	100	200	1.8	99.10
FLOURANTHENE	10	100	330	15	95.45
PYRENE	10	100	280	8.5	96.96
BENZO(a)ANTHRACENE	1	10	70	3.9	94.43
CHRYSENE	1	10	80	5.4	93.25
BENZO(b+k)FLOURANTHENE	1	10	120	7	94.17
BENZO(a)PYRENE	1	10	64	1.6	97.50
INDENO(1,2,3,c,d)PYRENE	1	10	42	2	95.25
DIBENZO(a,h)ANTHRACENE	1	10	11	0.73	93.36
BENZO(g,h,i)PERYLENE	1	10	38	1.7	95.53
TOTAL PAHs	20	200	1887.5	66.30	99.96
TOTAL EXTRACTABLE HC			3600	130	96.39
TOTAL OIL AND GREASE			1090	80	92.66
MINERAL OIL AND GREASE	1000	5000	860	<40	>95.35

TABLE 1



**INCOMING WASTE TYPE:**

Soil with high PAH and PCP contamination

PARAMETER	BC LEVEL		INPUT CONC.	OUTPUT CONC.	% REMOVAL
	B	C			
NAPTHALENE	5	50	840.0	0.21	99.98
ACENAPHTHYLENE	10	100	56.3	0.18	99.67
ACENAPHTHENE	10	100	750.0	3.30	99.56
FLOURENE	10	100	543.3	5.35	99.02
PHENANTHRENE	5	50	2506.7	44.93	98.21
ANTHRACENE	10	100	535.0	14.91	97.21
FLORANTHENE	10	100	867.2	28.43	96.72
PYRENE	10	100	550.0	17.88	96.75
BENZO(a)ANTHRACENE	1	10	124.7	5.76	95.78
CHRYSENE	1	10	137.2	5.68	95.86
BENZO(b+k)FLORANTHENE	1	10	99.5	5.43	94.54
BENZO(a)PYRENE	1	10	39.5	1.83	95.36
INDENO(1,2,3,c,d)PYRENE	1	10	6.2	0.71	88.54
DIBENZO(a,h)ANTHRACENE	1	10	1.8	0.24	86.29
BENZO(g,h,i)PERYLENE	1	10	4.7	0.55	88.24
TOTAL PAHs	20	200	7062.10	135.39	99.98
TETRACHLOROPHENAL	.5	5	77.7	4.34	94.41
PENTACHLOROPHENOL	.5	5	1476.7	58.03	96.07
TOTAL EXTRACTABLE HC			12683.3	25.33	99.80
TOTAL OIL AND GREASE			786.7	46.67	94.07
MINERAL OIL AND GREASE	1000	5000	461.7	<40	>91.34

**TABLE 2**

- vapour pressures
- soil type (clay/sand/silt)

**Process Application**

Thermal Phase Separation is well suited for treatment of soil contaminated with hydrocarbons and chlorinated organics. With the exception of mercury, this process is not effective in removal of metals from soil.

**Unique Features of This Process**

- ease of permitting
- can be set up in a densely populated area (public acceptance of the technology)
- it is a recovery process versus destruction process
- cost effective



## **THE IMPACT OF SULPHURIC ACID ON THE ENVIRONMENT**

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### **Abstract**

**Sulphuric acid is a corrosive liquid, well known since the Middle Ages. It has been an important commercial commodity for more than three centuries and, as a matter of fact, at one time a country's wealth and industrial activity were measured by the amount of sulphuric acid produced and consumed.**

**In a priority list ranking study of over 500 chemicals, in which major hazardous properties of these chemicals were compared and rated, sulphuric acid is considered the sixth most hazardous industrial chemical. It also has the highest spill and supply volumes.**

**While chemical burns are the most common hazards of this acid, a number of studies have shown association between sulphuric acid mists and laryngeal cancer. Changes in pulmonary flow resistance have been reported for different sizes and concentrations for sulphuric acid aerosols. Its main properties including physical, chemical, toxicological, behavioural and environmental fate will also be described.**

Up to the late sixties, sulphuric acid production used to be generally accepted throughout the industrialized world as an accurate barometer of a nation's commercial activity and wealth<sup>1</sup>. It is indispensable in many chemical and industrial processes.

The discovery of sulphuric acid occurred during the eighth century and has been credited to Abu-Bekr-Ahhas, a Persian alchemist who died in 940. Abu-Bekr-Ahhas distilled niter (potassium nitrate) with green vitriol (ferrous sulphate crystals) obtained from weathered iron pyrites. Several alchemists discussed, repeated, researched, and tried to improve on the methodology. These alchemists include Jabir Ibn Hayyan, Vincentius de Beauvais (1240), Albertus Magnus (1193-1280), Paracelsus, Gerhard Dornaeus (1570), Andreas Libavius (1595), Angelus Sala (1613), Nicholas le Fevre (1666), Nicholas Lemery and Cornelius Drebbel.

By the middle of the twelfth century the occidental alchemists were also producing sulphuric acid from sulphur and pyrites. Then, following the discovery of Lavoisier in the eighteenth century that sulphur is a chemical element and not a mixture, production of sulphuric acid from sulphur and pyrites was commercialized in many parts of the world<sup>2</sup>.

In Great Britain, around 1740, Ward started a large-scale production of the acid in Richmond, England by burning sulphur with potassium nitrate. In 1746, Dr. Roebuck of Birmingham introduced the lead chamber process and built a factory in Scotland to manufacture the acid<sup>2</sup>. The practice quickly spread throughout Europe and North America.

In North America, commercial production of sulphuric acid began in 1797, when John Harrison built a sulphuric acid in Philadelphia<sup>2</sup>. Much research has been done on the nature of the catalyst and feedstock. In the later part of nineteenth century, the lead chamber process was being gradually replaced by the contact process, patented by Phillips in 1831. Emil Jacob, in 1875, successfully demonstrated the new process and the modern contact acid manufacture began with a pyrite-burning gas as the source of sulphur dioxide.

Today a large proportion of the sulphuric acid produced in the world is what is termed "fatal" acid, which is solely manufactured to prevent substantial amount of waste sulphur dioxide formed in metallurgical and smelting processes such as non-ferrous metal smelting, iron production from pyrites, from entering the environment<sup>3,4</sup>. Many of the environmental and technical problems associated with large-scale production, handling and shipment of sulphuric acid are now fairly understood; emissions, effluent discharge, handling, shipping are now governed by several national and international regulations and codes.

## **SPILL PROFILE**

Canada places environmental concerns high on its list of national priorities and has enacted many Acts and Regulations to clean up the environment and combat spills. Even though the main purpose of these Acts is to provide safety for the people concerned, the public at large, as well as minimizing environmental impact, accidents still continue to happen. I would like to refer to our famous research study on the "Priority List Ranking of Hazardous Chemicals" done about

five years ago. Our main goal then was to determine the minimum number of hazardous chemicals that were most frequently spilled<sup>5</sup>. The list was developed by a simple ranking of: a) reported spill frequency b) supply volumes c) historical spill volumes and d) toxicities. Sulphuric acid places sixth on this list, with the highest supply volume (equalled only by ammonia). It also has one of the highest number of spills.

**Table 1: PRIORITY LIST RANKING OF SULPHURIC ACID**

CHEMICAL	RANKING	SPILL NUMBER	SPILL VOL.	SUPPLY VOL.
Ammonia	1	107	470	3700
Chlorine	2	36	120	1700
Tetraethyllead	3	4	72	26
Styrene	4	24	5000	630
PCBs	5	334	89	-
<b>Sulphuric acid</b>	<b>6</b>	<b>155</b>	<b>13000</b>	<b>3700</b>
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

Fig. 1 shows how the frequency of accidental spills varies from year to year from all sources. It appears the trend is increasing<sup>6</sup>. In this connection, I must mention that reporting of accidental spills to Environment Canada is not mandatory but all chemical spills must be reported to the provinces in which they occurred.

**Fig. 1: SPILL PROFILE OF SULPHURIC ACID 1988-93. YEARLY SPILL FREQUENCY.**

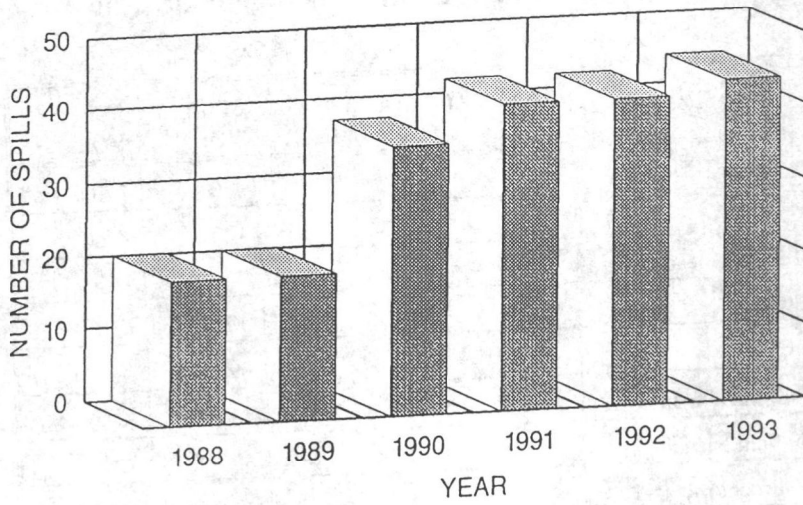




Fig. 2 shows how the spill frequency of sulphuric acid varies with the method of transportation. It appears rail spills the most, but a high percentage of sulphuric acid is transported by rail. However, one cannot conclude from this data which method is safest, since there are other factors involved.

**Fig. 2: SPILL PROFILE OF SULPHURIC ACID 1988-93. DISTRIBUTION BY MODE**

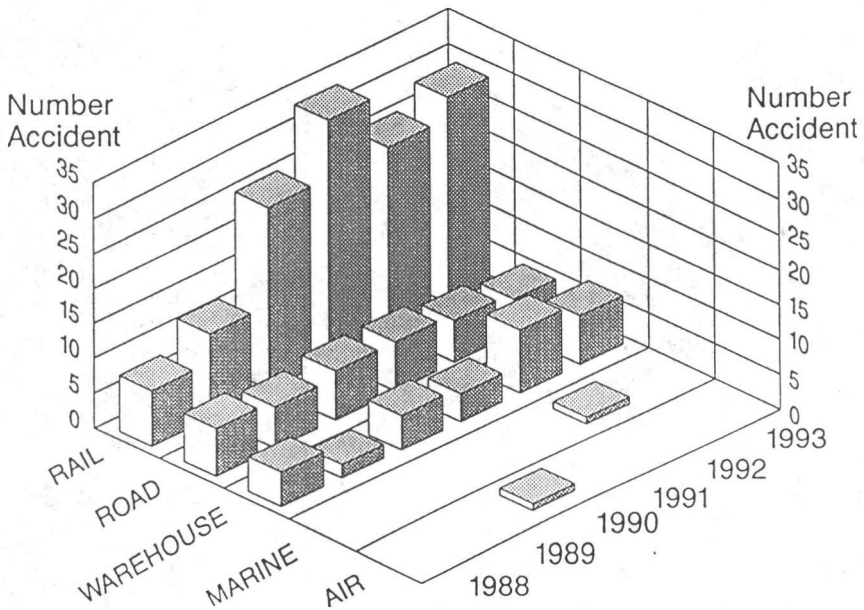


Fig. 3 shows how the spill frequency of the top five priority chemicals compare for the last six years. Sulphuric acid came second to ammonia eventhough their supply volume are the same. This is probably due to the fact that sulphuric acid is well known for its corrosive nature.

**Fig. 3: SPILL PROFILE OF SULPHURIC ACID 1988-93. TOP 5 PRIORITY CHEMICALS COMPARED.**

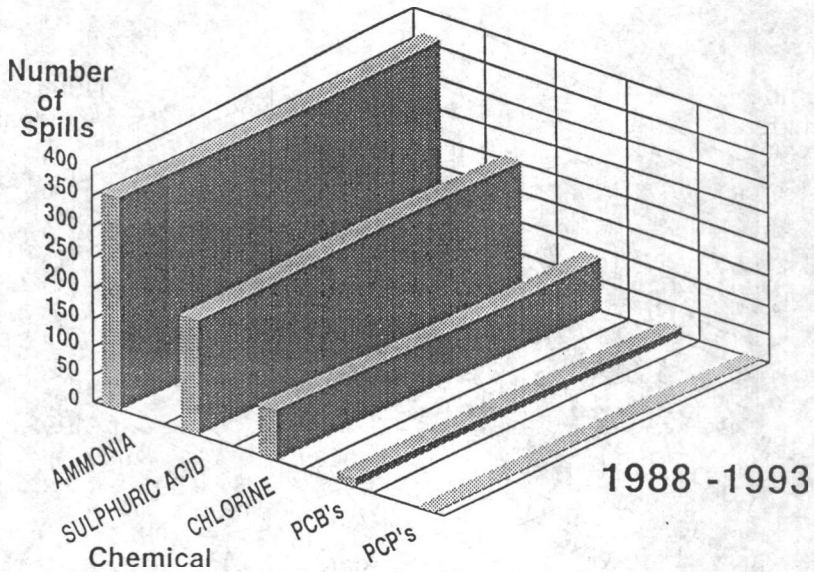
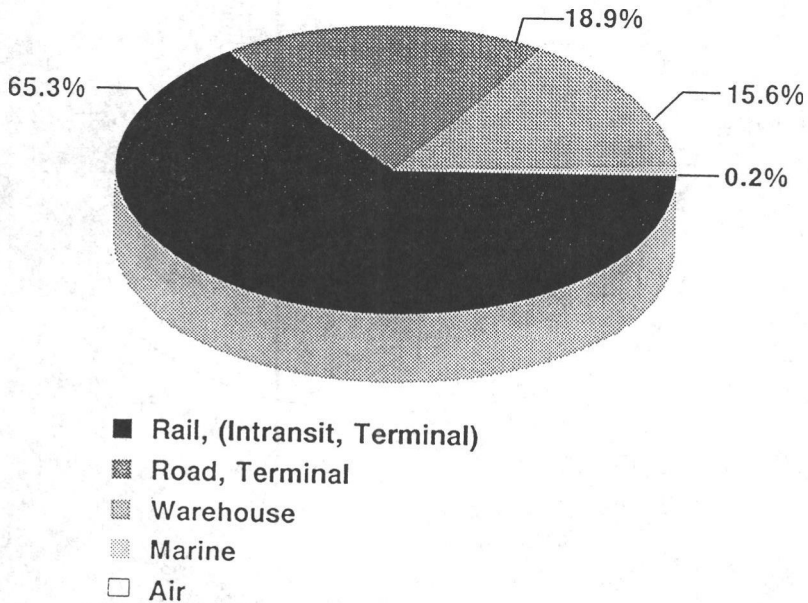


Fig. 4 shows at what phase of transportation is sulphuric acid being spilled. Most of the spills happen at the terminal. Warehouse spills also happen to make some contribution.

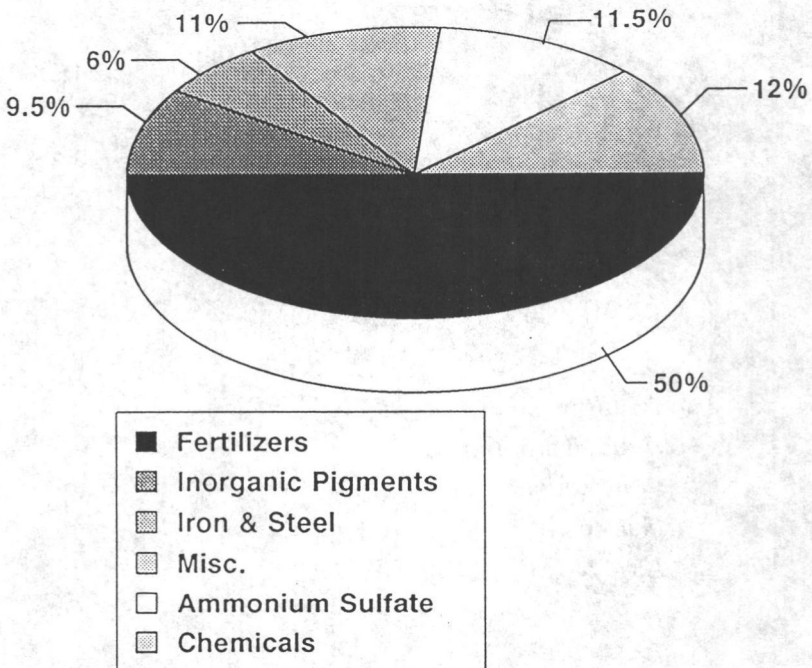
**Fig. 4: SPILL PROFILE OF SULPHURIC ACID 1988-93. DISTRIBUTION BY PHASE**



## USES

There are very few commercial and chemical products whose components or precursors that have not been at one time or the other touched by sulphuric acid. These products range from metals, to plastics, fertilizers, textiles, and pulp and paper<sup>1,7</sup>. For many decades sulphuric acid was a good index of economic activity.

Fig. 5: USES

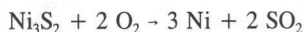
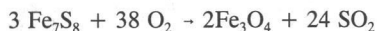


## PRODUCTION

As already been discussed, sulphuric acid was produced mainly by the lead chamber process (which uses nitrogen oxides as homogenous catalysts for the sulphur dioxide oxidation step) up to the later part of nineteenth century and was gradually replaced by the contact process. The feedstock were sulphur, iron-pyrites, non-ferrous-pyrites, hydrogen sulphide and spent sulphuric acid<sup>8,9</sup>. Nowadays, approximately 99% of all production is by the contact process. Sulphuric acid is at present manufactured for the sole purpose of preventing the substantial quantities of waste sulphur dioxide produced in metallurgical processes such as non-ferrous metal smelting and iron production from pyrites from entering the environment. Sulphur dioxide produced during roasting of sulphide ores sometimes referred to as roaster gas.

Below are the main essentials of the contact process:

1. As the sulphide ores (pyrites) are roasted, the roaster gas and the metal oxides produced are separated from each other in cyclones.



2. The roaster gas is mixed with additional air to complete the combustion of all volatilized products .

3. Any remaining metal oxides in the roaster gas are removed by cooling and contacting with sulphuric acid solution.

4. The roaster gas is then passed through a further stage of washing and drying followed by a wet precipitation stage.

5. The clean roaster gas then flows into the double-absorption plant consisting of two drying towers and a sulphur dioxide stripper where it is dried .

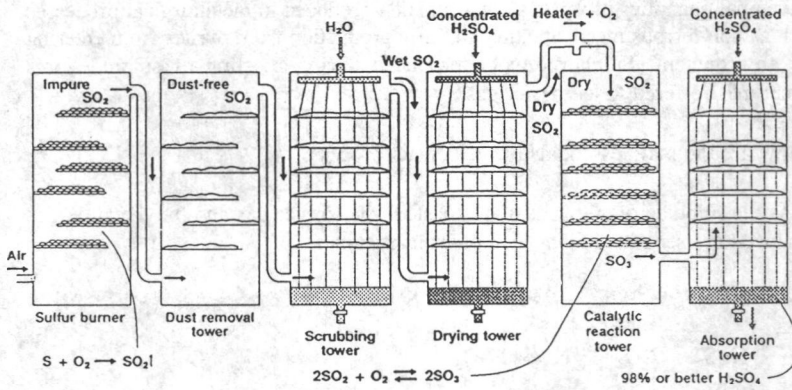
6. The roaster gas is catalytically oxidized to sulphur trioxide in a fixed bed converter which operates adiabatically with each catalyst pass.



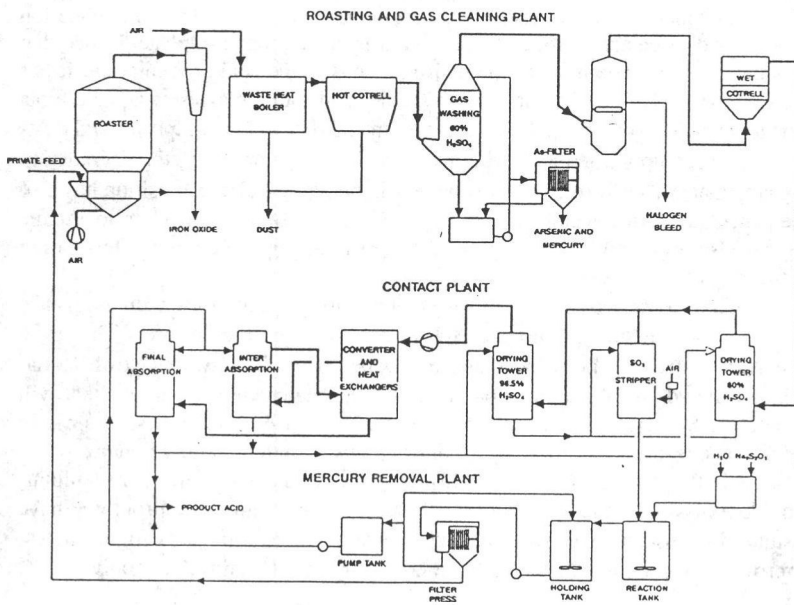
7. The gas is now cooled, and allowed to flow into the packed towers where it is absorbed. However, the production of fuming sulphuric acid (oleum) requires sulphur trioxide absorption in special absorption towers irrigated with oleum. The reaction is extremely exothermic.



Fig. 6: FLOW DIAGRAM OF THE CONTACT PROCESS



**Fig. 7: FLOW DIAGRAM OF A METALLURGICAL SULPHURIC ACID PLANT.**





## Environmental Considerations

Pollutant emissions occur during sulphuric acid manufacture, processing, storage, transport, accidents, uses, and disposal. Pollutant emissions during manufacture include sulphuric acid mist, sulphur dioxide, sulphur trioxide, dust and metal particulates.

Atmospheric sulphur dioxide deposition from smelters has long been shown to be mainly responsible for the acidity of surface water and lakes and the decline of several aquatic species. Acid precipitation has been attributed to the oxidation of sulphur dioxide and nitrogen oxides, but it is the hydrogen sulphate formed that is believed to provide most of the hydrogen ions in the acid precipitation. It has been observed that biodiversity in fish species and other classes of aquatic biota start to decrease when the pH of water systems fall below 6.0. Sulphates and dusts have also been implicated in causing reduced visibility, corrosion, the degradation of many materials and respiratory problems in humans. Acidic deposition has also been attributed to the decline of maple trees decline in Quebec and Ontario. Acidic fog has also been implicated as one of the agents causing white birch deterioration in the Bay of Fundy coast.

Canada is at the forefront of sulphur dioxide emissions reduction. The Eastern Canadian Sulphur Dioxide ( $\text{SO}_2$ ) Control Program is in force. The seven eastern provinces - Manitoba, Ontario, Quebec, New Brunswick, Nova Scotia, Prince Edward Island and Newfoundland - have implemented programs that will reduce the  $\text{SO}_2$  emissions from 4,516 kilotonnes in 1980 to 2,300 kilotonnes in 1994<sup>10</sup>. The main focus of these control programs is on ten major sulphur dioxide emitters in the mining and energy industries. The good news is, that some sulphur dioxide emission reductions that have been achieved with these programs have resulted in substantial recovery in surface waters, vegetation, less fog episodes, improvement in human health and better environment quality, generally.

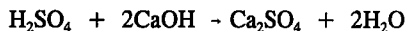
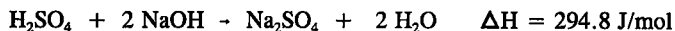
## CHEMISTRY

Some of the reactions which are encountered on regular basis during sulphuric acid spills are discussed below. One common element is the large quantity of heat that is given off in all these reactions. They are extremely exothermic. Some caution is therefore required during emergency response operations and spill mitigations.

### 1. Neutralization

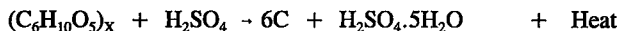
Like most strong mineral acids, sulphuric acid will react with bases to form salt and water. Hence substances such as slaked lime or sodium hydroxide are often added to sulphuric acid spills.





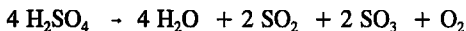
## 2. Reaction with Water and Hygroscopicity

Concentrated sulphuric acid is a strong dehydrating agent. It has enormous affinity for water. It will extract water and elements of water from most materials e.g. organic and inorganic with evolution of heat. Sometimes enough heat is generated to ignite surrounding combustible materials or vapour.



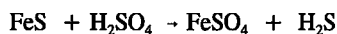
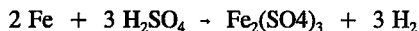
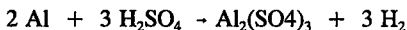
## 3. Fire and Intense Heat

Sulphuric acid itself is not combustible but can produce enough heat when reacting with other substances to self decompose.



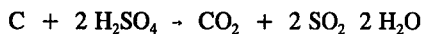
## 4. Reaction with Metals

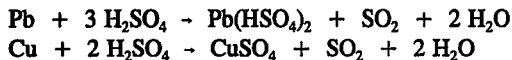
Sulphuric acid will react with many metals to produce salt and the flammable, explosive hydrogen gas. It will also corrode many materials to form innocuous substances. It will react with many sulphides, oxides and carbonates. So immediate neutralization is recommended during spills on soils, as some of these minerals may be present.



## 5. Oxidation.

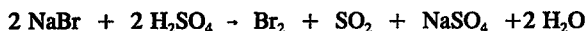
Concentrated sulphuric acid is a strong oxidizing agent and will oxidize carbon, non-metallic elements, and many metals. The potential hazard of these reactions is due to the formation of sulphur dioxide, a toxic gas.





## 6. Hazardous Reactions

Sulphuric acid will undergo many double-displacement reactions to produce new substances which may be hazardous. It is recommended that these substances be stored at distant locations.



## BEHAVIOUR AND ENVIRONMENTAL FATE

Sulphuric acid is a heavy, viscous, water-soluble, very corrosive liquid. It is not a volatile substance but fuming sulphuric (oleum) is. Since it does not rapidly evaporate (>96% will slowly evaporate), it is hard to detect by smell. Formation of sulphate aerosols and mist may occur in the atmosphere.

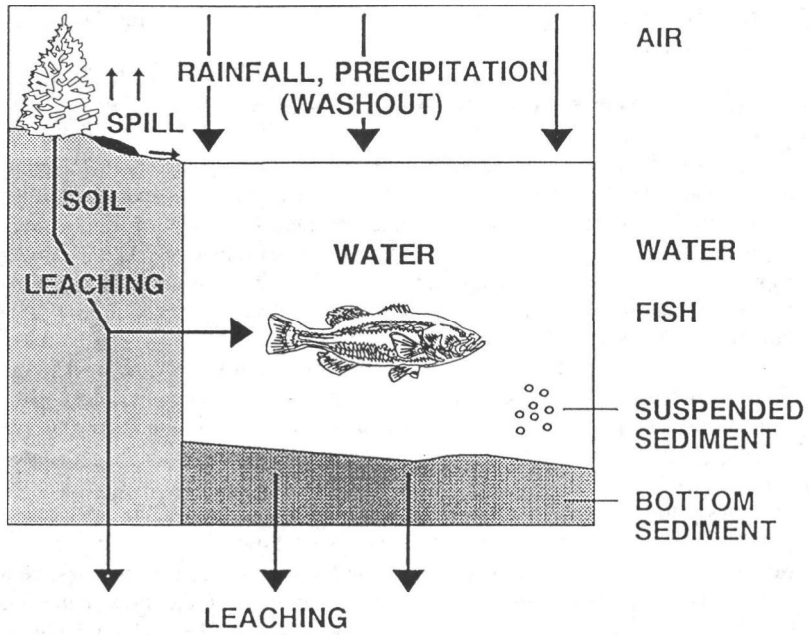
### Terrestrial Fate

When spilled on land, sulphuric acid will settle for few minutes before flowing away as it finds the lowest levels. It will sorb to the soil and char any vegetation with which it comes in contact. Because of its high viscosity, concentrated will not rapidly leach into the soil unless it rains or precipitation occurs. The process of soil acidification involves the replacement of exchangeable base cations such as calcium and magnesium by protons and aluminum ions, in other words, removal of bases and mobilization of aluminum are the key processes of concern. As it penetrates the soil, some of it will be neutralized by bases and carbonates, some will react with silicates and organic materials, some will exchange with metal cations and the rest may leach into ground water.

### Aquatic Fate

If spilled into water, sulphuric acid will dissolve in the water column as it sinks. It will also react with any bases and organic matter in the water. It has been shown that very low pH is extremely toxic to fish and aquatic organisms.

**Fig. 8: ENVIRONMENTAL FATE OF SULPHURIC ACID**



## **Research Study of a Sulphuric Acid Spill near Springhill, Nova Scotia (1985)**

On December 13, 1978, a railway tank car of concentrated sulphuric acid (93%) was spilled as a result of train derailment, about 10 km northwest of the town of Springhill, Nova Scotia<sup>12</sup>. The spill caused visible damage to vegetation over a limited area. In the fall of 1985, seven growing seasons after the spill, Environment, Canada contracted MacLaren Plansearch Limited, in association with P. Lane and Associates Limited to undertake a study to document the effects of the spill and make recommendations on appropriate response measures for future spills of sulphuric acid. Some Environment Canada scientists were also involved in the research project.

### **Description of Spill Event with Lessons to be learned**

At 13:55 hours on December 13, 1978, an eastbound freight train travelling at approximately 40 mph (64 km/h) derailed between mile 63.05 and 62.80 of the Springhill Subdivision of the CN mainline (see Fig. 9). A total of 51 cars were derailed. One railway tank car, containing concentrated sulphuric acid (93%), was ruptured and almost its entire contents spilled. The tank car came to rest lying transversely across the railway right-of-way, with acid leaking rapidly from a large hole in one end (see Fig 10).

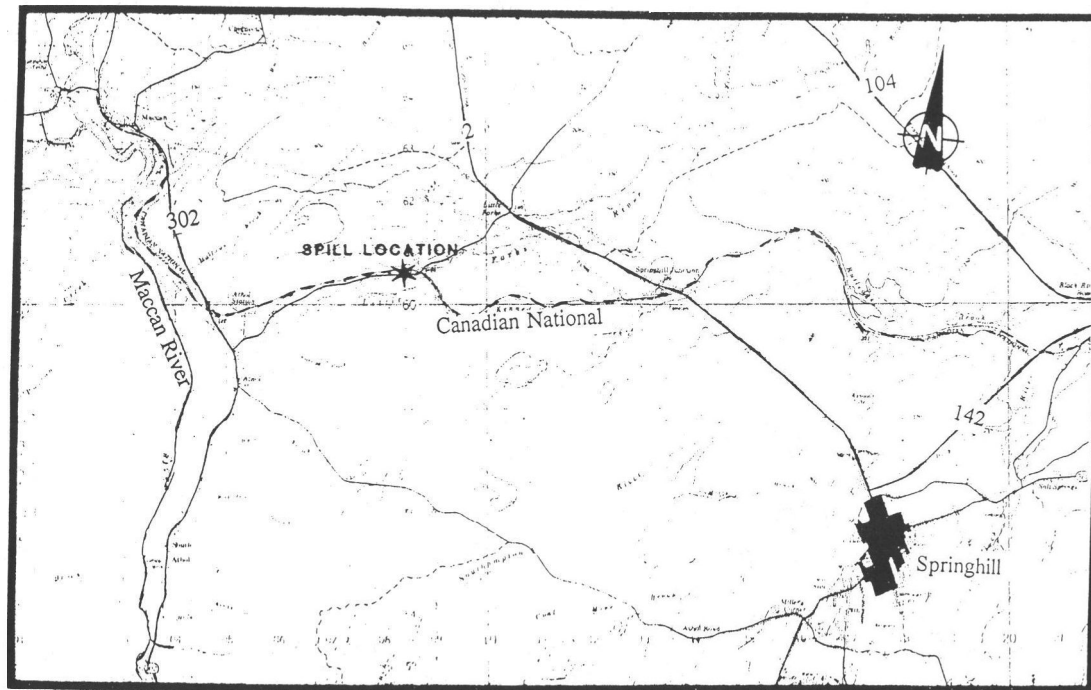
The acid pooled in a swale paralleling the south side of the tracks, and flowed downslope along three distinct paths (one major, two minor). Most of the spilled acid disappeared into a hole which opened up in the ground, flowing into an underground pit or cavity of unknown origin. Because of the highly fractured nature of the bedrock in the area, it is likely that most of the acid that reached the pit quickly found its way into the ground water. To our knowledge, no adverse effects on groundwater were reported. Overland flow of the acid was fairly restricted. Although the spill occurred at the top of a slope, eyewitnesses from Environment Canada (R. Simmons, L. Tripp) indicated that the three rivulets of acid flowed only partway down the slope. No acid reached the ditch on the north side of the highway at the bottom of the slope. A number of factors may have contributed to this:

- 1) The amount of acid flowing overland was greatly reduced because of the loss of liquid to the underground cavity.
- 2) The surface materials on the slope were highly permeable.
- 3) Although it was early winter and the ground was lightly snow covered, the ground was not yet frozen. This was confirmed by members of the spill response team who indicated there was no frost in the ground when an emergency road was bulldozed to the site.

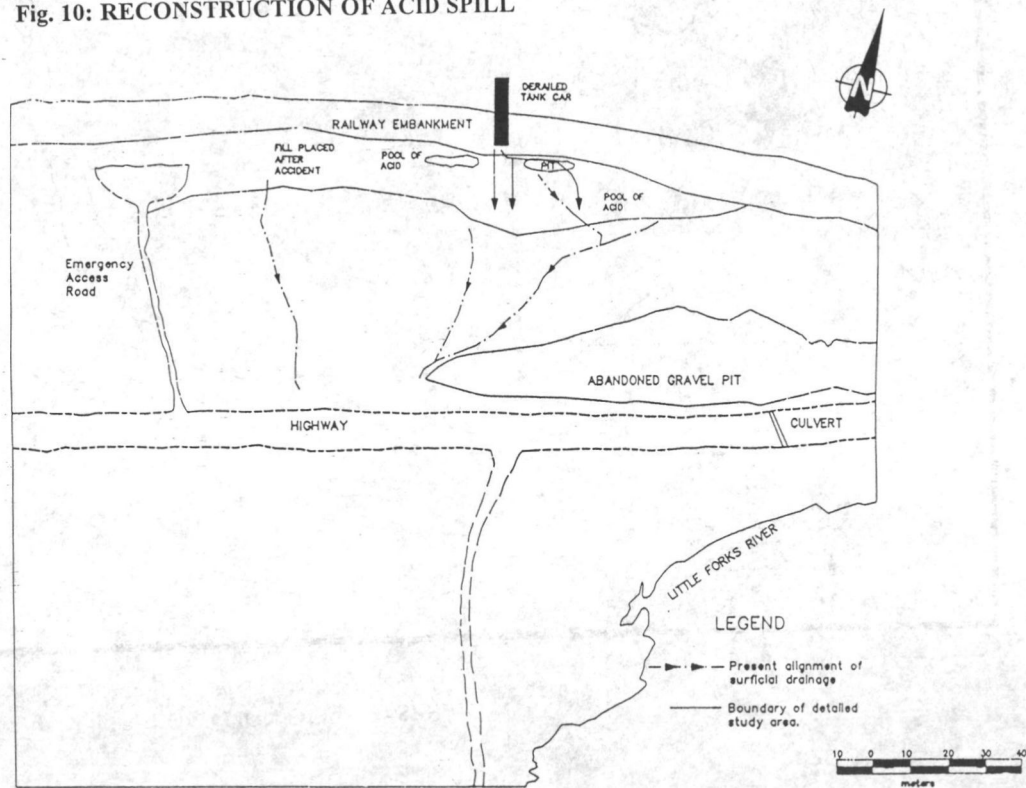
The Environment Canada report on the spill indicated that a CN employee and a local resident were injured as a result of stepping in a pool of acid.

After the derailment, the priority was to restore service on the mainline. The major area of activity was to the north of the railway right-of-way which could be accessed by a dirt road that joins the highway just east of the railway bridge spanning the highway and the Little Forks River. Removal of cars and railway

Fig. 9: LOCATION OF ACID SPILL



**Fig. 10: RECONSTRUCTION OF ACID SPILL**



repair activities resulted in considerable terrain disturbance north of the tracks. No action was taken to neutralize the spilled acid until a truckload of sodium hydroxide arrived on the site at 15:00 hours on December 14, 25 hours after the spill occurred. At that time an attempt was made to bulldoze a short access road from the highway to the spill site. The activity was halted when the bulldozer broke down. By the time the truckload of sodium hydroxide was pulled up to the trackside the following day (December, 15) almost two days has elapsed since the spill, the roadbed had been rebuilt and train had been restored. Neutralization was done selectively where pockets of acid could be reached. Sodium hydroxide was allowed to percolate through the new roadbed material to neutralize the acid underneath. Moreover, it is clear that significant amounts of sodium hydroxide were pumped into the cavity where much of the acid had flowed. (A solid block of sodium sulphate, the product of neutralizing sulphuric acid with sodium hydroxide, can still be seen in the pit to this day). The top of the slope where the spill occurred was severely impacted by physical disturbance associated with response to the spill. All of the natural vegetation was bulldozed and the site covered with up to 90 cm of sandy fill. Much of this fill remains almost barren of vegetation after seven growing seasons, and thus constitutes the major long-term disturbance associated with the spill.

The direct effects of the spill itself are relatively subdued after seven growing seasons. The ground vegetation in acidized areas is superficially indistinguishable from unaffected areas. Shrubs are reinvading areas where acid-induced shrub mortality was high. The main signs of a previous spill are the standing remains of dead shrubs. Fig. 11 shows the area of study and paths of flow for the sulphuric acid spill, while Figs. 12 and 13 show the results of pH measurements. It is surprising that even after seven years that all the spilled acid has not leached through. This clearly shows that the hydrogen ions are held in place by more than simple adsorption forces. Some effects on exchangeable soil minerals are also included (Figs. 14-17, 19-21).

## TOXICOLOGICAL PROFILE

### Human

The most common types of injuries during concentrated sulphuric acid spills are acid burns as a result of being in direct contact with this acid. Marked scarring of the skin often result from these burns<sup>13</sup>. The concentrated form destroys organic matter as a result of its severe dehydrating action. It is also a severe irritant to the eyes, respiratory tract and skin. Respiratory and teeth injuries usually result from chronic exposure to the acid aerosols and mists. Accidental exposure to liquid fuming sulphuric acid can result in skin burns as well as pulmonary edema from inhalation. Pulmonary fibrosis, residual bronchitis and pulmonary emphysema have also been reported. A single overexposure to sulphuric acid as in spills may lead to acute laryngeal, tracheobronchial, and pulmonary edema<sup>14</sup>. Concentrations around 5 mg/m<sup>3</sup> have been found quite objectionable, often causing coughs and respiratory disfunctions. The data below summarize

Fig. 11: STUDY AREA

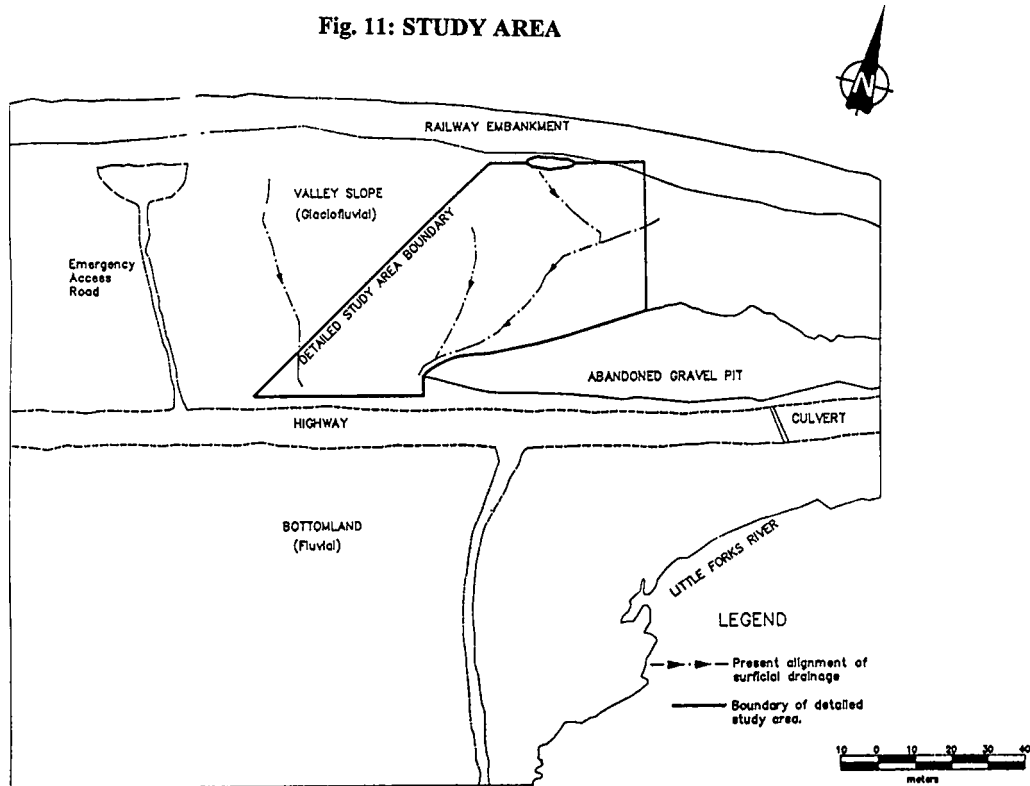
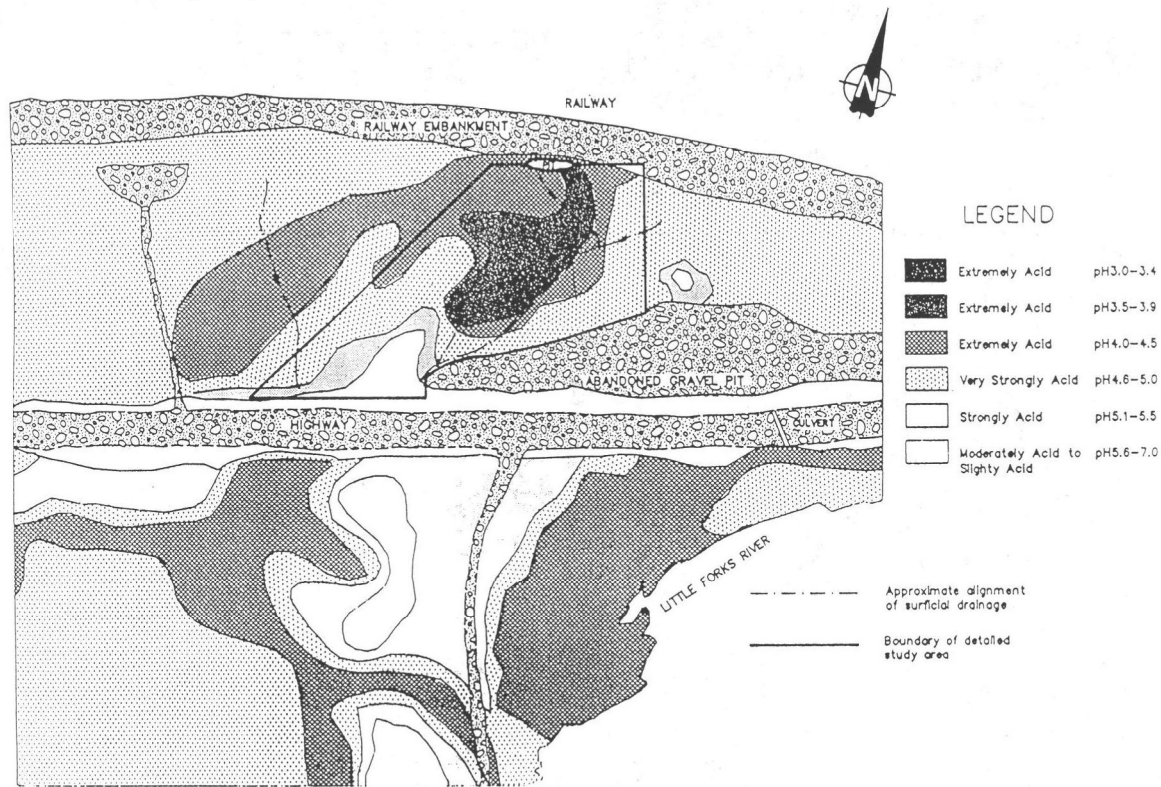




Fig. 12: pH MEASUREMENTS: TOTAL STUDY AREA



**Fig. 13: pH MEASUREMENTS: DETAILED STUDY AREA**

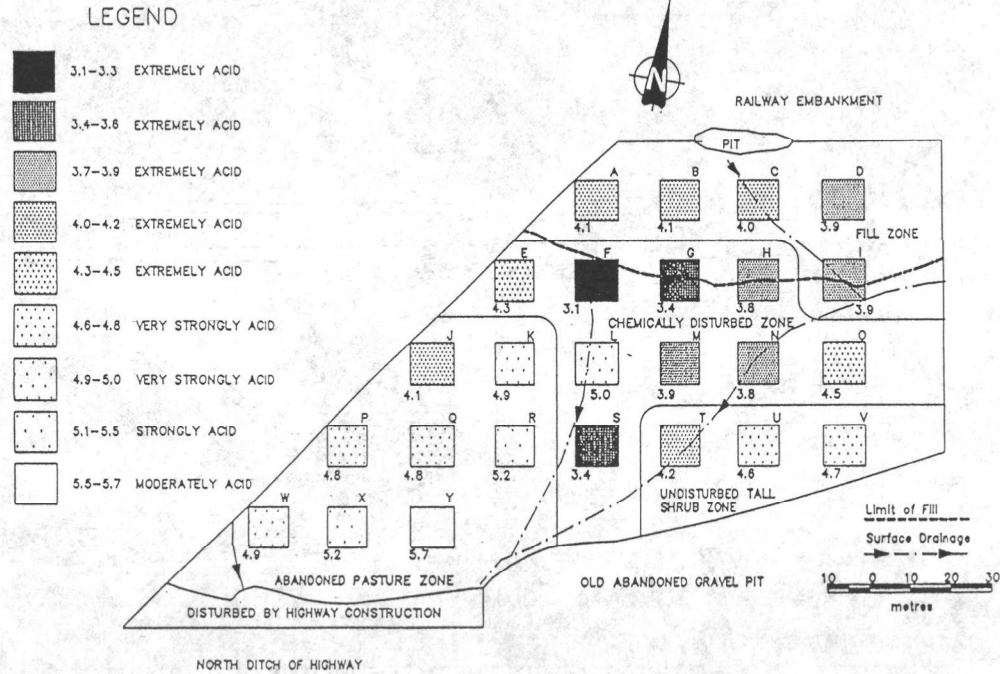


Fig. 14: EXCHANGEABLE SODIUM ( $\text{Na}^+$ )

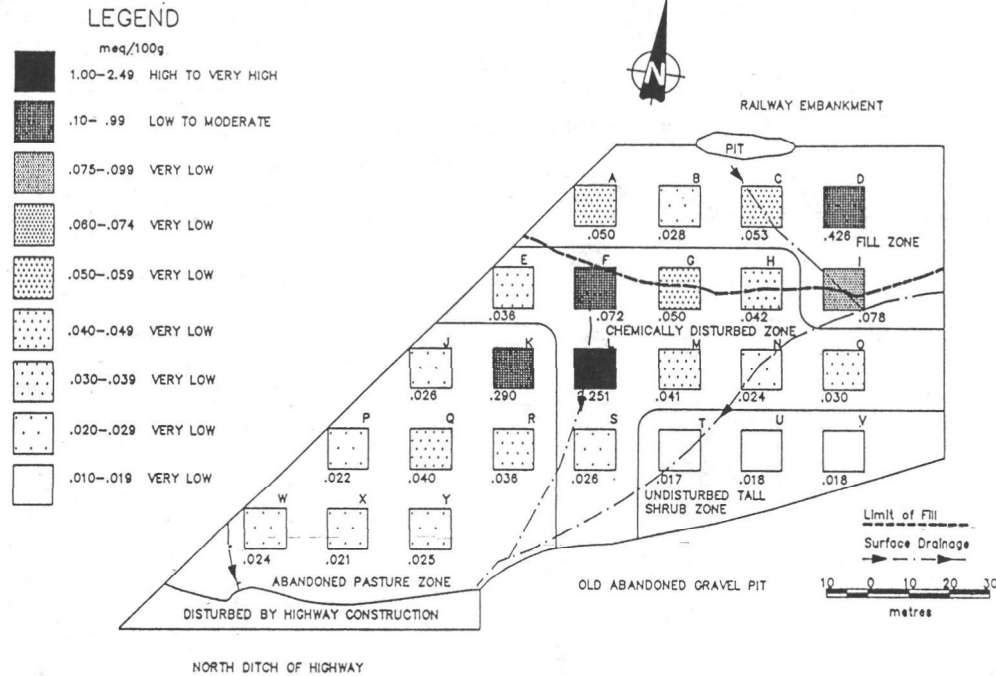


Fig. 15: EXCHANGEABLE MAGNESIUM ( $Mg^{3+}$ )

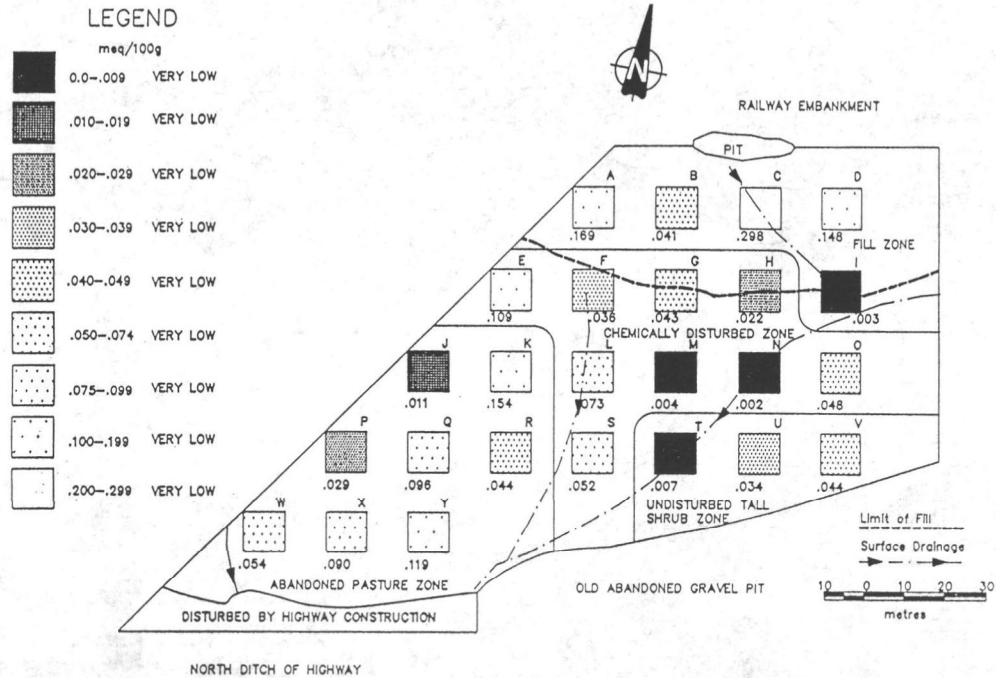


Fig. 16: EXCHANGEABLE CALCIUM ( $\text{Ca}^{2+}$ )

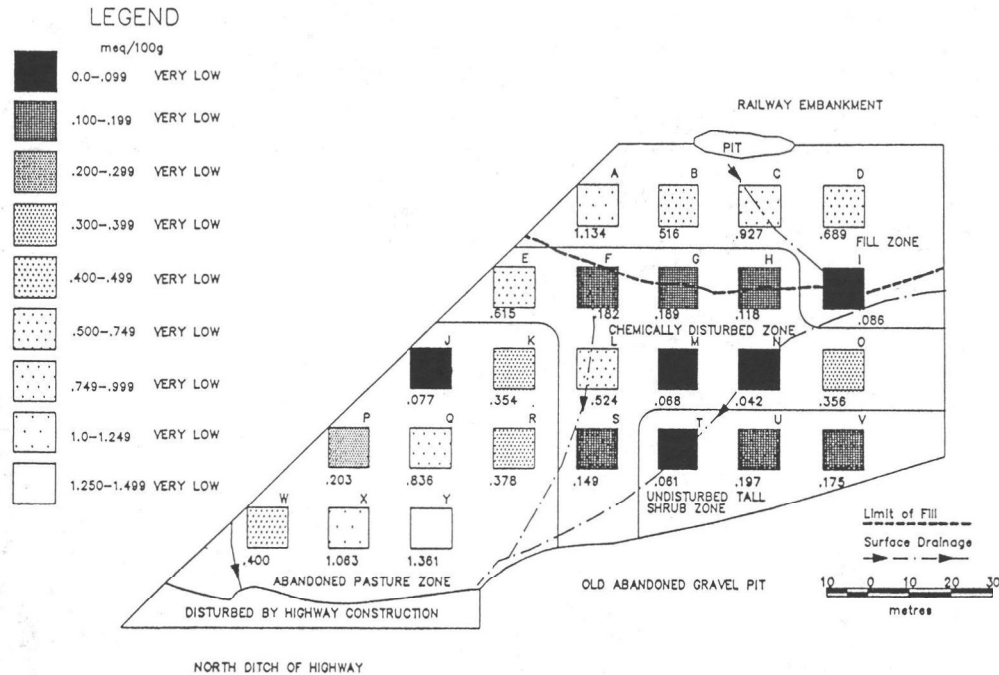
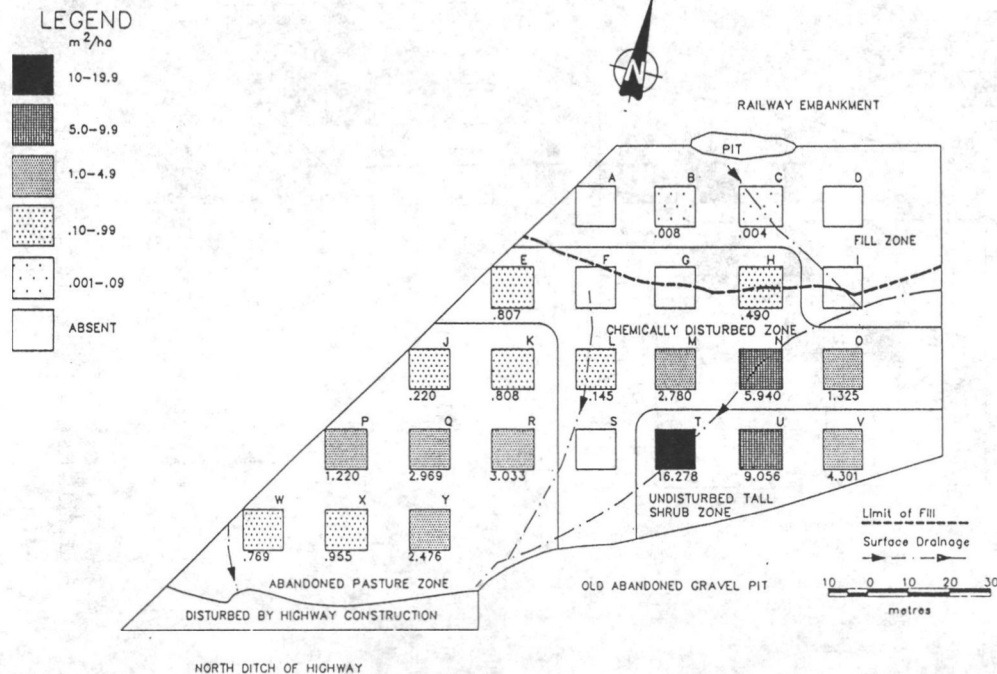


Fig. 17: DISTRIBUTION OF BASAL AREA OF HAWTHORN (*Crataegus macrosperma*)



**Fig. 18: DISTRIBUTION OF BASAL AREA OF PIN CHERRY (*Prunus pensylvanica*)**

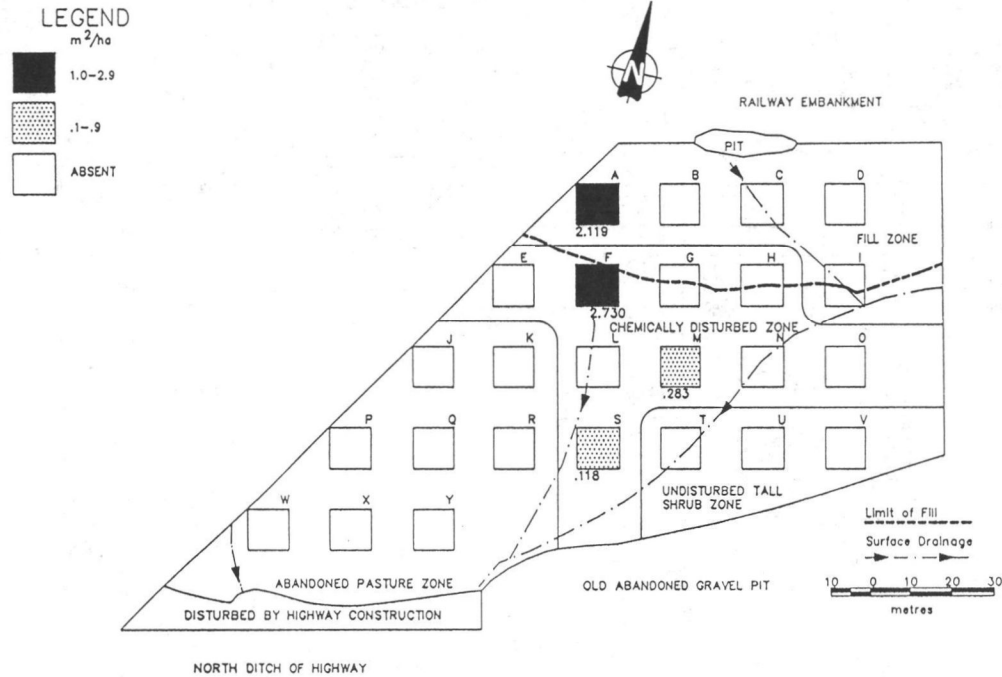


Fig. 19: SULPHATE ( $\text{SO}_4^{2-}$ )

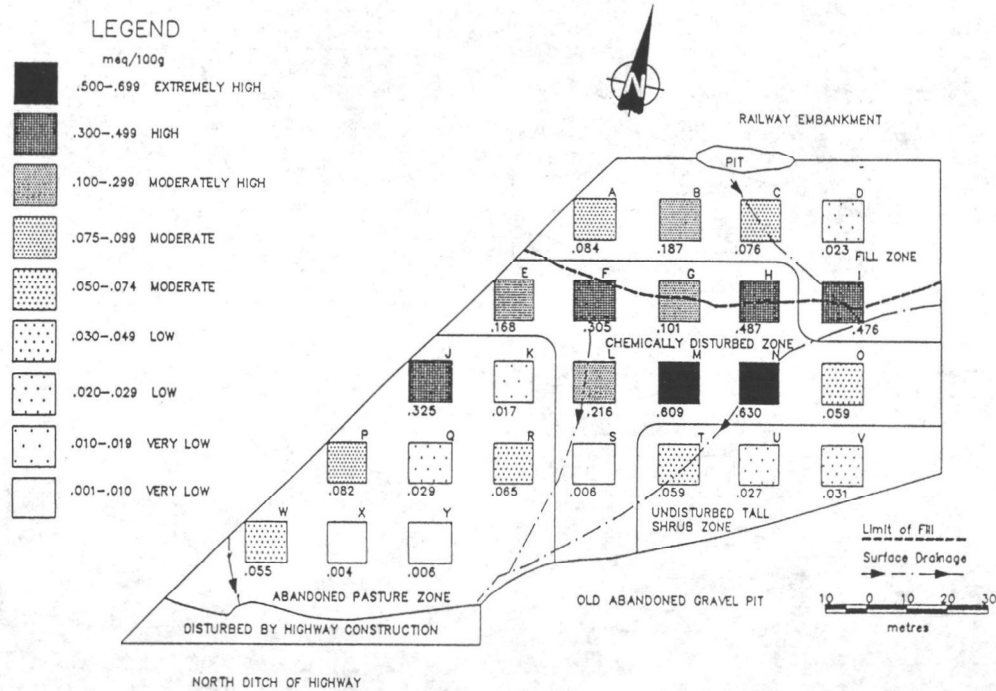




Fig. 20: EXCHANGEABLE ALUMINUM ( $Al^{3+}$ )

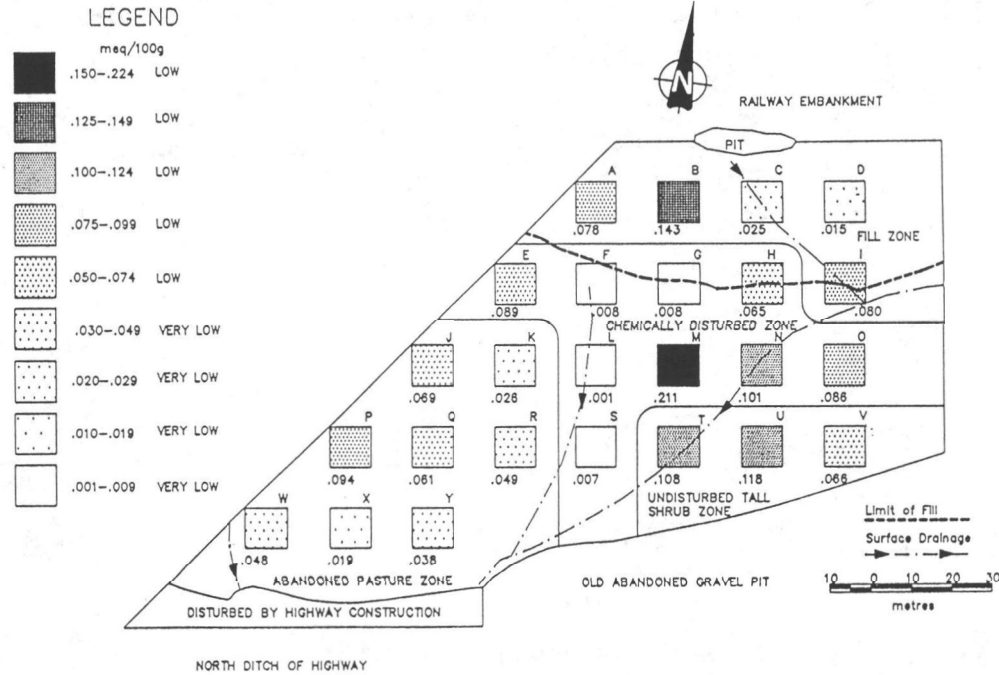
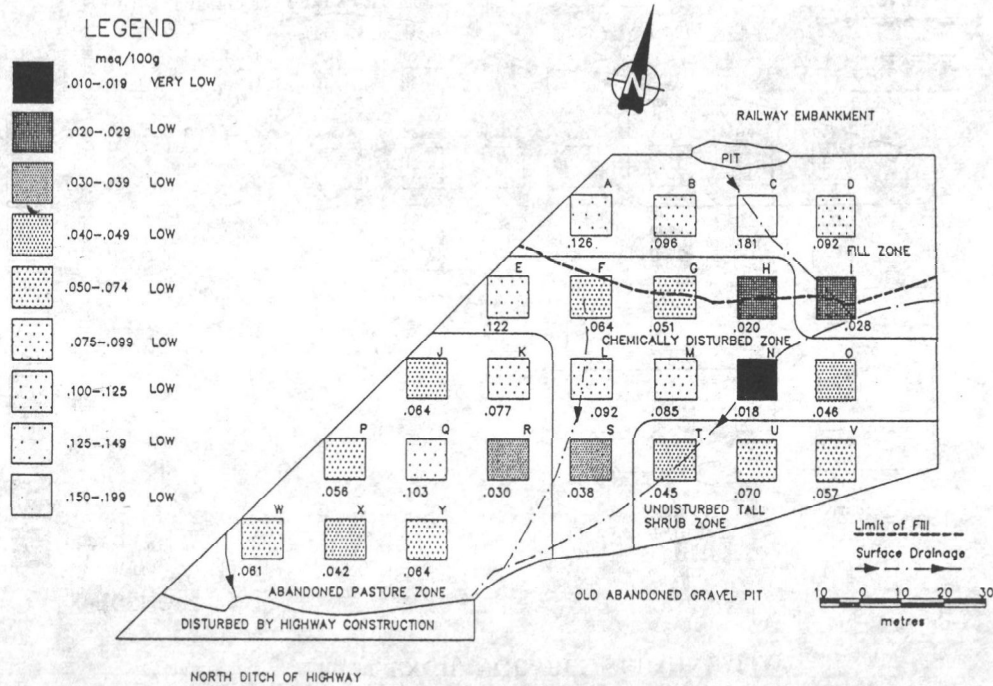


Fig. 21: EXCHANGEABLE POTASSIUM ( $K^+$ )



human responses to various levels of concentrations of sulphuric acid mist.

**Table 2: HUMAN RESPONSES TO SULPHURIC ACID MIST**

CONCENTRATIONS (mg/m <sup>3</sup> )	RESPONSE
0.5 - 2.0	Barely noticeable irritation
3.0 - 4.0	Coughing, easily noticeable
6.0 - 8.0	Decidedly unpleasant, marked alterations in respirations.

Results of many investigations on respiratory effects of sulphuric acid during acute exposures as in some spill cases are mixed, simply because there are many factors that influence its toxicity such as, particle size of the mist, humidity, presence of particulates, synergistic and protective agents, and pre-existing conditions of victims<sup>14,15,16,17,20</sup>. Bronchospasm in asthmatics has been shown to be of major concern. These effects are caused mainly by inhalation of the acid aerosols depositing on the surface of the respiratory tracts. The smallest aerosols often cause the greatest alteration in pulmonary function because they can penetrate further into the alveoli, whereas the larger particles deposit in the upper respiratory tract causing more harm. Increase in airway resistance at high acid concentrations has been demonstrated by several authors. Presence of ammonia in expired air has been reported to afford some protection in humans. Synergism has been demonstrated when sulphuric acid is deposited on zinc oxide dusts in the presence of sulphur dioxide, and also when in combination with nitrogen dioxide or sulphur dioxide, ozone, metallic aerosols and sulphuric acid.

Chronic exposure of the teeth to the corrosive action of sulphuric acid as in battery acid workers has resulted in etching or total loss of teeth substance. A number of studies have also shown some association between chronic exposure to sulphuric acid and laryngeal cancer<sup>18</sup>. For example, a 13-fold excess risk of laryngeal cancer was found among chemical refinery workers with the highest exposure, and 4-fold for moderately exposed as opposed very low exposure. Repeated exposures to sulphuric acid mists have been reported to cause dermatitis, stomatitis, conjunctivitis, and tracheobronchitis.

## Animals

Considerable body evidence exists on the sensitivity of laboratory animals to sulphuric acid. As discussed above, sulphuric acid inhalation causes changes in pulmonary flow resistance, which is sometimes irreversible. These changes could be seen as the first stage of bronchitis. The smaller the particles the more damage is done ( $< 2 \mu\text{m}$ ). Table 3 below shows results of some animal studies.

**Table 3: EFFECTS OF SULPHURIC ACID IN ANIMALS**

Conc. ( $\mu\text{g}/\text{m}^3$ ) Time	Species	Effects
100, 1h	Guinea pig	Pulmonary resistance increased 47%, pulmonary compliance decreased 27%.
500, 1h	Dog	Slight increases in tracheal mucociliary transport velocities immediately and 1 day after exposure. 1 week later clearance was significantly decreased.
510, 1h	Guinea pig	Pulmonary resistance increased 60%. Pulmonary compliance decreased 33%.
1000, 1h	Guinea pig	Pulmonary resistance increased 78%, pulmonary compliance decreased 40%.
190-1400	Donkey	Bronchial mucociliary clearance was slowed.
1000, 1h	Dog	Depression in tracheal mucociliary transport rate persisted at 1 week after exposure.

## Aquatic Species

The main cause of death in acid lakes is due to the excessive loss of sodium ions which cannot be rapidly replaced by active transport. Disruption of sodium/potassium pump mechanism has been attributed to the presence of high concentration of hydrogen ions.

Acidification of an experimental lake in Canada from 1975 by the addition of sulphuric acid, leading to a drop in pH from 6.8 to 5.0 resulted in the loss of many fish species. For example, as the acidification begins, the shrimps and the minnows were the first to go at about pH 5.8, followed by the young trout. At pH 5.6, the crayfish started to die as their exoskeleton started to lose its calcium and became infested with parasites. Table below provides a summary of the sensitivities of aquatic organisms to lowering of pH based on studies in Scandinavian lakes.

**Table 4: EFFECTS OF ACIDITY ON AQUATIC ORGANISMS**

pH	Effects
6.0	Crustaceans, molluscs, etc. disappear, white moss increases.
5.8	Salmon, char, trout and roach die. Sensitive insects, phytoplankton and zooplankton die.
5.5	Whitefish, grayling die.
5.0	Perch, pike die.
4.5	Eels, brook trout die.

## Plants

Direct contact of concentrated sulphuric acid with plants will result in perforation of the plant tissue and death of the plant may subsequently result. The most common response often reported of plants to acidic precipitation is the formation of foliar lesions or areas of dead tissue on the upper surface of the leaves, and low growth. Necrotic spotting of the epidermis of the leaves after exposure to sulphuric acid mist has been reported in previous investigations.

**Table 5: EFFECTS OF ACID PRECIPITATION ON PLANTS**

<b>pH</b>	<b>Plant</b>	<b>Effects</b>
2.5	Bean	Foliar aberrations, decrease in growth
3.1	Yellow birch	Foliar lesions, decrease in growth
3.1	Bean, sunflower	Foliar lesions
3.4	Hybrid poplar	Foliar lesions
3.4	Sunflower	Foliar lesions
4.04	Bean	Reduction in dry weight.

**GUIDELINES****STANDARDS**

The American Industrial Hygiene Association (AIHA) have provided some emergency response guidelines during large releases of sulphuric acid as follows<sup>19</sup>:

**ERPG -3: 30 mg/m<sup>3</sup> (as sulphuric acid mist)**

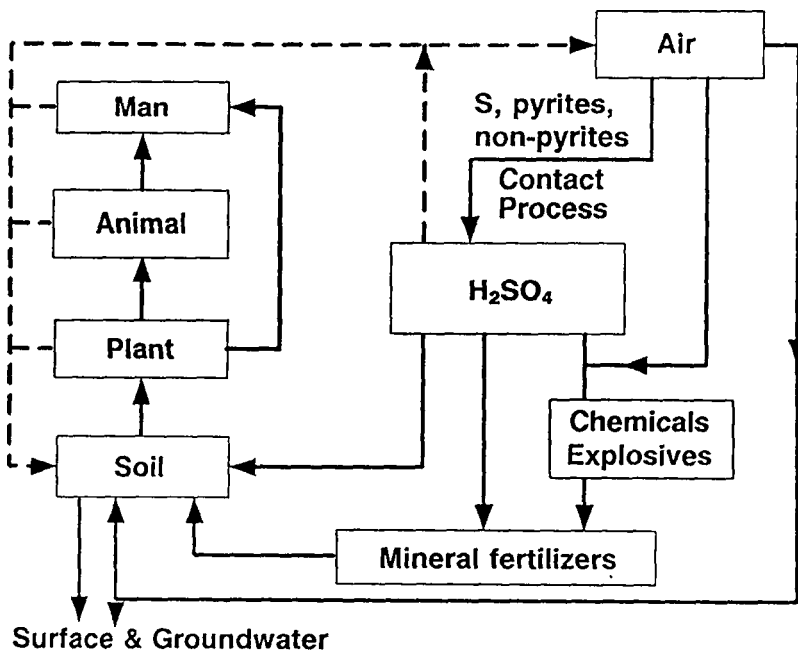
The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing life-threatening health effects.

**ERPG-2: 10 mg/m<sup>3</sup> (as sulphuric acid mist)**

The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without experiencing or developing irreversible or other serious health effects or symptoms which could impair an individual's ability to take protective action.

**ERPG-1: 2 mg/m<sup>3</sup> (as sulphuric acid mist)**

The maximum airborne concentration below which it is believed that nearly all individuals could be exposed for up to one hour without

**Fig. 22: A SIMPLIFIED SULPHURIC ACID CYCLE**

experiencing other than mild, transient adverse health effects or without perceiving a clearly defined objectionable odour.

### Threshold Limit Values

The American Conference Governmental Industrial Hygienists (ACGIH) have determined the threshold limit values - TWA(time weighted average) to be  $1 \text{ mg/m}^3$  and STEL (short term exposure limit) to be  $3 \text{ mg/m}^3$ . This proposed revision is under review. The ACGIH also recommends a TLV of  $1 \text{ mg/m}^3$  for sulphuric acid to prevent pulmonary irritation and injury to the teeth. The Occupational Safety and Health Administration (OSHA) permissible exposure limit (PEL) is  $1 \text{ mg/m}^3$ . The National Institute for Occupational Safety and Health (NIOSH) recommended exposure limit (REL) is  $1 \text{ mg/m}^3$  (10-hr TWA).

### CONCLUSION

In conclusion my main points are as follows:

- \* Sulphuric acid is an important substance that is widely used in industry.
- \* The effects of sulphuric acid spills are very localized and evidence suggests that sulphuric acid and oleum do not constitute a serious threat to the Canadian public at large.
- \* The Federal and Provincial Governments should be given credit for many of the successful, control programs towards reducing and mitigating its impact.

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**MTBE as a Contaminant****September, 1993****Prepared by:****R.M. Symington, MSc. Hydrogeology****University College London****(Pacific Hydrology Consultants Ltd., Vancouver)****1.1) Abstract**

MTBE is currently the fastest growing petrochemical in the world, and since its introduction in as a fuel oxygenate in 1979, and can form up to 15% by volume of unleaded gasolines. Driven by environmental legislation the long term anticipated trend is to increased use of MTBE in unleaded fuels. MTBE is recalcitrant in the groundwater environment and, despite its relatively low toxicity, more work is needed on long term effects.

The chemical properties of MTBE differ from those of the BTEX components and have led to concerns about its behaviour in aquifers. MTBE is hydrophobic in a ternary system of MTBE, fuel, and water, and under aquifer conditions will concentrate approximately 80% in the free product phase. MTBE is an order of magnitude (27 times) more soluble than benzene and has been recorded to travel at the same rate as stable tracers (chlorides) in groundwater. Contrary to first indications, MTBE shows no cosolubility effects with the BTEX components. The weight of experimental evidence points to fact that MTBE is nonbiodegradable.

Aqueous phase MTBE contaminant plumes have been observed as a "halo" around the plume of aqueous phase BTEX and MTBE. MTBE is commonly the first of the fuel components to be detected and, due to its low toxicity in comparison to the aromatic, is a comparatively "good" indicator of fuel spill.

**2.1) MTBE as a Fuel Oxygenate**

Fuel oxygenates are defined as fuel additives which have a substantial molecular oxygen content, and can be sub-divided into two major categories, the alcohols and the ethers. Oxygenates were first introduced in the 1920's as octane boosters. During the 1970's leaded additives were phased out and oxygenates were looked at for increasing octane rating and overall fuel quality. During the 1980's and 1990's atmospheric legislation has driven the development of fuel oxygenates.

Currently ethanol based fuels account for 1% of fuel sales in the United States. Experiments with Methanol, with TBA as a cosolvent, were considered unsuccessful in the United States. MTBE is the only ether blended in U.S. fuels and is the only ether used extensively in the world.

The combustion of fuels containing oxygenates require less atmospheric oxygen and theoretical complete combustion of the fuel components. The result is a reduction of carbon monoxide (smog), nitrous oxides (ozone depletion), and unburnt hydrocarbons (deforestation). EEC atmospheric legislation has targeted vehicle emissions (25% of the total volatile organic emissions) in recent directives. Vapour pressure limits, controlling evaporative losses (10% of the total volatile organic emissions), have been left to member states. Current EEC directives on oxygenates as fuel additives have limits of 10% or 15% by volume of MTBE, with Britain conforming to 10% maximum by volume MTBE.

Refiner and automotive acceptance has driven the move towards MTBE from the alcohol additives. The corrosive nature and low water tolerance of the alcohols would require added expenditures in the areas of automotive construction and fuel distribution systems. The lower blended vapour pressure of MTBE when compared with methanol will also play a significant role pending British legislation on fuel volatility.

MTBE, since its introduction as a fuel oxygenate 1979, is the fastest growing petrochemical in the world and is manufactured in Britain at one refinery. Current British legislation allows up to 10% MTBE, although personal communication with industry representatives estimates current use to be less than 1% by volume. The long term trend is to increased use of MTBE in unleaded fuels in Britain.

### **3.1) Physical Properties of MTBE**

The physical properties of MTBE differ from those of the BTEX components of fuel and lead to concerns about its behaviour under aquifer conditions. MTBE shows a solubility of 48,000 mg/l in water, 27 times that of benzene the most soluble aromatic. The solubility of MTBE is a reflection of the dipolar nature of the molecule (ie a more positive and negative end) which lead to concerns about its cosolubility effects on other fuel components.

Results of experimental data have indicated that the solubility of MTBE increases with decreasing temperature and at aquifer conditions a solubility of greater than 48,000 mg/l may be expected. No cosolubility effects were noted with the other BTEX components, and in fact, one set of data points to a slight decrease of the BTEX solubilities in the presence of MTBE. MTBE can be described as hydrophobic in a ternary system of water, fuel, and MTBE, and under aquifer conditions will concentrate approximately 80% in the fuel phase.

MTBE is an order of magnitude less volatile than the BTEX components of fuel and is therefore less susceptible to volatilisation techniques. The weight of experimental evidence, (three of four published experiments) points to the fact that MTBE is nonbiodegradable under aquifer conditions. MTBE is indicated to have a low carbon adsorption factor, and will adsorb only slightly to aquifer organic carbon. MTBE has a lower taste and odour threshold than the BTEX components of fuel.

Health studies are ongoing, although MTBE is currently classified as having a low toxicity. Although MTBE has been banned in Alaska due to its atmospheric persistence under cold climate conditions and perceived health effects, a more recent study questions the results and methodology of the Alaska survey and indicates MTBE to be a safe additive. A more comprehensive health study is expected to be available in 1993, published by the U.S. EPA.

The experimental evidence points to a persistent contaminant which will be recalcitrant under aquifer conditions. Due to its assumed low toxicity and low taste and odour detection thresholds, MTBE may be a "good" indicator of a spill of unleaded fuel.

Additional work is required in the area of biodegradation and health.

### **4.1) MTBE as a Groundwater Contaminant**

Field data on an MTBE contamination incident shows a "halo" of MTBE is observed developing around the plume of the MTBE and BTEX components which result from the release of unleaded fuel. Field experimental data using conservative tracers has shown that MTBE is recalcitrant in the environment over 476 days and that MTBE travels in groundwater at the same rate as conservative tracers.

The development of the contaminant "halo" testifies to the mobility and persistence of MTBE in the environment. MTBE will most likely be the first of the fuel components to be detected, due to its higher mobility when compared with the other fuel components and its low taste and odour detection threshold. MTBE will then be a comparatively "good" early warning indicator of an unleaded fuel spill due to its low toxicity in comparison to the BTEX components.

(The Merck Index 1989)

ColourAs MTBE concentrates 80% in the fuel phase the effectiveness of remediation of MTBE contaminated sites will be controlled by the ability of the remediation system to

recover the free product phase. Pump and Treat remediation of MTBE will be limited by the recovery of the floating free product phase and will not recover the MTBE partitioned in the fuel phase "bound" or "held" in the aquifer. Some form of Volatilization Extraction Techniques will prove more successful in remediation of the "bound" and "held" fuel phase components, and therefore the MTBE. The best remediation effort will probably involve a combination of the two systems, relying on the Pump and Treat to contain the contaminants and Volatilization Extraction to remove the remaining fuel phase

Remediation of the contaminated water is best undertaken by volatilization techniques, such as air sparging. Due to the early breakthrough of the MTBE verses the fuel components, activated carbon treatment, is an expensive option.

### Summary Table of Physical Properties

Physical State:	Liquid, (The Merck Index, 1989)
Odour Threshold:	680 micrograms/l, 680ppb, (Angle, 1991)
Taste Threshold:	2 - 3 micrograms/l, (Personal Communication)
Water Solubility:	48 g/100g 20 C, (The Merck Index, 1989)
Cosolubility Effect:	None, (Stephenson R.M., 1992).
Density:	0.7404 g/ml @20 C, (The Merck Index, 1989)
Vapour Pressure:	32.66 kpa @ 25 C, (The Merck Index, 1989)
Aqueous Half Life:	540 minutes
Adsorption:	0.004 grams organic per 1.0 gram activated carbon, (API 1991)
Henrys Law Constant:	4.5 E10-4(atm*m3*mol-1), (USA EPA 1986)
Molecular Mass:	88.15, (The Merck Index, 1989)
Melting Point:	-110 C, (The Merck Index, 1989)
Boiling Point:	55C, (The Merck Index, 1989)
Log Octanol/Water Partition	
Co-efficient (Kow):	0.94 - 1.30
Log Fuel Water Partition	
Co-efficient (Kfw):	15.5 at 22 C, (Cline et al 1991)
Drinking Water Standards:	
EEC, WHO, EPA:	None
Recommendations:	200 ppb, (Hartly et al 1992) 50 ppb, (Garrett et al 1986)
Biodegradation	
Aerobic:	Weight of evidence points to Nonbiodegradable
Anaerobic:	Nonbiodegradable
Atmospheric	
Half Life:	4 days under summer conditions
Reactivity (OH):	$2.8 * 10^{-12} \text{cm}^3 \text{molecule}^{-1} \text{second}^{-1}$

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78/665 Atmospheric Emissions

83/851 Atmospheric Emissions

85/536 Oxygenates as Fuel Additives

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## **DESIGN AND DEVELOPMENT OF A PERSON-PORTABLE INSTRUMENTATION SYSTEM FOR EMERGENCY RESPONSE AND FIELD STUDIES.**

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### **THE PERSON-PORTABLE INSTRUMENTATION SYSTEM**

The term person-portable refers to a unit carried and operated by one person. The Emergencies Science Division has set its own criteria for this type of instrument: it must weigh no more than 20 kg, operate on batteries and be self-contained (internal cylinders if gases are required). The person-portable instrumentation system is the ensemble of instruments and equipment used for emergency response or field studies.

### **TRANSPORTATION**

The person-portable instrument system can be transported to a spill site aboard a cube van with custom-designed shelving and storage. The van has outside dimensions which allow transportation by a Hercules plane. A kit, packed in cases, will also be prepared for transportation by regular air cargo.

This paper describes the person-portable instrumentation system developed by the Emergencies Science Division. The construction of the vehicle, its contents (including the person-portable instrumentation) and some field tests will be discussed.

### **CONSTRUCTION OF THE VEHICLE**

Two vehicles were acquired by the Emergencies Science Division in 1992. Both vans are of identical construction and only vary by their contents. Therefore, the following section applies to both vehicles.

The vehicle consists of a 1992, Ford F-350 series truck, with automatic transmission and four wheel drive capability. The 8 cylinder engine is diesel-fuelled. For convenience, the vehicle has two tandem diesel tanks (total 70L) and the operator can change the tank that is in use by simply pressing a switch. Based on specifications set by ESD, the cargo area was custom designed and built by a private contractor.

Some modifications were made to the truck; running boards were installed along the side of the truck to reduce the size of the step to get into the vehicle and a second set

of batteries was added to serve as back-up. The spare batteries had to be mounted externally under the cube because of the lack of room under the hood.

The truck is equipped with a remote alarm system and with emergency flashers which consist of a rooftop mounted light bar and two rear mounted flashing lights. The highest point of the vehicle is 105 inches permitting allow loading on board of a Hercules, C130 plane (maximum height 108 inches). An Onan 2.5 KV generator operating on LPG (liquid propane gas) is located in a side compartment of the cube. The output is 2500 watts, 20.8 A, 120 V @ 60 Hz. The generator can provide AC power to on-board systems - heating, refrigeration, and internal and external grounded outlets. The heating system and refrigerator can be powered by propane. A 12V battery is required to power up the generator, as well as to provide power to thermostats.

All shelving and drawers are made of oak and are labelled with a letter to indicate the location and simplify the organization of the equipment. The work bench is covered with Teflon sheeting to protect against chemicals. The wall behind the bench is made of special material on which water-soluble markers can be used. For convenience, the outside compartments and the back door of the van all use the same key. One side compartment contains the generator and the cube battery whereas the other one is for storage and is accessible from outside or inside the van. A pair of high intensity flood lights powered through the 12V battery is mounted at the rear exterior of the vehicle.

An array of communication equipment was set-up in the cab of the vehicle and includes programmable UHF and VHF radios (Motorola HT1000), portable cellular phone (Motorola) with hands free adapter and Fax connector and CB radio (Uniden). Three power points were added inside the cube to allow the operation of the portable cellular, the portable fax and other devices which have a cigarette lighter plug.

Among essential utilities added to the vehicle are: heavy duty booster cables (to charge the generator battery if required), windshield fluid, gas line anti-freeze, motor oil, shovel, snowbrush, first aid kits (in back and front) and blankets.

## **CONTENTS OF THE EMERGENCY RESPONSE VEHICLE**

The contents of the emergency response vehicle are, for the most part, stored in the cube part which has dimensions of 3.7 metres long x 1.6 metres high (floor to ceiling) x 1.9 metres wide. The choice of the items placed in the truck was governed by various factors such as size, cost and necessity. Care was taken to ensure that the items chosen were small because of the limited space in the cube. The best quality/price items were purchased. Many items are necessary to be able to fully respond to all imaginable scenarios, but the size of the vehicle and weight of equipment are limiting factors. Thus, the equipment chosen should allow the team to perform its duties for a day or two; a period long enough to have any required extra equipment shipped.

The shelves and various compartments were assigned a letter for location (see Figures 1 & 2, where units are in inches). The complete inventory of the contents includes a letter location for each item. The list is kept in an Excel format file which can be sorted according to item or location (see appendices A & B).

To simplify the inventory, some items were organized into kits. Therefore, the main inventory list contains a series of kits which are detailed separately. The following table is a listing of the kits found in the emergency response vehicle and a brief summary of their contents.

**Table 1** - Description of the kits found aboard the emergency response vehicle.

TYPE OF KIT	CONTENTS
audio kit	hand-held tape recorder, lapel microphone, tapes, batteries
air kit	filter cassettes, tubing, cyclones, impingers, sorbent tubes
tool kit	screwdrivers, drill, hammer, nails, screws, etc.
calibration field kit	flow rate calibration units
computer kit	computer cables, adapters, ink cartridges
emergency kit	field survival equipment
extension kit	power bars, 2-3 prong adapters, extension cords
fastening kit	bungee cords, duct tape, polypropylene rope
first aid kit	for minor medical emergencies
food kit	cups, cutlery, coffee maker, water container
chemistry kit	beakers, graduated cylinders, pipettes, flasks
housecleaning kit	soap, rags, window cleaner, paper towels
office kit	pens, paper, file folders, stapler, diskettes
oil kit	tools required to collect and characterize oils
safety equipment kit	respirator masks and cartridges, coveralls, safety glasses, hard hats
sampling kit	various jars and vials, spatulas, spoons, syringes
tubing kit	Tygon, rubber and Teflon tubing
radio kit	hand-held UHF and VHF portable radios
wipe kit	to collect known quantities of samples on surfaces (eg. walls)

The emergency response vehicle, sometimes referred to as WK9 136 for its plate number, is setup to be driven to a site by two or three people, and can be ready to leave the Centre within an hour from the time it is requested. The other vehicle, WK9 137, is the special project vehicle and will be discussed later.

The full contents of WK9 136 are listed in Appendix A and, apart from the kits listed in Table 1 and miscellaneous items, it includes an array of person-portable instruments. A copy of the inventory is always kept in the truck and is located by the door in a protective folder.

### *Analytical instrumentation*

The selection of the instruments was based on the top 150 spill priority list which identifies the minimum number of chemicals that would account for the maximum number of spills. The list is established by ranking of supply volume, reported spill frequency, historical spill volumes, and toxicity<sup>1</sup>. The goal of the person-portable analytical system is to be able to identify, and quantify when possible, the largest number of compounds found on the list. Appendix C is a list of the top 150 priority spill list. The following sections describe briefly some of the major equipment found on-board of WK9 136. The number in parenthesis refers to the quantity in the truck.

#### •Armstrong CD-1 carbon dioxide analyzer (2)

This instrument uses a rechargeable battery and has an analog display. The voltage output can be connected to a datalogger and the values converted to accurate ppm concentrations of carbon dioxide using a factory provided conversion chart.

#### •Berthold LB122 radiation meter

Both beta and gamma types of radiations can be measured with this instrument which operates from a rechargeable battery.

#### •Briel & Kjaer 1302 gas monitor

Commonly called the B&K Analyzer, it consists of an infra-red analyzer using photoacoustics to measure the concentration of the contaminants in air. An array of filters with different wavelengths is available for selectivity, but the filters are not compound specific and one has to be aware of the possible interferences. This instrument is more complex than others and requires a greater chemistry knowledge. However, once it is set-up for a specific analysis, it is quite simple to operate. The B&K Analyzer can be operated with a battery pack contained in the bottom of a back-pack. The instrument itself weighs approximately 14 kg and the battery pack, 4 kg, making this the heaviest instrument amongst the portable equipment.

### ►Biosystems Cannonball

The Cannonball is a multisensor gas detector which is set-up to monitor %Oxygen, %LEL (lower explosive limit) of combustible gases, and two toxic gases, sulfur dioxide and carbon monoxide. The toxic gas and oxygen cells are electrochemical whereas the combustible gas cell is a thermal conductivity sensor. It is equipped with an internal datalogger. The Cannonball is a rugged instrument which has a water protective cover and special mechanism which stops the pump if any liquid gets into the system. It also operates from rechargeable batteries but can use 4 D-cells if necessary.

### ►Clor-n-Oil, Clor-n-Soil, Hydro-Clor

These kits are designed to detect the presence of organic chlorine, more specifically PCBs, in oil, soil and water. The tests are quick and inexpensive (between \$10-18) and provide a positive/negative response according to a certain level of contamination.

### ►Draeger pump

The Draeger pump is used in conjunction with colorimetric tubes and can be used to characterize contaminants present in the air. The tubes are calibrated to indicate concentrations but have an error of 50%, 25% at best. They are mostly used to characterize, not quantify the contaminants. The list of tubes kept on-board the emergency response vehicle is in appendix D.

### ►Gilian 513A pump

The Gilian 513A air pump has a flow rate capability of about 50 cc/min to 4L/min. It is used for long term sampling with the accessories contained in the air kit (see Table 1).

### ►Gilian Aircon2

The Aircon2 has a similar purpose to the 513A but has higher flow rate capacities, from 4 to 30 L/min.

### ►Hach kit

The kit contains some battery operated items: small balance, magnetic stirrer, DL2000 spectrophotometer. It also contains pH paper, a variety of reagents and some glassware. These tools allow to perform quantitative analysis of contaminants using colorimetric or titrimetric reactions.

### ►Hazcat kit

The Hazcat kit is manufactured by Sensidyne and consists of about 40 different

chemicals, test tubes, propane torch, spatulas, pH paper, oxidizer paper and other miscellaneous accessories. The kit is used to characterize unknown solids and liquids by an elimination process. It does not necessarily achieve a positive identification of the unknown but can assign it to a class of compounds. This allows the response team to take the appropriate safety precautions.

►Heath Detecto-pak II

The Detecto-pak is an organic vapour analyzer (OVA) which uses flame ionization detection. A rechargeable battery powers the instrument and the result is indicated on an analog display. A convenient feature is the fuel supply which consists of a hydrogen/air mixture and comes in a refillable cylinder. The cylinder is of small size and can be placed in a belt pocket, making the instrument still person-portable.

►HNU PI-101 and DL-101

The HNU instruments are photoionizing devices which can detect volatile compounds that have an ionization potential lower than that of the photoionization lamp used. Both PI-101 and DL-101 models have the same detection capabilities and run off rechargeable batteries but there are some slight differences. The PI-101 has an analog display whereas the DL-101 is digital and has internal datalogging capabilities. The recorded information can be viewed on the LCD screen or uploaded by a computer using the RS-232 cable.

►Horiba U-10

The U-10 water checker is an instrument which can simultaneously measure 6 water parameters; pH, temperature, conductivity, turbidity, dissolved oxygen and salinity. It is powered with a 9V cell and also has an internal datalogger from which the information can be uploaded.

►Monitoring station

The monitoring station consists of a small weather station manufactured by Earth and Atmospheric Sciences, Inc. and operating on a 12V sealed acid battery. A solar panel is also mounted on the weather station to maintain the battery charge. Information about temperature, humidity, barometric pressure, wind speed and direction is recorded by a datalogger and can also be uploaded via a RS232 cable connected to the serial port of a computer.

►Neotronics Exotox 75 (2)

The Exotox 75 is a multisensor gas detector which is set-up to monitor %Oxygen, %LEL of combustible gases, sulfur dioxide, nitrogen dioxide and carbon monoxide. The toxic gas and oxygen cells are electrochemical whereas the combustible gas cell is a thermal conductivity sensor. An internal datalogger records the concentrations



and the information can be retrieved from a computer.

►Photovac 10Splus

The Photovac 10Splus is a portable gas chromatograph (GC) equipped with a photoionization detector. The lamp used has an energy of 10.2 eV, and therefore, can detect most organic substances. A capillary column is used and can be heated up to 65°C. This low temperature means that only volatile compounds can be analyzed. The injection can be done directly using a gas-tight syringe or with the gas inlet (direct or using a Tedlar bag containing the contaminant of interest). Zero air is used as a carrier gas. This is a convenient feature since SCBAs (self-contained breathing apparatus) are always brought to a site and this eliminates the need for a supplementary gas cylinder. The GC is controlled by an integrated computer which uses RAM (256KB or 2MB) cards for storing information. A library containing calibration data about the compounds of interest can be programmed prior to arrival at the site and a quick check with only one compound is required to adjust the instrument.

►PS-1 Hi-volume sampler (2)

The high volume sampler is used to collect samples from large volumes of air or to collect samples in very short times. A combination of polyurethane foam and glass fibre filter is used to collect samples. It has a pumping capacity anywhere from 100 to 280 L/min, depending on the condition of the brushes in the pump. The main disadvantage of this sampler is that it requires AC power.

►MIE RAM-1

The RAM is a real-time aerosol monitor which detects total particulates or particulates of less than 10 microns by light scattering. The more light scattered, the higher the concentration of particulates in the air. The RAM uses a rechargeable battery and possesses a data output for optional datalogging equipment.

►Summa canisters (4) and orifices (2)

The Summa canister is a 6L polished stainless steel canister which collects air samples via vacuum through a restricted orifice set at a specific intake rate. The restricted orifices are set at a flow rate of 50 cc/min so that an appropriate sample can be collected in about 1.5 hours. The flow rate can be adjusted as required.

►Miscellaneous

To complement the analytical equipment, the van is equipped with a reference library containing: US EPA (US Environmental Protection Agency) methods, instrument manuals, handbooks, TIPS (Technical Information for Problem Spills) manuals, toxicology manuals, etc... A complete list appears in Appendix A.

Each member of the emergency response team has its own kit bag which contains issued gear a personal SCBA and totally encapsulated suit. Kit bags include winter outerwear, spring/summer workwear and marine accessories such as a floater jacket and floater vest.

Other equipment which is essential at a site includes: laptop computers, cellular phones, video camera, instant camera, cellular fax, photocopier, binoculars. Those are not necessarily included in the inventory list as some items are assigned on a personal basis to the team member.

### **SPECIAL PROJECTS VEHICLE**

The special projects vehicle is equipped with almost the same items found in the emergency response vehicle. However, instead of having the equipment placed in the various compartments, everything is packed in cases. If an emergency occurs in an area which is not within a short driving distance, the vehicle can be driven to the airport and the equipment flown by cargo.

When the vehicle is needed for special projects, only the general equipment such as safety equipment, sampling kits, communications devices remain on-board. Specific instruments related to the project are placed on-board as required.

Two fourteen-foot tag along trailers are currently being built and should be completed soon. The trailers will have windows on each side, a fixed ladder, a reinforced roof to hold external equipment, and shelving and power outlets on the inside. They will be used for special projects and also to provide more working room in the cube van by removing large size equipment such as the oil kit, the weather station and the remote-controlled helicopter.

### **FIELD TESTS**

The emergency response vehicle has never been used in a real spill situation. However, there were a few occasions where the vehicle was tested.

The first field test was done by driving WK9 137 to Petawawa in May 1993. Remote-sensing tests on oil evaporation were done and a lot of equipment was required on site. The vehicle was used to carry some equipment and the generator was crucial to provide AC power for one of the analytical instruments. The soil was still muddy at the time the experiment was conducted and it would have been useful to have a winch to tow other vehicles. The trucks have since been equipped with a winch. It was also noticed that the floor of the cube, which consisted of plain plywood, became dirty and difficult to clean. Upon return, the floors of both trucks were cleaned and painted with a special floor paint containing an anti-skid compound (very fine sand).

WK9 136 was tested in the summer of 1993 when a trailer containing four customized aluminum boats (total length of the trailer 40', total weight 7000 lbs) had to be hauled

from Ottawa, ON to St-John's, NF. The boats were required for the Newfoundland Offshore Burn Experiment. The heavy weight of the trailer only permitted a maximum driving speed of 80 km/hr, otherwise the trailer would pull sideways. The drive from Ottawa to North Sydney, NS took approximately 25 hours (2000 km), plus another hour after the ferry crossing to Argentia, NF (about 1 hour away from St-John's). No major difficulties were experienced except for one flat tire on the trailer on the way back! It was observed that stabilization bars would be a nice addition if a trailer of such weight had to be hauled again. It nevertheless demonstrated that WK9 136 was able to haul a trailer of such dimensions and weight, on a very long course and on roads ranging from the highway to more rural types.

To prevent problems which may be caused by cold weather ( $-40^{\circ}\text{C}$ ), such as frozen fuel lines and dead batteries, a maintenance program was designed to check the trucks weekly for diesel, windshield fluid, battery charge (see Appendix E).

## CONCLUSION

Although a lot of effort has been made to try to accommodate all response situations, it is likely that some items are probably still missing. Only real emergency situations will tell. It is hoped that the experience described here and that the difficulties encountered will be helpful to those who plan to set up their own emergency response system. When a response vehicle is being set-up, it is a good idea to obtain advice from people who have already experienced the process with a similar system.

Future plans for the vehicles include field studies, operation practice with spill simulations and real emergency response, when required.

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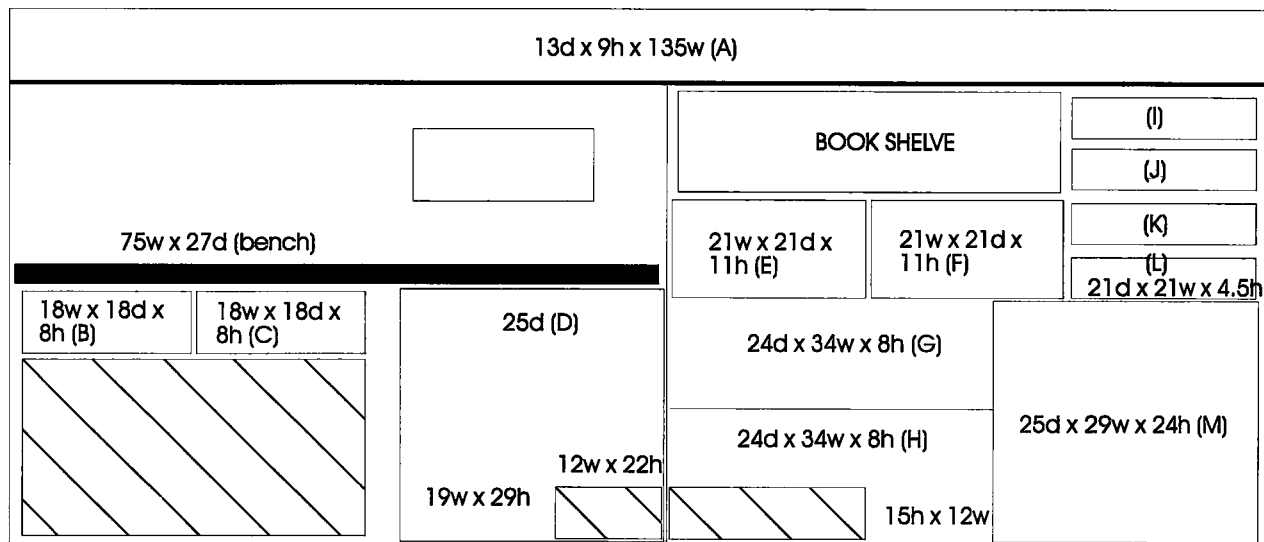


Figure 1 - Compartment dimension and location for right side of van.

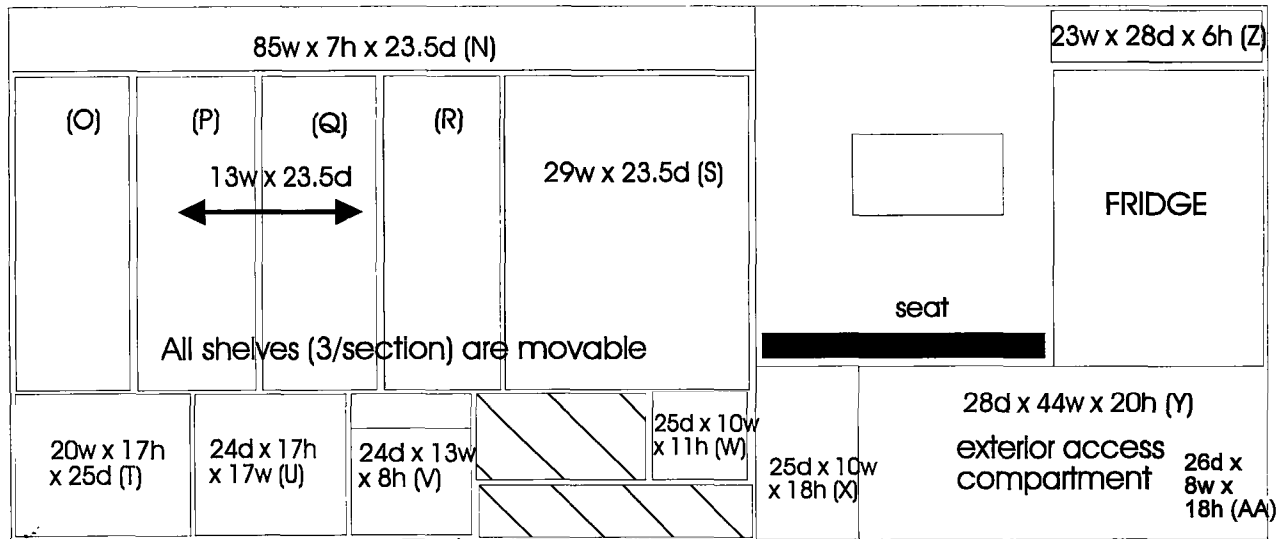


Figure 2 - Compartment dimensions and locations for left side of van.

## Appendix A

## VEHICLE INVENTORY WK9 136 -- BY ITEM

Item	Compartment	Item	Compartment
Acetone (1L)	Solvent cooler	Horn	S
Agrochemical handbook	Bookshelf	Housecleaning kit	B
Air kit	W	Hydro-chlor (2)	Fridge
Armstrong CD-1 (2)	O	Ice paks	Fridge
Armstrong CD-1 charger	K	Instruments manual	Bookshelf
Audio kit	A	Isopropanol (1L)	Solvent cooler
Balance-Acculab	see Hach kit	Jack	V
Berthold LB122	N	Kimwipes	J
Black toolbox	T	Kit batteries	Fridge
Boot tray for clean-up	Q	Kleenex	J
Broom	Aisle	Label maker	W
Bruel & Kjaer charger	K	Ladder	Aisle
Bruel and Kjaer 1302	X	Large jug of deionized water	R
Bruel and Kjaer 1302 accessories	A	Metal shovel	Y
Bucket	Q	Methanol (1L)	Solvent cooler
Calibration field kit	H	Microwave	Q
Cannonball	O	Monitoring station	M
CB radio	Cab	Monitoring station gel cell	AA
Cellular phone	Cab	Motor oil	V
Chlor-n-oil (1)	Fridge	Neotronics Exotox 76 (2)	Z
Chlor-n-soil (2)	Fridge	Office supplies kit	L
Coffee warmer	C	Oil kit	Aisle
Cola-Parmer Strirrer	see Hach kit	Oil spill manual (Exxon)	Bookshelf
Collapsible water carrier	C	Paper towel (2)	I
Compressed gases	Gas cooler	pH meter	A
Computer kit	see serial	pH paper (2)	see Hach kit
Computer cables	O	Photocopier	N
Crow bar	Y	Photocopier paper	Bookshelf
Dangerous goods-response guide	Bookshelf	Photocopier toner	N
Dangerous properties of Industrial mat	Bookshelf	Photovac 10S plus	S
Dichloromethane (1L)	Solvent cooler	Photovac 10S plus manual	Bookshelf
Disposable bench mats	J	Photovac accessories	A
Draeger pump	O	Photovac power supply	K
Draeger tubes (60)	Fridge	Plastic spray bottle	I
Drill	T	Polaroid camera	B
Dust pan	I	Portable decontamination unit	
EE manuals (110-115-118-134)	Bookshelf	Portable FAX	N
Emergency blanket	V	Portable (2)	A
Emergency fire blanket	Door	PS-1 HI-vol sampler	Y
Emergency kit	A	PUF pre-cleaned	Fridge
Emergency shower		Rags	J
EPA standard response	Bookshelf	RAM drierite	I
Extension kit	T	RAM-1	O
Eye Wash station		Recycling paper can	A
Fastening kit	T	Rite in the rain notebooks	Bookshelf
Field books (different sizes)-12	Bookshelf	Safety equipment (	E/F/J/H/Aisle
First Aid kit	J/Cab	Sampling kit	G
Fixed UHF radio	Cab	Sampling kit pole	A
Fixed VHS radio	Cab	Sensidyne MSDS manual	Bookshelf
Foil (2)	J	Serial printer	O
Folding chairs (2)	Y	Slides camera film (12)	Fridge
Folding table	Bench	Solvent cooler	Aisle
Food kit	C	Sorbent mats	V
Garbage bags (medium & large)	J	Spill of hazardous substances	Bookshelf
Garbage can	A	Stool	A
Gas catalogue-Scott	Bookshelf	Stopwatches (2)	K
Gas cooler	Aisle	Summa canisters (4)	R/S
General chemistry kit	G	Summa orifices (2) @ 100 cc/min	I

## Appendix A

### VEHICLE INVENTORY WK9 136 -- BY ITEM

Gillan 513A (5H/5L)	U	Summa pressure gauge	I
Gillan Aircon2-AC	S	Tarp	N
Gillan Aircon2-DC (2)	S	TDG course manual	Bookshelve
Gillan charger	K	Tedlar bags	Gas cooler
Gillibrator	U	TIPS manuals	Bookshelve
Hach Kit	P	Thermometer/humidity meter	K
Hach manual	Bookshelve	TLV Handbook	Bookshelve
Hand-held UHF radio	A	Trailer hitch	V
Hand-held VHS radio	A	Truck manuals	Bookshelve
Hazcat kit	R	Tubing kit	Q
Heath Detecto-Pak II	H	UHF/VHF radio kit	A
Heavy duty flashlight	U	Video camera	AA
Helicopter and accessories	Aisle	Washer fluid	V
Hexane (2L)	Solvent cooler	Waste container (2)	Q
Hnu DL-101	S	Winch strap	V
Hnu PI-101	O	Wind speed/direction meter	K
Hnu PI-101 charger	K	Wipe kit	H
Horiba U-10	S	Ziploc bags (S & L)	J

## Appendix B

## VEHICLE INVENTORY WK9 136 -- BY COMPARTMENT

Item	Compartment	Item	Compartment
Audio kit	A	Kinwipes	J
Bruel and Kjaer 1302 accessories	A	Kleenex	J
Emergency kit	A	Rags	J
Garbage can	A	Ziploc bags (S & L)	J
Hand-held UHF radio	A	First Aid kit	J/Cab
Hand-held VHS radio	A	Armstrong CD-1 charger	K
pH meter	A	Bruel & Kjaer charger	K
Photovac accessories	A	Gillan charger	K
Portafille (2)	A	Hnu PI-101 charger	K
Recycling paper can	A	Photovac power supply	K
Sampling kit pole	A	Stopwatches (2)	K
Stool	A	Thermometer/humidity meter	K
UHF/VHF radio kit	A	Wind speed/direction meter	K
Monitoring station gel cell	AA	Office supplies kit	L
Video camera	AA	Monitoring station	M
Broom	Aisle	Berthold LB122	N
Gas cooler	Aisle	Photocopier	N
Helicopter and accessories	Aisle	Photocopier toner	N
Ladder	Aisle	Portable FAX	N
Oil kit	Aisle	Tarp	N
Solvent cooler	Aisle	Armstrong CD-1 (2)	O
Housecleaning kit	B	Cannonball	O
Polaroid camera	B	Computer cables	O
Folding table	Bench	Draeger pump	O
Agrochemical handbook	Bookshelve	Hnu PI-101	O
Dangerous goods-response guide	Bookshelve	RAM-1	O
Dangerous properties of industrial materials	Bookshelve	Serial printer	O
EE manuals (110-115-118-134)	Bookshelve	Hach Kit	P
EPA standard response	Bookshelve	Boot tray for clean-up	Q
Field books (different sizes)-12	Bookshelve	Bucket	Q
Gas catalogue-Scott	Bookshelve	Microwave	Q
Hach manual	Bookshelve	Tubing kit	Q
Instruments manual	Bookshelve	Waste container (2)	Q
Oil spill manual (Exxon)	Bookshelve	Hazcat kit	R
Photocopier paper	Bookshelve	Large jug of deionized water	R
Photovac 10S plus manual	Bookshelve	Summa canisters (4)	R/S
Rite in the rain notebooks	Bookshelve	Gillan Aircon2-AC	S
Sensidyne MSDS manual	Bookshelve	Gillan Aircon2-DC (2)	S
Spill of hazardous substances	Bookshelve	Hnu DL-101	S
TDG course manual	Bookshelve	Horiba U-10	S
TIPS manuals	Bookshelve	Horn	S
TLV Handbook	Bookshelve	Photovac 10S plus	S
Truck manuals	Bookshelve	Balance-Acculab	see Hach kit
Coffee warmer	C	Cole-Parmer Strirrer	see Hach kit
Collapsible water carrier	C	pH paper (2)	see Hach kit
Food kit	C	Computer kit	see serial
CB radio	Cab	Acetone (1L)	Solvent cooler
Cellular phone	Cab	Dichloromethane (1L)	Solvent cooler
Fixed UHF radio	Cab	Hexane (2L)	Solvent cooler
Fixed VHS radio	Cab	Isopropanol (1L)	Solvent cooler
Emergency fire blanket	Door	Methanol (1L)	Solvent cooler
Safety equipment	E/F/J/H/Aisle	Black toolbox	T
Chlor-n-oil (1)	Fridge	Drill	T
Chlor-n-soil (2)	Fridge	Extension kit	T
Draeger tubes (80)	Fridge	Fastening kit	T
Hydro-chlor (2)	Fridge	Gillan 513A (5H/5L)	U
Ice paks	Fridge	Gillibrator	U
Kit batteries	Fridge	Heavy duty flashlight	U
PUF pre-cleaned	Fridge	Emergency blanket	V
Slides camera film (12)	Fridge	Jack	V
General chemistry kit	G	Motor oil	V
Sampling kit	G	Sorbent mats	V
Compressed gases	Gas cooler	Trailer hitch	V



## Appendix B

## VEHICLE INVENTORY WK9 136 – BY COMPARTMENT

Tedlar bags	Gas cooler	Washer fluid	V
Calibration field kit	H	Winch strap	V
Heath Detecto-Pak II	H	Air kit	W
Wipe kit	H	Label maker	W
Dust pan	I	Brueel and Kjaer 1302	X
Paper towel (2)	I	Crow bar	Y
Plastic spray bottle	I	Folding chairs (2)	Y
RAM drierite	I	Metal shovel	Y
Summa orifices (2) @ 100 cc/min	I	PS-1 Hi-vol sampler	Y
Summa pressure gauge	I	Neotronics Exotox 75 (2)	Z
Disposable bench mats	J	Emergency shower	
Foil (2)	J	Eye Wash station	
Garbage bags (medium & large)	J	Portable decontamination unit	

Appendix C  
LIST OF THE TOP 150 MATERIALS

Acetic acid	Diphenyl ether	Phthalic anhydride
Acetic anhydride	Diquat	Picloram
Acetone	Endrin	Potassium chloride
Acetylene	Ethyl alcohol	Potassium cyanide
Acrylonitrile	Ethyl chloride	Potassium hydroxide
Aldrin	Ethylbenzene	Potassium permanganate
Aluminum sulfate	Ethylene	Propionic acid
Aminocarb	Ethylene dichloride	Propylene
Ammonia	Ethylene glycol	Propylene glycol
Ammonium chloride	Ethylene oxide	Propylene oxide
Ammonium hydroxide	Ethylhexanol	Pyridine
Ammonium nitrate	Fenitrothion	Sodium carbonate
Ammonium phosphates	Ferric chloride	Sodium chlorate
Ammonium sulfate	Formaldehyde	Sodium chloride
Aniline	Formic acid	Sodium cyanide
Atrazine	Hexane	Sodium fluoride
Azinphosmethyl	Hydrazine	Sodium hydrosulfite
Benzene	Hydrochloric acid	Sodium hydroxide
Benzene hexachloride (Lindane)	Hydrofluoric acid	Sodium hypochlorite
Benzolic acid	Hydrogen peroxide	Sodium silicate
Benzotrifluoride	Isopropyl alcohol	Sodium sulfite
Bromoform	Lead oxide	Styrene
Butyl alcohol	Lignin sulfonate	Sulfur
Calcium chloride	Malathion	Sulfur dioxide
Calcium cyanide	Maleic anhydride	Sulfuric acid
Calcium hydroxide	Maneb	Terephthalic acid
Calcium hypochlorite	MCPA	Tetraethyl lead
Calcium oxide	Mercury	Thallium sulfate
Calcium phosphate	Methoxychlor	Thioglycolic acid
Carbaryl	Methyl alcohol	Titanium dioxide
Carbofuran	Methyl chloride	Toluene
Carbon tetrachloride	Methyl ethyl ketone	Toluene-2,4-diamine
Chlordane	Methyl methacrylate	Toluene-2,4-diisocyanate
Chlorine	Methylamine	Tributyl phosphate
Chlorophenol	Methylene chloride	Trichloroethane
Chromic acid	Naphthalene	Trichloroethylene
Cobaltous nitrate	Nitric acid	Trichlorofon
Copper cyanide	Nitroaniline	Trifluralin
Copper sulfate	Nitrogen (liquefied)	Trinitrotoluene
Cresol	Nonylphenol	Uranyl nitrate
Cyclohexane	Oxygen (liquefied)	Vinyl acetate
Diazinon	Paraquat	Vinyl chloride
Dicamba	Parathion	Xylene
Dichlorvos	PCBs	Zinc chloride
Dieldrin	Pentachlorophenol	Zinc cyanide
Diethanolamine	Perchloroethylene	Zinc oxide
Diethylamine	Phenol	Zinc phosphate
Dimethylamine	Phosphamidon	Zinc sulfate
Dinitramine	Phosphoric acid	2,4,5-Trichlorophenoxyacetic (2,4,5-T)
Dinoseb	Phosphorus	2,4-dichlorophenoxyacetic acid (2,4-D)

## Appendix D

### Draeger tube inventory WK9 136

Qty	Item	Primary compounds detected	Secondary compounds detected
10	Ammonia 5/a	Ammonia, Hydrazine	
5	Benzene 2/a	Benzene	Toluene, Xylene, hydrocarbons
10	Chlorine 0.3b	Chlorine, Bromine, Chlorine dioxide	
5	Hydrogen sulfide 5/b	Hydrogen sulfide	
6	Nitrous fumes 2/a	Nitric oxide, Nitrogen dioxide	Ozone, Chlorine
10	CO 200/a + CO <sub>2</sub> 2%/a	Carbon dioxide, Carbon monoxide	Acetylene
10	Hydrocarbon 0.1%/b	Propane, Butane	Hexane, Acetylene, Ethylene
5	Natural gas test	Methane-qualitative	
9	Sulfuric acid 1/a	Sulfuric acid	other mists, sulfates
5	Sulfur dioxide 1/a	Sulfur dioxide	
6	Toluene 25/a	Toluene, Xylene, Ethylbenzene, Cumene	
5	Monostyrene 10/b	Styrene	Xylene, Toluene, Ethylbenzene
5	Hydrochloric acid 1/a	Hydrochloric acid, Nitric acid	Chlorine
5	Phenol 1/b	Phenol, Cresol, Xylenols	
5	Formaldehyde 0.002	Formaldehyde	Acetaldehyde, Acrolein, Styrene
10	Acetic acid 5/a	Acetic acid	Acetic anhydride, other acids
5	Methanol 50/a	Methanol, Diethyl ether	Ethanol, Isopropanol, Butanol, Acetone, THF
10	Vinyl chloride 1/a	Vinyl chloride	Ethylene dichloride
5	Ethylene oxide 25/a	Ethylene oxide	Propylene oxide, alcohols
5	Perchloroethylene 10/b	Perchloroethylene	Trichloroethylene, petroleum alkanes, aromatics, carbon monoxide
5	Carbon tetrachloride 5/c	Carbon tetrachloride	Phosgene, alcohols
6	Ethyl acetate 200/a	Ethyl acetate, Methyl ethyl ketone	Vinyl acetate, Acetone, Benzene, petroleum alkanes, alcohols
5	Carbon dioxide 0.1%/a	Carbon dioxide	

Appendix E  
TRUCK MAINTENANCE CHECKLIST

Truck I.D.: Vehicle Serial No. \_\_\_\_\_  
Vehicle License No. \_\_\_\_\_

Date: \_\_\_\_\_

Odometer Reading: \_\_\_\_\_

### TRUCK ENGINE AND RUNNING SYSTEMS

Start-up: \_\_\_\_\_

Check all indicator lights on dash: \_\_\_\_\_

Check that alternator level returns to neutral at idle: \_\_\_\_\_

Fuel Level: Front \_\_\_\_\_ Back \_\_\_\_\_ [ Fill if total is less than 3/4 ]

Signals and Lights \_\_\_\_\_

Tire Pressure: DSF \_\_\_\_\_ DSR \_\_\_\_\_ PSF \_\_\_\_\_ PSR \_\_\_\_\_

Check Wheel Lug Tightness \_\_\_\_\_

Oil Level: \_\_\_\_\_

Washer Fluid \_\_\_\_\_

Engine Coolant \_\_\_\_\_

Front Tire Rotation: [ every 12 000 km] Odometer reading at last rotation

Engine Oil/Filter/Water Drain: [ every 6 months or 8000 km ]

Date of Last Change \_\_\_\_\_

Odometer Reading at last change \_\_\_\_\_

Date of last Lubrication: \_\_\_\_\_ [ Should not exceed 6 months ]

Date of Last Check of Non-Silicone Hoses: \_\_\_\_\_ [ 12 months or 24 000 km ]

Odometer Reading at last Brake Check: \_\_\_\_\_ [ Should not exceed 24 000 km ]

Date of last Engine Coolant Change: \_\_\_\_\_ [ Should not exceed 36 months ]

### CONTENTS OF TRUCK CAB

UHF Radio: (Dash) Power \_\_\_\_\_ Send/Receive \_\_\_\_\_

VHF Radio: (Dash) Power \_\_\_\_\_ Send/Receive \_\_\_\_\_

UHF Radio: (Portable) Power \_\_\_\_\_ Send/Receive \_\_\_\_\_

VHF Radio: (Portable) Power \_\_\_\_\_ Send/Receive \_\_\_\_\_

CB Radio: Power \_\_\_\_\_ Send/Receive \_\_\_\_\_

Cellular Phone: Power \_\_\_\_\_ Send/Receive \_\_\_\_\_

### CONTENTS OF TRUCK BOX

Generator Service Hours: \_\_\_\_\_

Hours Since Last Check: \_\_\_\_\_

Hours since last Oil Change: \_\_\_\_\_ [ Should not exceed 100 hours ]

Date of Last Oil Change: \_\_\_\_\_ [ Should not exceed 6 months ]

Hours Since Battery Check: \_\_\_\_\_ [ Should not exceed 100 hours ]

Hours Since Last Servicing: \_\_\_\_\_ [ Should not exceed 200 hours ]

Propane Level: \_\_\_\_\_

Appendix E  
TRUCK MAINTENANCE CHECKLIST

Regulator Pressure: \_\_\_\_\_  
Oil Level: \_\_\_\_\_

Generator Starting: \_\_\_\_\_  
Heater Operational: \_\_\_\_\_  
Fridge Operational: \_\_\_\_\_  
Interior Lights Check: \_\_\_\_\_

Service Check Performed By: \_\_\_\_\_

General Notes: \_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_  
\_\_\_\_\_



THE ENVIRONMENTAL RESPONSE TEAM'S USE of FIELD-PORTABLE  
X-RAY FLUORESCENCE INSTRUMENTS for ANALYZING LEAD (Pb) in  
SOILS

by

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The USEPA's Environmental Response Team (ERT) is presently using field-portable x-ray fluorescence (FPXRF) instruments for analyzing lead (Pb) in soils and sediments. Both in situ and prepared soil procedures are being used by the ERT.

Energy-dispersive XRF provides a nondestructive near real-time simultaneous multi-elemental analysis of liquid, powder, and solid samples. The ERT has used the OEI X-MET 880 and the Spectrace 9000 FPXRF analyzer for rapid on-site screening of soils for metallic contaminants. These instruments were selected for their capability to provide multi-elemental analysis and to correct for sample matrix effects. The instruments differ in their energy-resolving and consequently in their calibration and analytical methodology. The instruments have allowed the ERT to perform the following services at hazardous waste sites:

- Extent of Contamination Studies
- On-site Metal Analysis to Support Cleanup
- Paint Analysis for Lead
- Air samples for Metal Analysis

#### INSTRUMENTATION AND CALIBRATION

##### OEI X-MET 880 Instrument

The OEI X-MET 880 that was used was equipped with a double-source surface probe (DOPS) for both in-situ soil analysis and XRF sample cup analysis with the probe in the upright geometry and the safety shield attached. The DOPS probe was equipped with a 30 mCi  $\text{Am}^{241}$  radioisotope sources for Pb analysis.

The OEI DOPS probe employ a gas proportional detector with a typical energy resolution of 850 eV at the full width

at half of the maximum (FWHM) of the manganese (Mn) K x-ray line. The resolution of this detector does not allow for universal and efficient use of a fundamental parameter (FP)-based program to calculate elemental concentrations. An empirical or site-specific calibration curve that uses elemental standards, a suite of site standards, and regression mathematics is used to determine elemental response and matrix effects. This provides the operator with the flexibility to configure the instrument to analyze for any element from aluminum to uranium.

Since the site-specific calibration standards (SSCS) must be representative of the matrix and target element concentration range that may be found at site, some site samples need to be analyzed using atomic absorption (AA) or inductively coupled plasma emission spectroscopy. The highest and lowest SSCS samples are then used to determine the linear calibration range for the instrument. Guidelines for sampling, preparation of SSCS samples, for calibrating the X-MET 880 for hazardous materials applications can be found in ERT's SOP 1707 and the X-MET 880 Operator's Manual.

Since the DOPS probe is sensitive to temperature, the operator must activate a software-controlled gain-control circuit for five minutes for every 5° F change in the ambient operating temperature or every half hour to prevent possible errors due to shifts in the gain.

The electronic unit of the X-MET 880 is capable of holding 32 calibration models. Each model can be calibrated to analyze for six target elements. The electronic unit does not provide internal storage for spectrum or analytical results. An RS-232 serial port is provided for downloading data and spectra to a peripheral device.

### SPECTRACE 9000

The Spectrace 9000 surface probe provides for both in-situ soil analysis and XRF sample cup analysis with the probe in the upright geometry and the safety shield attached. It is furnished 5 mCi Cd<sup>109</sup>, 50 mCi Fe<sup>55</sup>, and 5 mCi Am<sup>241</sup> radioisotope sources.

The Spectrace 9000 utilizes a mercuric iodide semiconductor detector with an energy resolution of less than 300 eV at the FWHM of the Mn X-ray line. The improved energy resolution of the detector allows for efficient of FP-based program to calculate elemental concentrations. The FP-based program is a mathematical treatment of chemical matrix effects used in conjunction with a pure element or known standard element responses to develop an interactive for algorithm for analysis of a specific sample type (e.g., soil, oil, thin film, paint). Fundamental parameter method does not require site-specific calibration samples, only the selection of one of the FP-based applications from the menu is required. The following applications are provided with the instrument; soil, K and L-line Pb in paint, and thin film. Only soil application will be addressed in this



paper.

The X-ray intensities, derived from the spectra of the three sources, allows for 25 elements to be analyzed simultaneously. The soil application presently analyzes for potassium (K), calcium (Ca), titanium (Ti), Cr, Mn, iron (Fe), cobalt (Co), Ni, Cu, Zn, As, selenium (Se), strontium (Sr), zirconium (Zr), molybdenum (Mo), mercury (Hg), Pb, silver (Ag), thorium (Th), uranium (U), rubidium (Rb), Cd, tin (Sn), antimony (Sb), and Ba. Soil samples may be analyzed for any or all these elements without developing a calibration model.

A spectrum-energy calibration is performed automatically with each analysis to prevent error due to gain shift. The electronic unit provides internal nonvolatile memory for storage of 120 spectra and 300 multi-element analytical reports. An RS-232 serial port is provided for downloading data and spectra to a peripheral device. The multi-element analytical reports and the 2000 channel spectra can be displayed on the instrument's LCD panel.

The ERT's SOP 1713 "Spectrace 9000 Field Portable X-ray Fluorescence Operating Procedure," gives guidelines for start-up, check-out, operation, calibration, and routine use of the Spectrace 9000 for field use in screening of hazardous or potentially hazardous inorganic materials.

## **ANALYSIS METHODOLOGY**

### **IN-SITU FPXRF**

A complete procedure for conducting in situ soil analysis can be found in ERT's SOP 1707 "X-MET 880 Field Portable X-ray Fluorescence Operation Procedures<sup>2</sup>" and ERT's SOP 1713.

Large rocks and organic debris are removed from the soil within a 10 in. by 10 in. area to a depth of 1 inch. The soil is then mixed to reduce gross heterogeneity and flattened with a stainless steel trowel. Two or three different points in the area are then analyzed with the field portable XRF surface probe and the average of the measurements are recorded.

A soil moisture content of up to 20 percent is acceptable for most analyses. If the moisture content is greater than 20 percent, the soil and or sediment is placed in an aluminum pan and allowed to air dry. Large rocks and organic debris is removed and the sample is mixed to reduce gross heterogeneity. The sample is shaped into a 1 inch thick cake and flattened with a stainless steel trowel. Two or three different points are then analyzed with FPXRF surface and the average is reported.

### PREPARED SAMPLES FPXRF

Soil or sediment is collected from a 10 in. by 10 in. area to a 1 in. depth. The sample is allowed to air dry or dry in a conventional oven at 105° C. The sample is broken up and passed through a ten-mesh sieve. The oversized material is then discarded, and the undersized portion is mixed. A 31 mm sample cup is filled and covered with 0.2mil polypropylene x-ray film. The cup is analyzed once with the FPXRF surface probe in the upright geometry.

Confirmation samples, using the same sample cup used for FPXRF analysis, are submitted to a laboratory for analysis following EPA publication "Test Methods for Evaluating Solid Waste," SW-846, 3rd Edition.

### QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

Data produced by the XRF meet the requirements of QA objective 1 (QA1), and QA2 which are stated in OSWER Directive 9360.4-01, "Quality Assurance/Quality Control Guidance for Removal Activities-Sampling QA/QC Plan and Data Validation Procedures," April 1990. For screening a site QA1 is used. It allows for a quick preliminary assessment of sites contamination. Calibration or performance check of the method along with a verification of detection limit is required for QA1. No other QA data is required for QA1.

Since QA2 is a verification objective, ten percent of the XRF samples must be confirmed by a U.S. EPA certified laboratory using AA or ICP methods. In order to meet QA2 objectives, the regression analysis of AA/ICP vs XRF data sets must have a coefficient of determination ( $R^2$ ) of 0.7 or greater.

Precision is monitored by analyzing a sample with target elements concentrations above the method detection limit (MDL) at the start and periodically throughout the day. The FPXRF field MDL is calculated from the measurement of a soils matrix blank at the start and end of sample analysis, and after approximately every tenth sample. The MDL is defined as three times the calculated standard deviation of the mean for each target element. Precision is determined from the MDL data by calculating the coefficient of variation (COV). The COV should be within  $\pm 20\%$  for the data to be considered adequately precise.

### RESULTS

Table 1 summarizes the MDL, precision, and confirmation regression data for the X-MET 880 FPXRF analyses of Pb in a variety of soils and waste matrices. Table 2 has similar data for the Spectrace 9000.

## DISCUSSION OF RESULTS

The in situ and prepared sample methodologies were evaluated at a battery breakage and a scrap metal site using X-MET 880 (the first and last site in Table 1). These methodologies were also evaluated using the Spectrace 9000 at the scrap metal site (site 2 in Table 2). Both methodologies meet QA2 data objectives for these sites.

A statistical comparison of slopes (regression coefficient) was performed to compare AA/in-situ FPXRF, and AA/prepared sample FPXRF regression results for the battery breakage and the scrap metal sites. A methodology was utilized which is similar to that of testing the difference between two population means (the Student's t test). The null hypothesis for this test is  $\beta_1 = \beta_2$  where  $\beta$  represents the true population regression coefficient. The alternative hypothesis is  $\beta_1 \neq \beta_2$ . In all cases, alpha was set equal to 0.05.

Comparison of X-MET 880 battery breakage AA vs in-situ FPXRF, and AA vs prepared sample FPXRF regression results indicate slope of 0.92 and 0.84, respectively. When applying the Student's t methodology, no significant difference could be found between these two slopes (p-value < 0.50) indicating that these two slopes came from the same  $\beta$  population and that the regression lines can be assumed to be parallel.

Similar results were achieved from the data at the scrap metal site for the X-MET regression and the Spectrace 9000 regression. Results of the X-MET 880 in-situ FPXRF regression (slope = 1.98) vs prepared sample FPXRF regression (slope = 1.78), also showed no statistical difference between the slopes with  $0.10 < \text{p-value} < 0.20$ . The Spectrace 9000 comparisons gave similar result, with in-situ FPXRF slope = 1.09 and prepared sample FPXRF slope = 1.04 and with  $0.20 < \text{p-value} < 0.50$ .

In all three of these cases, the null hypothesis could not be rejected. Lending support to the theory that the true population regression coefficient are, in fact, the same between in-situ and prepared sample FPXRF results. Therefore, the pairs of regression lines can be assumed to be parallel in each case.

The Pb detection limits in Table 1 and Table 2 are significant below typical Pb action levels of 500 - 2000 mg/kg, and the precision is normally less than 20% for analysis times of 30 - 60 seconds. The results from Pb analysis using the FPXRF generally meet QA2 data objective with close to 1:1 proportionality between AA/ICP and XRF data sets.

## CONCLUSIONS

Field portable XRF instruments can achieve QA Level 2 objectives providing quick on-site multi-elemental analysis of a large number of in-situ and prepared samples. The on-site availability of reliable metal analysis by FPXRF provides site managers with real-time needed during site contamination studies and during site cleanup activities.

The mention of trade names of commercial products does not constitute an endorsement or recommendation for their use by EPA.

## REFERENCES

- [1] "Spectrace 9000 Field Portable X-ray Fluorescence Operation Procedures," U.S. Environmental Protection Agency/Environmental Response Team, SOP #1713.
- [2] "X-MET 880 Field Portable X-ray Fluorescence Operation Procedures," U.S. Environmental Protection Agency/Environmental Response Team, SOP #1707.

**TABLE 1**  
**LEAD RESULTS FOR THE X-MET 880 FPXRF**

WASTE TYPE	MET HOD	MDL PPM	CONC mean ppm	COV%	MEAS TIME SEC.	N	R <sup>2</sup>	SLOP E
BATTERY BREAK- AGE	P	123	300	13.7	60	21	0.97	0.84
	I	123	300	13.7	60	21	0.85	
	I	81	---	---	60	46	0.85	0.92
								0.85
SMEILTER STACK	I	165	485	11.3	60	9	0.84	0.53
SCRAP METAL	P	111	159	23.3	60	22	0.78	1.16
SCRAP METAL	P	606	----	----	60	24	0.64	1.01
IND. SLAG	P	73	1513	16.1	60	14	0.98	1.21
BATTERY BREAK- AGE	I	129	266	16.2	60	26	0.89	0.96
SMEILTER SLAG	P	119	256	15.6	60	261	0.98	0.96
PLATING	P	186	551	11.3	240	34	0.99	6.5
SCRAP METAL	I	93	772	4.0	240	30	0.89	1.98
	P	93	772	4.0	240	70	0.92	1.78

P = Prepared samples,

I = In-situ analysis,

COV = Coefficient of variation,

N = number of  
observations,R<sup>2</sup> = Coefficient of determination for the regression

**TABLE 2**  
**LEAD RESULTS FOR THE SPECTRACE 9000 FPXRF**

WASTE TYPE	METHOD	MDL PPM	MEAN CONC PPM	COV%	MEAS TIME SEC.	N	R <sup>2</sup>	SLOPE
PLATING	P	114	1124	3.4	240	32	0.71	0.67
SCRAP METAL	I	123	972	4.4	240	40	0.87	1.09
	P	123	972	4.4	240	72	0.83	1.04
JUNK YARD	P	30	136	19.1	60	12	0.86	1.17
BATTERY BREAK AGE	I	42	1049	5.0	60	20	0.97	0.69
BATTERY BREAK AGE	I	33	1750	4.3	60	13	0.99	1.62
SMEILER WASTE	P	38	1151	8.0	60	180	0.89	1.34
BURNED ELECTRONICS	I	40	175	12.2	60	212	0.82	0.93
	P	59	164	16.4	30			

P = Prepared samples,

I = In-situ analysis

COV = Coefficient of variation,

N = Number of observations,

R<sup>2</sup> = Coefficient of determination for the regression

## **Air Monitoring and Sampling Techniques Used in Support of a Cleanup of an Abandoned Plating Facility**

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### **Abstract**

The U.S. Environmental Protection Agency's Environmental Response Team ( ERT ) was established in October 1978 to provide scientific support to Federal On-Scene Coordinators ( OSC's ), Remedial Project Managers ( RPM's ), Regional Response Teams ( RRT's ), Federal / State and foreign governmental agencies in the area of hazardous waste sites, oil spills and environmental emergencies.

This paper will summarize ERT's air monitoring and sampling procedures used during bulking and transferring operations at a plating facility in Sarasota, Florida. The paper will compare results from sampling monitoring for cyanide and inorganic acids.

**PAPER NOT AVAILABLE AT TIME OF PRINTING**





cannot be used in  
a composite chemical

## **The Use of Remote-controlled Helicopters for Air Sampling in An Emergency Response Situation**

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### **Abstract**

The use of remote-control (RC) helicopter to monitor vapour concentration or take air samples in hazardous spills without endangering the lives of emergency responders was first reported by Emergencies Science Division (ESD), Environment Canada in 1989. This paper addresses the design of such helicopters as developed by ESD and their use in emergencies response and oil burn projects. With emphasis on the most recent development, technical data of the airframe and various sampling devices onboard are presented. The value of current experience and analytical data from actual field trials are assessed. Finally the strength and weakness of this novel sampling device, and a consolidation of the current RC helicopter technology will be discussed.

### **Background**

There has been published references to research and development projects involving remotely piloted aircraft. Most of them, however, have military, law enforcement and telemetry application and tend to be expensive and costly to develop. Reports on using low cost, reliable, mobile environment sampling/monitoring with miniature RC airborne crafts have been scarce (1).

ESD has pioneered the use of RC helicopter to sample and monitor vapour cloud over highly toxic spills. The rationale of employing this novel means of sampling/sensing is that in cases of extremely hazardous toxic spills or access to the site cannot be attained by any other means, an unmanned, airborne platform with sensing/sampling equipment can be flown over the spill site for a quick assessment. The highly mobile nature of this sampling platform also enables plume movements be tracked easily. If necessary, instantaneous or composite samples can be taken using particulate filters or sorbent tubes.

Once brought back to the ground, they can be analyzed using Level 2 person-portable instruments. If more sophisticated analysis is warranted, Level 3 vehicle-portable instrumentation is employed. An example is ESD's Level 3 emergencies response vehicle, designed to be self-sufficient for field analysis, it is a fully functional lab equipped with a small fume hood and a lab grade GC/MS/data system (Hewlett-

Packard GC/MSD) system. Upon desorption (either thermally or solvent extraction) and injection into the GC/MSD operated in scan mode, the generated spectra can be searched against a 75,000-compound NIST library. Qualitative and quantitative information can then be established very quickly. When deployed together, the entire system can provide responders with vital information about the nature and magnitude of the spill under investigation.

With the objectives thus defined, the ideal package should possess the following attributes:

- can be operated within a 1000 feet radius, within visual sight of the operator,
- be fairly portable and easy to setup for deployment in a confined area,
- be able to carry an on-board video camera for positioning and surveillance purpose; a data telemetry system will send real time imagery to nearby ground control station,
- be able to monitor real time concentration measurement with on-board vapour or gas sensors and sampling device for subsequent analysis,
- have sufficient endurance to linger over the site for a minimum of 15 min, and finally,
- be reasonably inexpensive, easy to fly and maintain.

### **Development of RC Helicopter sampling technology in ESD**

The first prototype, designed and built in 1988, was essentially a custom-built helicopter with many fabricated components because common hobby helicopter kits did not meet the 20-lb payload requirement. The completed helicopter carried a variety of sampling equipment, among them a photoionisation-based gas detector, a Gilan high flow sampler and an onboard video camera with a data telemetry system transmitting real time imagery via data downlink to the ground. Measuring about 5 ft long and with a rotary span about 6.5 ft, the helicopter was a highly sophisticated sampling platform which had a useful payload of about 15 lbs. Unfortunately, because of the heavy loading and weight distribution on the airframe, this helicopter was found to be difficult to fly. Also, since most of the components were non-stock items, the airframe was not as rugged as production models and thus difficult to maintain.

Based on the experience gained from the prototype, the second generation of RC helicopters was constructed in 1991 and was based largely on a commercially available GMP 60-size Legend using mostly off-the-shelf components. With emphasis on low development cost and ease of operation, the video positioning/data telemetry system were left out to match the payload of the now much lighter airframe. The Legend carried a Gilian high flow sampler, drawing air samples through a stainless-steel probe protruding about 18-in beyond the nose of the helicopter to clear the downwash of the rotary blades. Particulate filters and sorbent tubes were used to trap and concentrate contaminants.

In anticipation of an offshore oil burning experiment, the third generation of RC helicopters were constructed in 1993 to take air/smoke samples. They were primarily

based on Miniature Aircraft (Orlando, FL) 60-size X-Cell helicopter kits and custom-modified with floatation devices for over water operation. Sampling equipment consisted of a Gilian sampling pump for smoke sampling and mini-summa canisters to take air samples over the burning pool of oil contained by the apex of a fire-resistant boom.

### **Description of Equipment**

The first prototype has been described by earlier ESD publications (2) and will not be repeated here. The second- and third-generation helicopters platform are described as follows:

#### **Legend**

<b>Airframe:</b>	GMP/Legend with Hiller Stabilised flybar system
<b>Radio:</b>	Futaba FP-7UHF 7-channel digital proportional RC system
<b>Gyro:</b>	Quest rated gyro
<b>Fuel:</b>	12 % nitro/methanol
<b>Engine:</b>	Single cylinder glow engine, Enya 60XF-4H, 0.61 cu in (10 cc); cruising power, 1.5 hp
<b>Dimension:</b>	18 in (46 cm) high, 50 in (127 cm) long; rotary span 58 in (145 cm)
<b>Weight:</b>	15 lbs (7 kg) all-up weight
<b>Payload:</b>	5 lbs (2.5 kg)
<b>Sampling equipment:</b>	Gilian HFS-513A hi-flow sampler; 2 l/min sampling rate (nominal)

#### **X-Cell**

<b>Airframe:</b>	Miniature/X-Cell modified with a set of glass-fibre floats for over water operation
<b>Radio:</b>	JR C-347 7-channel digital proportional RC system
<b>Gyro:</b>	JR rated gyro
<b>Fuel:</b>	12 % nitro/methanol
<b>Engine:</b>	OS Max SF, 0.61 cu in (10 cc); cruising power, 3 hp
<b>Dimension:</b>	24 in (61 cm) high, 52 in (132 cm) long; rotary span 58 in (145 cm)
<b>Weight:</b>	18 lbs (8 kg) all-up weight
<b>Payload:</b>	8 lbs (3 kg)

**Sampling equipment:**

**Activation--**On/off switch servo-activated on an unused channel.

**Sample probe--**0.5-in diameter aluminum tubing mounted on the right side of helicopter, protruding approx. 1.5-ft from the nose to clear the rotary blades. Air

samples were drawn through a Teflon filter to screen out particulate and through a concentric 1/4-in diameter Teflon tubing.

**Smoke/soot sampling**—Gilian LFS-113 lo-flow sampler; 1 l/min sampling rate (nominal); sampling media: 37-mm Teflon filter and 6\*70 mm XAD sorbent tube (PAH sampling).

**Inert gas/VOC sampling**—1- or 2-litre evacuated summa canisters, with restricted orifice drawing at 50 cc/min (nominal).

#### Solenoid valve driver for Summa or Gilian pump

A custom-designed solenoid latching valve driver (Figure 1) was constructed and installed on each of the X-Cell so that the sampling device could be remotely activated. This type was chosen due to the short electrical pulse required to actuate it rather than a continuous drain on the battery pack. The circuitry comprised a double pole double throw relay which was controlled by a dedicated channel on the radio control system. Initially, the latching capacitor was connected to the solenoid latch lead and the unlatching capacitor connected to a pair of 9-v batteries for charging. When the channel was activated, the latching capacitor returned to 12 v for re-charging while the unlatching capacitor discharged into the corresponding lead causing the valve to open. The subsequent closure of the channel returned all conditions to the initial states. In this manner the toggle operation of the valve was obtained by an actuation mechanism equivalent to that of a dedicated radio channel.

#### Floatation device for X-Cell

To improve survivability in case of a crash or forced landing on water, a pair of floats were fitted to each X-Cell helicopter in lieu of the normal landing skids. Each float was constructed from a hollowed-out foam cylinder 20-in long\*4-in diameter. They were made water-proof by fibre-glassing and given a final coat of fuel-proof paint. To facilitate visual orientation, each float was painted a different colour. The weight of floats had to be kept at below 2 lb to maximize the useful payload of the helicopter. The bright colour floats greatly improved the visibility factor and turned out to be indispensable for over water operation. On two occasions, one a forced landing due to mechanical difficulty, the other a crash caused by pilot dis-orientation in fog, both helicopters were saved along with all sampling equipment.

#### **Actual Field Trials of ESD Helicopters**

The Legends were employed in two land oil burn experiments in 1991 and 1992 at the Fire and Safety Test Detachment Center, Mobile, Alabama. The X-Cell took part in an off shore oil burn experiment in St. Johns, Newfoundland in 1993. In these experiments, crude oil, ranging from 500-3000 gallons for the land burns and 10,000 gallons for the offshore burn was contained in a manner so that the thickness could be varied. Upon ignition, the smoke plume was sampled by a variety of samplers positioned in the air as well as on the ground in an array of ground stations. Operational details are described as follows:

### **Mobile 1 Burns (1991)**

Carried out during June 1991 on Sand Island in Mobile Harbour, a series of 13 burns were conducted by a consortium of 15 agencies from US and Canada. The ESD helicopters were shipped on site in custom-made aluminum cases. Through the help of A. M. A. (Academy of Model Aeronautics in Reston, VA), a pilot from the local flying club was enlisted. A demonstrative flight was performed on May 27 to 'climatise' the helicopter to local conditions. On the following day, a sample was collected during the burn. NIST was operating a blimp tethered at 250-ft from the fire. In order to clear the line, a oval-shaped flight path was drawn up such that the helicopter would fly towards the fire in an upwind leg, boring through the cone of smoke plume. At about 300 feet downwind from the fire, the helicopter exited the plume and turned around in a downwind leg and re-entered the plume at a point about 600 feet from the fire. At that point the helicopter was flown well beyond the shore line of the sand island. After about 15 min, the helicopter was landed and the filter/XAD sample recovered. The blades were wiped down with acetone-moistened tissues to recover the fine layer of soot.

The recovered sample was analyzed by ESD using the following procedure: soxhlet extracted in dichloromethane/benzene and cleaned up by silica column chromatography. The extract was injected on a GC/MSD by which 26 PAH compounds ranging from 2 to 6 rings were determined.

### **Mobile 2 Burns (1992)**

Additional burns were carried out in the fall of 1992 at the same site. With the experience gained from the first burn, two helicopters were employed during each burn. The first helicopter, operated by a contract pilot of ERT (Emergency Response Team, EPA), was designated to fly at a point 100 feet downwind from the fire. The second one was operated by the same local pilot as in Mobile 1 burn and flew at about 500 feet from the fire. The blimp was positioned in between at about 250 feet. The operation of the ERT helicopter turned out to be difficult because of the very limited air space assigned to it. The smoke plume at that point was also very dark and the air extremely turbulent. In the third burn, the ERT pilot lost eye contact with the helicopter and, in order not to endanger the personnel manning the ground sampling stations, he opted to force-land the helicopter before it flew out of control, resulting in serious damages to the equipment. Hence, for the remaining 3 burns, only one helicopter was employed to collect the soot samples, at distances 300-600 feet from the fire.

In all cases, Teflon filter/XAD samples were collected together with the blade wipes. They were analyzed by ESD using the methodology described above (3).

### **NOBE Burn (1993)**

For this offshore burning experiment, the third generation ESD X-Cell helicopters were constructed and outfitted with floats. A new provision was made to carry

evacuated summa canisters to collect whole air samples in addition to the normal filter/sorbent sampling system. Two teams of expert pilots were recruited from members of various flying clubs: among them the Canadian national champion, the field representative of Miniature Aircraft (maker of X-Cell) and a local expert builder and pilot who has been involved with the design/building of ESD's helicopters in the past.

The two teams, each with a principle pilot, a backup and a scientific coordinator, were positioned in cutters at 100 and 500 feet off to one side from the apex of the boom which contained the burning pool of crude oil. Take off and landing was made from a 12\*8 feet plywood platform atop the fore section of the vessel. Previously thought to be almost impossible to operate a hobby-style helicopter from a small, pitching platform, the extremely difficult operation was successfully carried out. Only one crash took place which happened during the rehearsal on August 7. The accident was attributed to lost of orientation in the fog and to motion sickness suffered by the pilot. Nevertheless, the crashed helicopter was repaired in time to participate in the actual burn experiment.

Before the oil was discharged, background summa samples were taken. Samples were also taken after oil discharge to assess the amount of VOC present before ignition. Once the burning was underway, two summa runs were made collecting the clear air around the smoke plume (for VOC and inert gases analysis) and one run made with the helicopter traversing the smoke plume (for PAH/soot analysis). This sampling scheme was repeated for the second burn (4).

## Results and Discussion

Results of PAH analysis on soot collected from filter/XAD tubes and blade wipes are summarised in Tables 1-3. On the whole, only traces of PAH were found on the filter/sorbent samples. This is due to the limited drawing capacity of the Gilian pump and the short residence time inside the smoke plume (5-10 min). The blade wipes, however, had appreciable amount of soot (up to 89 mg) and some had significant concentration of PAH. This is due to the high rotational speed of the blades which functions in effect as a very efficient passive soot collector. Figure 2 shows a chromatogram of PAH analysis of a soot sample collected from the blades in Mobile 2 Burn. The helicopter was flown approx. 350 feet from the fire. The profile of the 6-rings PAH, characteristic of combustion of crude oil, is compared to that from a ground station.

Table 4 summarises the findings from the NOBE burn. The mini-summa canisters were analysed for VOC as well as CO<sub>2</sub>. More or less ambient levels of CO<sub>2</sub> was measured around the smoke plume.

Detailed VOC results are given in Table 5. On the list are 150 target VOC as reported by Pollution Measurement Division, Environment Canada in their ozone precursor analysis. The VOC background samples collected at various times before the actual burn ranged from 78-325 ug/m<sup>3</sup>. With the oil in place and before ignition, VOC were

measured at 254 ug/m<sup>3</sup>. The first burn generated VOC concentration of approx. 300 ug/m<sup>3</sup> at distances 100 and 500 feet from the fire, with a high one at 2083 ug/m<sup>3</sup>; this canister was collected by team 1 under the smoke plume at about 100 feet from the apex. For the second burn, the VOC concentration averaged about 100 ug/m<sup>3</sup>, the highest VOC concentration was found to be 1005 ug/m<sup>3</sup> under the plume at an altitude of approx 18 metres at a distance about 500 feet from the fire.

### **Safety and performance limitations**

As stipulated by the safety regulation of M.A.A.C. (Model Aeronautical Association of Canada), there should be a minimum clearance of 20 feet around the take off/landing area. The pilot is also forbidden to fly the helicopter above people. When fully loaded, the package weighs at about 16 lbs. At hover speed, the blades spin at about 2500 RPM; the amount of energy stored could cause severe injuries if proper caution is not exercised.

For emergencies response application, it is also essential to have a 'spotter' who functions as an extra eye for the pilot. As a coordinator between the ground control and pilot, he would warn the pilot of any obstacles or disturbances in the flight path, to backup the pilot if necessary and control the crowd who may otherwise affect the concentration of the pilot.

Despite the potential advantages of the helicopters over other remotely piloted sampling devices, there are some practical limitations in its use. When the helicopter is fully equipped with the sampling devices, handling can become increasingly difficult because of the overall weight, and weight distribution on the airframe may not be optimal. Without any power reserve, operating in windy days may become marginal. For example, in the case of the fully loaded X-cell, flying should be confined to days with winds calmer than 8-10 km/hr.

Furthermore, in order to take a meaningful sample so that the data can be properly interpreted with information such as altitude and proper orientation in the vapour plume, fairly precise flight manoeuvres are required from the pilots. Often times the pilot is required to fly the helicopter at the extreme range of operation at 1000 feet. All those factors, plus the presence of a myriad of other activities at an emergency site, demand a maximum skill level from the pilot/operator. In our experience, the flyer needs to be in the 'good' to 'excellent' class and generally would have logged about 150-200 hrs of flying. It is also preferable that the pilot has competition experience, so that he has accustomed to stress and tension. These requirements would normally place the prospective flyer in a category well beyond the intermediate level of most hobby flyers.

### **Future development**

There are several new instruments and development now on the market which have potential application in RC helicopter sampling. They are briefly described below.

Pocket-portable gas sensors available at present can monitor on a continuous basis spot concentration of toxic and combustible gases. Their sensors are generally electrochemical or catalytic and some have data-logging capability. For example, Matheson's MAT 5100 Personal Monitor offers over 140 gases and ranges. Weighing less than 1-pound each, they are rugged and some have multi-channel detectors for multiple gas analysis (5).

Onboard video camera is now available the size of a pack of cigarettes. Once exacting a heavy weight penalty, the new video-on-a-board plus UHF transmitter kit are relatively inexpensive and light weight (Supercircuits, Texas). This can bring back the video positioning/surveillance capability, and should make flying and sampling more precise.

The technology of RC helicopter has been improved steadily in terms of durability and versatility of the equipment. Helicopters that can lift 15-lbs of equipment are now available using mostly stock components. Costing about \$4000 each with an all-up weight of 26-lbs, such helicopters have been employed routinely in aerial photography work (Flight craft, Kitchener). Helicopters that have even bigger payloads (up to 20 lbs) can even be supplied in a ready-to-fly configuration.

Flight simulation for RC helicopter (Dave Brown Products, Hamilton, Ohio) has improved and now features solid graphics which gives a much more realistic view of the helicopter. Supplied with a modified radio transmitter which plugs into the game port of a PC, the software is indispensable to beginners. It is an excellent way to train the novice the proper view orientation and feel for the stick as well as learning the difficult transition to nose-in manoeuvres.

## Conclusions

From three years of operational experience, we have identified the potential applications for RC helicopter in the following situation:

1. preliminary assessment of situations where highly toxic vapour is suspected, by taking whole air samples or absorption tubes;
2. monitoring/mapping of hazardous (HAZMAT level 3) spills when access is impossible;
3. situations where full size aircraft is precluded by F.A.A regulation, pilot/crew or cost.

Among the various airborne crafts, a RC helicopter was chosen because of the following advantages:

- can carry a reasonable payload given the size of the craft (compare with lighter than air crafts);
- the ability to hover the spill site with no or little ground speed; take off and land in restricted areas (compare to fixed wing crafts);
- not as sensitive to high wind conditions and thus can be flown upwind from the



- suspected site, thus minimising risks to the operator;
- with the blades folded back, transportable in a fairly small package and easy to deploy;
- components readily available using hobby-style helicopters;
- using whole air samplers such as evacuated summa canisters or tedlar bags, a quick grab sample can be taken and multiple analysis can be performed.

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• Hygroscopic →

• there is a window of opportunity  
 • incorporating later a GPS on  
 on board. etc

Table 1

PAH in XAD and Wipe samples, Mobile 2 Burn (1992)

Sampling Date	Nov-03				Nov-05				Nov-06				Nov-07		Nov-09		Nov-10	
Helicopter Designation	ERT	ERT	EC	EC	ERT	ERT	EC	EC	ERT	ERT	EC	EC	ERT	ERT	EC	EC	EC	EC
Sampling Location (estimate)	150 ft		500 ft		150 ft		500 ft		150 ft		500 ft		Background		500 ft		500 ft	
Sample Description	Filter	WIPE	Filter	WIPE	Filter	WIPE	Filter	WIPE	Filter	WIPE	Filter	WIPE	Filter Blank	WIPE Blank	Filter	WIPE	Filter	WIPE
Sample wt (mg)	<0.1	37.00	LOST	16.00	<0.1	<0.1	<0.1	23.00	<0.1	Heli crashed	<0.1	88.00	<0.1	<0.1	<0.1	lost	lost	78.00
Sample volume (liters)	10.00	20.00	20.00	10.00	10.00	20.00	20.00	10.00	20.00	20.00	20.00	10.00	10.00	20.00	20.00	20.00	20.00	20.00
COMPOUND	ug/m3	ug/gm	ug/m3	ug/gm	ug/m3	ug/gm	ug/m3	ug/gm	ug/m3	ug/gm	ug/m3	ug/gm	ug/m3	ug/gm	ug/m3	ug/gm	ug/m3	ug/gm
1-NAPHTHALENE	ND	21.56	14.00	ND	ND	ND	13.20	ND	ND	7.68	ND	ND	ND	ND	ND	2.04		3.20
2-METHYLNAPHTHALENE	ND	4.20	4.89	ND	ND	ND	3.55	ND	ND	1.67	ND	ND	ND	ND	ND	0.57		0.70
1-METHYLNAPHTHALENE	ND	2.40	2.58	ND	ND	ND	2.07	ND	ND	1.00	ND	ND	ND	ND	ND	0.34		0.35
2-FLUORENE	ND	5.12	3.99	ND	ND	ND	31.61	ND	ND	1.30	ND	ND	ND	ND	ND	3.63		1.84
2,6-DIMETHYLNAPHTHALENE	ND	1.46	1.50	ND	ND	ND	1.35	ND	ND	0.69	ND	ND	ND	ND	ND	0.32		0.19
1,8-DIMETHYLNAPHTHALENE	ND			ND	ND	ND		ND	ND		ND	ND	ND	ND	ND			
ACENAPHTHYLENE	ND	19.66	5.35	ND	ND	ND	6.44	ND	ND	2.37	ND	ND	ND	ND	ND		0.71	2.19
ACENAPHTHENE	ND	2.08	<0.5	ND	ND	ND	0.79	ND	ND	0.69	ND	ND	ND	ND	ND		<0.5	<0.5
3,3,5-TRIMETHYLNAPHTHALENE	ND	0.66	<0.5	ND	ND	ND	0.88	ND	ND	1.61	ND	ND	ND	ND	ND		<0.5	<0.5
10-METHYLNAPHTHALENE	ND			ND	ND	ND		ND	ND		ND	ND	ND	ND	ND			
FLUORENE	ND	8.99	2.00	ND	ND	ND	2.54	ND	ND	1.06	ND	ND	ND	ND	ND		0.39	1.01
PHENANTHRENE	ND	71.92	22.16	ND	ND	ND	19.86	ND	ND	8.38	ND	ND	ND	ND	ND		4.58	31.76
ANTHRACENE	ND	10.21	3.00	ND	ND	ND	2.10	ND	ND	0.86	ND	ND	ND	ND	ND		0.62	6.88
1-METHYLPHENANTHRENE	ND			ND	ND	ND		ND	ND		ND	ND	ND	ND	ND			
2-METHYLPHENANTHRENE	ND	1.54	1.78	ND	ND	ND	1.41	ND	ND	1.34	ND	ND	ND	ND	ND		0.60	2.25
FLUORANTHENE	ND	44.26	17.37	ND	ND	ND	11.31	ND	ND	4.10	ND	ND	ND	ND	ND		3.23	36.73
PYRENE	ND	46.91	5.66	ND	ND	ND	11.46	ND	ND	3.71	ND	ND	ND	ND	ND		3.41	37.08
1-BENZOPHANTHRENE	ND	4.38	<0.5	ND	ND	ND	2.74	ND	ND	1.10	ND	ND	ND	ND	ND		1.40	7.85
CHRYSENE	ND	6.59	<0.5	ND	ND	ND	<0.5	ND	ND	<0.5	ND	ND	ND	ND	ND		<0.5	9.46
BENZOFULY	ND	7.46	<0.5	ND	ND	ND	<0.5	ND	ND	<0.5	ND	ND	ND	ND	ND		<0.5	12.86
BENZOPYRENE	ND	3.74	<0.5	ND	ND	ND	<0.5	ND	ND	<0.5	ND	ND	ND	ND	ND		<0.5	5.14
BENZOPYRENE	ND	4.82	<0.5	ND	ND	ND	<0.5	ND	ND	<0.5	ND	ND	ND	ND	ND		<0.5	9.33
PERYLENE	ND	2.15	<0.5	ND	ND	ND	<0.5	ND	ND	<0.5	ND	ND	ND	ND	ND		<0.5	1.82
1-BENZOPYRENE	ND	1.41	<0.5	ND	ND	ND	<0.5	ND	ND	<0.5	ND	ND	ND	ND	ND		<0.5	11.61
1-BENZOPYRENE	ND	<0.5	<0.5	ND	ND	ND	<0.5	ND	ND	<0.5	ND	ND	ND	ND	ND		<0.5	1.10
1-BENZOPYRENE	ND	3.38	<0.5	ND	ND	ND	<0.5	ND	ND	<0.5	ND	ND	ND	ND	ND		<0.5	8.73
TOTAL, ug/gm		273		84			111					38				22		191
SURROGATE RECOVERY %																		
d10-ACENAPHTHENE	77	77		73	85	39	57	40	29			76	87	64			50	51
d10-PHENANTHRENE	78	78		78	83	58	79	61	41			91	76	88		77	69	62
d12-8-QUANTHRACENE	84	84		74	88	62	70	69	47			78	73	72		83	58	82
d12-PERYLENE	61	61		49	40	29	42	41	25			44	43	38		66	<0.5	74

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Note: <0.5 denotes less than method detection limit of 0.5ppm; assuming sample wt = 20 mg  
 ND denotes non detectable because of non-measurable sample weight  
 Lost samples were due to breakage

Table 2

## PAH In Helicopter XAD Samples, NOBE Burn.

Sample Size (m3)	0.023	0.006	0.0120	0.006	0.005	0.005	0.0100	0.007	
Description	Team 1	Team 1	Team 1	Team 1	XAD blk	Team 1	Team 2	Team 2	XAD trip blank
	Burn 1	Burn 1	Burn 2	Burn 2	Burn 2	Bkg	Burn 2	Burn 2	
Compound	Air	Plume	Air	Plume	Static blk		Plume	Plume	
	ug/gm	ug/gm	ug/gm	ug/gm	ug/gm	ug/gm	ug/gm	ug/gm	ug/gm
Naphthalene	<4.35	77.62	<8.3	78.25	0.12	<20	<20	41.39	0.33
1-Methylnaphthalene	<4.35	<16.7	<8.3	16.70	<0.1	<20	<20	<14.3	<0.1
2-Methylnaphthalene	<4.35	26.66	<8.3	33.24	<0.1	<20	<20	17.61	0.11
Biphenyl	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
2,6-Dimethylnaphthalene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Acenaphthalene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Acenaphthene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
2,3,5-Trimethylnaphthalene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Fluorene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Phenanthrene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Anthracene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
1-Methylphenanthrene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Fluoranthene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Pyrene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Benz(a)anthracene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Chrysene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Benzo(b)fluoranthene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Benzo(k)fluoranthene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Benzo(e)pyrene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Benzo(a)pyrene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Perylene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Indeno(1,2,3-c,d)Pyrene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Dibenz(a,h)anthracene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Benzo(g,h,i)Perylene	<4.35	<16.7	<8.3	<16.7	<0.1	<20	<20	<14.3	<0.1
Total:	0	104	0	128	0	0	0	59	0
<b>Surrogates (percent recovery)</b>									
d8-Naphthalene	108	95	88	89	78	93	94	88	88
d10-Acenaphthene	108	97	89	93	82	95	96	89	88
d10-Phenanthrene	103	94	86	89	83	91	94	87	86
d12-Chrysene	76	85	70	86	88	81	86	86	80
d12-Perylene	58	76	61	79	82	63	73	76	68
d14-Terphenyl(I.S. area *1000)	253	277	261	277	374	294	324	303	311

**Table 3**

**PAH on Helicopter Wipe Samples, NOBE burn.**

Sample Size (g)	0.037	0.0169	0.0578	0.1222	0.0023	0.0004
Description	Team 1, Burn 1	Team 1, Burn 2	Team 2, Burn 1	Team 2, Burn 2	Field Blank	Field Blank
Compound	ug/gm	ug/gm	ug/gm	ug/gm	ug/gm	ug/gm
Naphthalene	12.58	11.44	8.80	5.48	N/D	N/D
1-Methylnaphthalene	<3	<6	<2	<1	N/D	N/D
2-Methylnaphthalene	<3	<6	<2	1.10	N/D	N/D
Biphenyl	<3	<6	<2	<1	N/D	N/D
2,6-Dimethylnaphthalene	<3	<6	<2	<1	N/D	N/D
Acenaphthalene	8.94	19.92	5.67	5.24	N/D	N/D
Acenaphthene	<3	<6	<2	<1	N/D	N/D
2,3,5-Trimethylnaphthalene	<3	<6	<2	<1	N/D	N/D
Fluorene	<3	<6	<2	1.05	N/D	N/D
Phenanthrene	19.82	52.47	14.15	10.68	N/D	N/D
Anthracene	18.33	50.72	13.66	2.36	N/D	N/D
1-Methylphenanthrene	<3	<6	<2	<1	N/D	N/D
Fluoranthene	13.13	34.58	12.72	11.18	N/D	N/D
Pyrene	12.32	33.63	12.81	10.54	N/D	N/D
Benz(a)anthracene	<3	<6	<2	1.18	N/D	N/D
Chrysene	<3	<6	2.03	<1	N/D	N/D
Benzo(b)fluoranthene	<3	11.16	5.45	5.48	N/D	N/D
Benzo(k)fluoranthene	<3	6.80	3.32	3.34	N/D	N/D
Benzo(e)pyrene	<3	<6	<2	1.67	N/D	N/D
Benzo(a)pyrene	<3	<6	2.26	2.16	N/D	N/D
Perylene	<3	<6	<2	<1	N/D	N/D
Indeno(1,2,3-c,d)Pyrene	<3	<6	<2	<1	N/D	N/D
Dibenz(a,h)anthracene	<3	<6	<2	<1	N/D	N/D
Benzo(g,h,i)Perylene	<3	<6	<2	4.23	N/D	N/D
<b>Total:</b>	<b>85.12</b>	<b>220.72</b>	<b>80.88</b>	<b>65.70</b>	<b>N/D</b>	<b>N/D</b>
<b>Surrogates</b>						
d8-Naphthalene	64	30	56	49	25	39
d10-Acenaphthene	62	62	75	79	44	52
d10-Phenanthrene	64	77	76	88	61	67
d12-Chrysene	83	79	78	90	78	69
d12-Perylene	49	77	74	85	54	45
d14-Terphenyl(I.S. area *1000)	Not added	Not added	218	212	208	197

150

"< " symbol indicates below method detection limit.

"N/D" indicates not detectable.

## Table 4

### Helicopter Summa CO2/VOC results, NOBE Burn.

Sample #	Cannister #	Event	Site	Time	Description	ppm CO2	VOC, ug/m3
Hel-1	13871	Burn 1	207		Team 1, flight 1, background before discharge, 6 min.	396	325
Hel-2	13875	Burn 1	207		Team 1, flight 2, evaporation, 5 min.	368	254
Hel-3	13876	Burn 1	207		Team 1, flight 3, in frt of plume, 6 min.	310	283
Hel-4	13377	Burn 1	207		Team 1, flight 4, under smoke, 6 min.	347	2083
Hel-5	13872	Burn 1	209		Team 2, flight 1, background before discharge, 4 min	346	271
Hel-6	13877	Burn 1	209		Team 2, flight 2, under plume @20m high, 6.5 min	380	405
Hel-7	13870	Burn 1	209		Team 2, flight 3, under plume @40m high, 6 min	308	264
Hel-8	13869	Burn 2	207		Team 1, flight 1, in frt of plume, 6 min.	373	43
Hel-9	13868	Burn 2	207		Team 1, flight 2, under plume, 6 min.	na	109
Hel-10	13376	Burn 2	209		Team 2, flight 1, under plume @18m high, 6 min.	359	1005
Hel-11	13874	Burn 2	209		Team 2, flight 2, under plume @20m high, 8 min.	na	96
Hel-blk0	13873	Background			Team 1, taken on Aug 7, background sample, crashed helicopter	276	271
Hel-blk1	KC-09	Burn 2	207		Team 1, after burn, using 2-l summa, 6 min.	na	78
Hel-blk2	KC-14	Burn 2	207		Team 1, static blank after burn, using 2-l summa	na	80

note: 'na' denotes sample not analysed

TABLE 5

Helicopter Summa data, NOBE Burn, ug/m3														
	HE-1	HE-2	HE-3	HE-4	HE-5	HE-6	HE-7	HE-8	HE-9	HE-10	HE-11	HE-BLK0	HE-BLK1	HE-BLK2
Compounds	MS65F.D	MS48G.D	MS83F.D	MS41G.D	MSDUP.D	MS53G.D	MS56G.D	MS49G.D	MS42G.D	MS51G.D	MS54G.D	MS50G.D	MS36F.D	MS28F.D
Propene	125.49	16.57		0.87	22.79	38.57	19.76	20.39	34.77	54.01	10.21	26.02	1.03	1.14
Propene	2.56	2.44	0.00	60.85	3.75	8.89	0.59	0.31	2.58	0.09	0.69	1.95	0.28	0.77
Freon22 (Chlorodifluoromethane)	0.74	0.56	0.00	0.26	0.33	0.49	0.61	0.26	6.00	0.48	1.08	0.59	0.73	1.36
Freon12 (Dichlorodifluoromethane)														
Propyne	4.73	0.22	0.00	0.00	0.18	0.35	0.00	0.00	0.00	0.00	0.00	0.62	0.00	0.00
Chloromethane	0.79	1.35	1.73	0.73	0.77	0.79	0.83	0.57	0.23	0.65	0.24	2.69	0.43	0.73
Isobutane (2-Methylpropane)	3.87	7.62	4.00	83.63	1.79	8.45	1.07	0.49	2.17	0.65	0.31	2.94	0.56	0.38
Freon114 (1,2-Dichlorotetrafluoroethane)	1.03	0.53	0.48	0.37	0.39	0.48	0.46	0.30	0.45	0.37	0.40	0.44	0.34	0.23
Vinylchloride (Chloroethene)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Butene/2-Methylpropene	10.28	8.34	10.63	3.45	5.85	3.34	3.14	1.10	3.12	3.21	3.37	6.61	2.05	4.61
1,3-Butadiene	8.87	1.29	1.09	1.48	0.63	0.30	0.22	0.20	0.00	0.10	0.10	0.20	0.00	0.00
Butane	6.90	15.33	9.67	251.59	4.26	26.17	3.23	1.21	2.23	1.11	0.48	2.36	0.89	0.70
1,3-Butene	1.19	0.00	1.85	0.23	0.47	0.26	0.21	0.00	0.17	0.15	0.17	0.49	0.13	0.14
2,2-Dimethylpropane	0.00	0.00	0.00	1.02	0.00	0.12	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bromomethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.47	0.00	0.00
1-Butyne	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
c-2-Butene	1.31	1.96	2.79	0.29	0.72	0.38	0.36	0.15	0.19	0.31	0.29	1.33	0.11	0.13
Chloroethane	0.00	0.83	0.00	0.00	0.56	0.70	0.60	0.15	0.54	0.77	0.40	0.65	0.36	0.48
2-Methylbutane	16.63	27.62	9.31	254.17	8.91	26.51	3.46	1.42	1.97	1.74	0.36	3.89	1.49	1.13
Freon11 (Trichlorofluoromethane)	1.11	1.44	1.13	3.75	1.01	0.95	0.85	1.06	0.53	6.28	1.55	8.16	0.91	0.13
1-Pentene	1.47	1.03	0.51	0.68	0.67	0.46	0.37	0.11	0.49	0.44	0.82	0.57	0.17	0.36
2-Methyl-1-Butene														
Pentane	8.56	15.91	11.77	260.28	6.11	27.36	3.81	1.02	1.93	1.22	0.48	2.85	0.85	1.03
Isoprene (2-Methyl-1,3-Butadiene)	0.76	0.76	0.40	0.46	0.35	0.17	0.19	0.00	0.00	0.19	0.18	0.24	0.00	0.38
Ethylbromide	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2-Pentene	0.83	1.44	0.17	0.16	0.47	0.47	0.11	0.07	0.08	0.23	0.05	0.32	0.09	0.13
1,1-Dichloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
c-2-Pentene	1.29	1.27	0.00	0.21	0.42	0.31	0.09	0.07	0.00	0.16	0.06	0.24	0.08	0.00
Dichloromethane	0.67	0.52	1.79	0.93	1.12	2.30	6.65	0.29	7.83	124.07	7.54	2.96	8.31	1.87
2-Methyl-2-Butene														
Freon113 (1,1,2-Trichloro-1,2,2,2-tetrafluoroethane)	6.61	2.74	3.41	2.74	3.34	3.38	3.89	2.08	2.88	2.75	3.52	2.70	5.38	7.45
2,2-Dimethylbutane	1.59	2.41	0.24	5.14	0.60	1.25	0.14	0.10	0.00	0.16	0.00	0.40	0.14	0.10
Cyclopentene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,1,2-Dichloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
4-Methyl-1-Pentene														
3-Methyl-1-Pentene														
1,1-Dichloroethane	0.00	0.00	0.00	0.24	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cyclopentane	1.20	1.75	1.13	27.80	0.91	2.72	0.40	0.11	0.24	0.19	0.00	0.44	0.11	0.10
2,3-Dimethylbutane	2.00	3.13	0.57	18.18	1.08	2.30	0.32	0.12	0.21	0.29	0.00	0.57	0.16	0.13
1,4-Methyl-2-Pentene	0.00	0.16	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2-Methylpentane	8.64	16.54	7.80	125.93	5.16	17.54	2.42	0.53	1.40	2.62	4.97	2.87	0.72	0.52
c-4-Methyl-2-Pentene	0.37	0.43	0.00	0.00	0.15	0.11	0.00	0.00	0.00	0.00	0.00	0.13	0.00	0.00

3-Methylpentane	5.71	9.35	5.03	81.48	3.93	9.03	4.60	0.10	1.10	39.38	1.42	2.60	0.72	0.43
4-Hexadecyl-2-Methyl-1-Pent	3.53	1.30	0.00	0.99	1.06	0.55	0.55	0.19	0.87	0.59	0.83	0.65	0.20	0.37
2-1,2-Dichloropentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Heptane	6.05	11.88	91.80	182.19	11.89	22.81	90.62	2.83	13.43	892.03	28.51	22.45	3.79	2.18
Chloroform	0.00	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00	0.12	0.59	0.00	0.00
1,3-Hexane	0.39	0.99	0.12	0.00	0.26	0.27	0.08	0.00	0.00	0.17	0.00	0.23	0.05	0.08
2-Ethyl-1-Butene														
1,3-Methyl-2-Pentene	0.50	0.65	0.36	0.00	0.26	0.22	0.08	0.00	0.00	0.13	0.00	0.18	0.00	0.00
2-2-Hexane	0.32	0.52	0.00	0.00	0.22	0.16	0.06	0.00	0.00	0.12	0.00	0.20	0.00	0.00
6-3-Methyl-2-Pentene	0.66	0.80	0.43	0.00	0.32	0.28	0.11	0.04	0.00	0.13	0.05	0.21	0.05	0.07
2,2-Dimethylpentane	0.26	0.45	0.00	3.90	0.19	0.41	0.07	0.00	0.00	0.00	0.00	0.11	0.00	0.00
1,2-Dichloroethane	0.00	0.00	0.00	0.64	0.00	0.00	0.09	0.00	0.00	0.61	0.00	0.00	0.00	0.00
Methylcyclopentane	3.81	8.69	11.21	109.29	4.74	10.32	10.80	0.59	1.93	97.97	4.20	5.35	0.57	0.44
2,4-Dimethylpentane	0.86	1.83	0.33	8.67	0.56	1.07	0.19	0.06	0.17	0.16	0.00	0.38	0.09	0.07
1,1,1-Trichloroethane	0.49	0.84	1.74	0.98	0.83	0.89	0.35	0.45	0.73	1.01	0.00	1.06	1.77	1.72
2,2,3-Trimethylbutane	0.18	0.43	0.26	0.65	0.43	0.40	0.42	0.06	0.34	0.00	0.00	0.22	0.08	0.14
1-Methylcyclopentane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Benzene	9.25	2.17	1.03	6.32	3.33	2.72	0.97	0.34	0.38	1.62	0.16	3.97	30.88	23.43
Carbon tetrachloride	0.44	0.54	0.22	0.36	0.36	0.27	0.24	0.40	0.04	0.17	0.00	0.19	0.03	0.19
Cyclohexane	1.59	3.14	2.39	76.15	2.48	8.60	2.62	0.17	0.35	0.81	0.07	0.99	0.17	0.17
2-Methylhexane	1.94	2.47	0.88	0.00	1.47	2.18	0.49	0.00	0.21	0.41	0.00	0.00	0.13	0.11
2,3-Dimethylpentane	1.43	2.48	0.49	14.24	1.08	1.82	0.37	0.11	0.27	0.38	0.00	0.78	0.00	0.10
Cyclohexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Methylhexane	3.47	5.95	1.86	44.61	3.15	5.00	1.26	0.19	0.85	0.88	0.00	2.22	0.36	0.53
Dichloromethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,2-Dichloropropane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bromodichloromethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Trichloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Heptene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.33
2,2,4-Trimethylpentane	1.13	1.73	0.34	2.27	0.71	0.84	0.30	0.08	0.48	0.00	0.00	0.53	0.19	0.20
1,3-Heptene	0.05	0.08	0.09	0.07	0.13	0.13	0.04	0.00	0.06	0.06	0.07	0.00	0.00	0.03
6-3-Heptene														
Heptane	2.77	6.39	5.04	97.06	4.97	8.63	2.26	0.27	0.64	1.23	0.39	2.81	0.29	0.37
1,2-Heptene	0.21	0.32	0.26	0.18	0.29	0.33	0.17	0.07	0.18	0.28	0.17	0.32	0.00	0.11
2-3-Heptene	0.00	0.00	0.00	0.00	0.45	0.00	0.00	0.00	0.00	0.00	0.38	0.29	0.00	0.00
1,3-Dichloropropane	0.14	0.23	0.00	3.42	0.00	0.28	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,2-Dimethylhexane	1.57	5.11	3.67	19.36	4.94	10.16	2.21	0.25	0.86	0.90	0.00	1.14	0.15	0.17
Methylcyclohexane	0.46	0.72	0.15	3.98	0.38	0.51	0.14	0.00	0.00	0.14	0.00	0.31	0.00	0.00
2,5-Dimethylhexane	0.61	1.08	0.00	5.19	0.58	0.78	0.22	0.00	0.00	0.20	0.00	0.48	0.00	0.00
2,4-Dimethylhexane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,1,3-Dichloropropane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.21	0.00	0.00	0.00	0.00	0.00	0.00
1,1,2-Trichloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Bromodichloromethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
2,3,4-Trimethylpentane	0.49	0.78	0.00	0.85	0.28	0.47	0.11	0.00	0.00	0.18	0.00	0.28	0.11	0.04
Octane	11.55	7.57	10.85	121.2	25.61	58.45	35.35	0.60	3.47	18.26	0.54	30.63	4.04	3.28
2-Methylheptane	1.20	2.15	0.97	21.98	1.91	2.23	0.73	0.07	0.18	0.62	0.47	1.32	0.12	0.11

4-Methylpentane	0.00	1.09	0.00	0.00	0.73	0.92	0.32	0.00	0.00	0.28	0.00	0.73	0.00	0.00
1-Methylcyclohexane	0.00	0.00	0.00	0.00	15.08	0.00	10.76	0.00	0.00	0.00	0.00	0.00	18.65	0.00
Dibromochloromethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
3-Methylpentane	1.63	3.02	0.65	2.28	2.68	0.82	0.12	0.15	0.78	0.05	0.00	0.13	0.13	0.11
e-1,3-Dimethylcyclohexane	0.24	0.90	0.69	20.26	1.00	1.74	0.40	0.96	0.00	0.16	0.00	0.39	0.36	0.00
e-1,3-Dimethylcyclohexane	0.00	0.40	0.27	11.52	0.45	0.71	0.20	0.00	0.00	0.00	0.00	0.12	0.00	0.00
EDB (1,2-Dibromoethane)	0.00	0.00	0.00	0.00	0.24	0.15	0.28	0.07	0.00	0.00	0.00	0.00	0.00	0.00
2,2,5-Trimethylhexane	0.19	0.22	0.00	0.00	0.00	0.00	0.00	0.00	0.07	0.32	0.00	0.11	0.20	0.00
1-Octane	1.29	0.84	0.00	0.00	1.00	0.19	0.63	0.00	1.28	0.32	1.56	0.34	0.00	0.24
Octane	0.96	2.14	2.27	34.40	3.14	3.66	1.20	0.10	0.39	0.73	0.10	1.92	0.18	0.28
1,1,2-Dimethylcyclohexane														
1,2-Octane														
Tetrachloroethane	0.00	0.00	0.00	0.00	0.11	0.14	0.10	0.12	0.00	0.13	0.00	0.18	0.00	0.00
e-1,4e-1,3-Dimethylcyclohexane	0.21	0.47	0.17	4.68	0.36	0.58	0.18	0.00	0.00	0.11	0.00	0.22	0.00	0.00
e-2-Octane	0.00	0.39	0.00	0.00	0.00	0.32	0.00	0.00	0.00	0.00	0.00	0.40	0.00	0.00
e-1,2-Dimethylcyclohexane														
Chlorobenzene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.05	0.00	1.68	2.08
Ethylbenzene	2.86	2.07	2.53	2.59	5.41	4.71	2.65	0.21	0.42	2.70	0.11	8.54	1.92	0.24
m,p-Xylene	9.55	6.36	9.59	8.67	17.60	14.92	8.67	0.71	1.42	8.65	0.36	27.31	1.31	0.78
Bromodrom	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1,4-Dichlorobutane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Styrene	0.48	0.25	1.53	0.62	0.55	0.29	0.30	0.00	0.00	0.35	0.10	0.85	0.17	0.00
1,1,2,2-Tetrachloroethane	0.00	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00	0.00	0.03	0.00	0.00	0.00
e-Xylene	1.1,2,2-Tetrachloroethane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
1-Norane	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Norane	0.55	1.17	2.82	14.37	2.69	3.34	1.21	0.07	0.76	0.86	0.24	1.44	0.26	0.48
iso-Propylbenzene	0.19	0.18	0.46	0.51	14.47	0.42	0.31	0.00	0.00	0.23	0.06	0.57	0.04	0.04
3,6-Dimethylcyclohexane	0.00	0.00	0.00	0.62	1.39	0.19	0.47	0.10	0.00	0.14	0.19	0.03	0.21	0.09
iso-Propylbenzene	0.66	0.72	1.16	0.87	2.07	1.51	1.05	0.06	0.25	0.78	0.18	2.31	0.10	0.22
3-Ethylbenzene	2.08	1.95	3.43	2.20	6.56	4.28	2.83	0.13	0.41	1.85	0.15	7.62	0.18	0.32
4-Ethylbenzene	0.95	0.98	1.74	0.99	3.16	2.02	1.34	0.07	0.22	0.93	0.12	3.81	0.10	0.19
1,3,5-Trimethylbenzene	1.04	1.08	2.18	1.51	3.43	2.44	1.59	0.10	0.37	1.18	0.13	3.91	0.14	0.02
2-Ethyltoluene	0.68	0.70	1.49	0.90	2.18	1.57	1.01	0.06	0.21	0.73	0.08	2.39	0.10	0.18
1-Decene	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
tert-Butylbenzene														
1,2,4-Trimethylbenzene	3.23	3.42	8.87	4.36	11.63	7.68	5.14	0.31	1.16	3.64	0.90	12.08	0.42	1.04
Decane	0.68	0.78	8.34	8.33	3.73	4.30	2.46	0.14	1.53	1.67	0.29	1.24	0.48	1.62
1,3-Dichlorobenzene	0.00	0.16	0.00	0.00	0.15	0.07	0.06	0.00	0.00	0.00	0.13	0.00	0.00	0.00
1,4-Dichlorobenzene	0.00	0.13	1.40	0.21	0.81	0.82	0.78	0.00	0.70	0.65	0.24	0.32	0.11	0.11
iso-Butylbenzene	0.08	0.09	0.19	0.13	0.19	0.13	0.10	0.00	0.00	0.06	0.04	0.15	0.00	0.00
iso-Butylbenzene	0.09	0.09	0.39	0.25	0.23	0.22	0.13	0.00	0.00	0.11	0.04	0.17	0.00	0.05
1,2,3-Trimethylbenzene	0.68	0.78	2.60	1.45	2.84	1.93	1.30	0.11	0.42	0.99	0.15	2.32	0.16	0.48
p-Cymene	0.00	0.77	2.60	0.00	0.42	0.77	0.44	0.32	0.00	0.71	0.00	1.17	0.00	0.00
1,2-Dichlorobenzene	0.00	0.19	0.00	0.00	0.07	0.07	0.06	0.00	0.00	0.00	0.14	0.00	0.00	0.00
Indane	0.30	0.37	0.71	0.30	1.20	0.69	0.47	0.04	0.00	0.33	0.07	1.19	0.00	0.09
1,3-Diethylbenzene	0.23	0.27	0.60	0.26	0.70	0.39	0.25	0.00	0.00	0.16	0.10	0.49	0.00	0.11



1,4-Diethylbenzene	1.00	0.71	0.00	1.62	2.45	1.07	0.89	0.00	0.00	0.47	0.28	1.36	0.00	0.60
n-Butylbenzene	0.24	0.26	0.71	0.40	0.70	0.36	0.30	0.00	0.00	0.18	0.14	0.37	0.00	0.12
1,2-Diethylbenzene	0.00	0.13	0.25	0.00	0.18	0.14	0.08	0.00	0.00	0.09	0.11	0.00	0.00	0.07
Undecane	0.55	0.96	7.95	7.20	4.05	3.29	2.15	0.18	1.67	1.33	0.52	1.38	0.54	5.11
1,2,4-Trichlorobenzene														
Naphthalene	2.03	1.49	1.24	1.42	1.84	0.00	0.69	0.00	0.00	0.00	1.92	0.00	0.38	0.97
Dodecane	1.55	1.97	1.70	5.57	1.62	2.84	0.87	0.40	1.32	0.45	1.32	0.54	0.37	3.76
Hexachlorobutadiene														
Hexylbenzene	6.31	2.47	0.00	3.90	0.00	0.00	0.00	0.00	0.00	0.00	4.06	0.00	0.00	2.40
<b>TOTAL VOC</b>	<b>325</b>	<b>254</b>	<b>283</b>	<b>2083</b>	<b>271</b>	<b>405</b>	<b>264</b>	<b>43</b>	<b>109</b>	<b>1005</b>	<b>96</b>	<b>271</b>	<b>78</b>	<b>80</b>
Sample ID:	MS85F.D	MS48G.D	MS83F.D	MS41G.D	MSDUP.D	MS53G.D	MS56G.D	MS49G.D	MS42G.D	MS51G.D	MS54G.D	MS50G.D	MS36F.D	MS25F.D
Canister ID:	T1,BLK	T1BKPRE	T1B1R1F3	F4T1B1R2	13872.00	T2B1R2	T2B1R3	T1B2R1	T1B2R2	T1B1R1	13868.00	BKHELIC	KC-09	KC-14
Dilution Factor:	1.00	1.53	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Sample Date:														
Sample Volume (mL):	249.00	246.00	256.00	248.00	270.00	246.00	270.00	246.00	248.00	246.00	270.00	246.00	489.00	489.00

## HELI-SUMMA CANISTERS

Figure 1

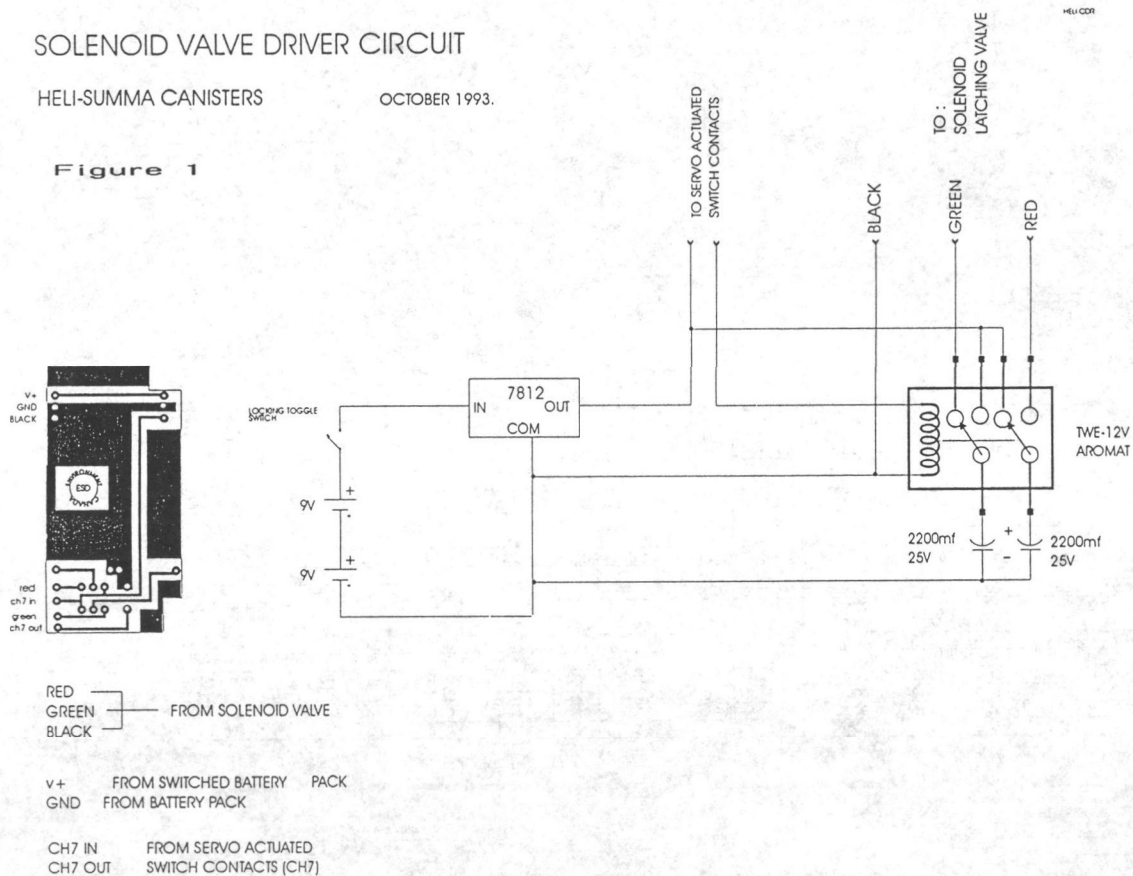
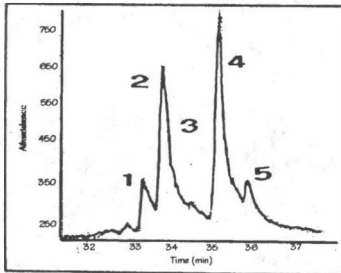


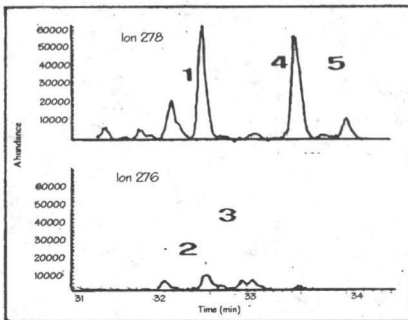
Figure 2  
Extracted Ion Chromatogram of PAH

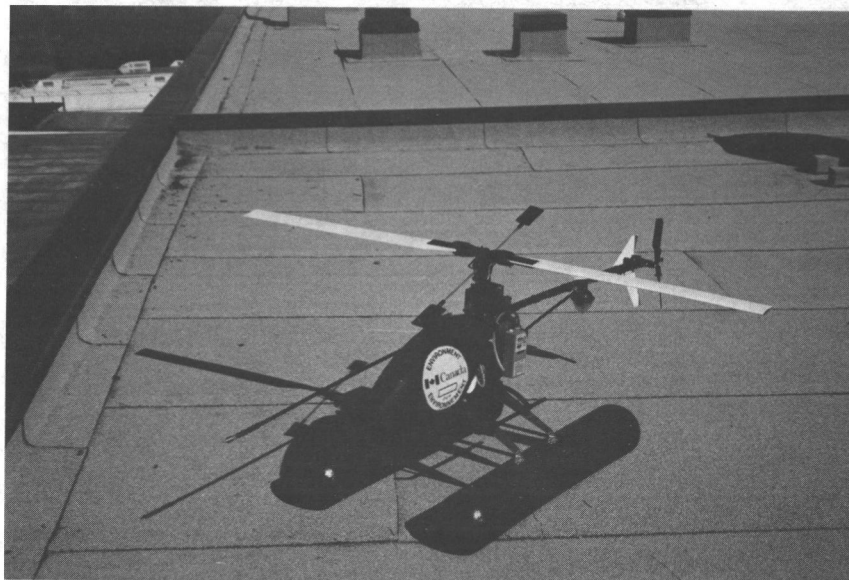
Blade wipe sample



1. Indenopyrene
2. Dibenzo (a,h)anthracene
3. Pentaphene
4. Benzo(ghi)perylene
5. Anthanthrene

Ground Filter/PUF sample





### X-CELL

Emergencies Science Division  
Remote Control Helicopter  
for air sampling

**AIR MONITORING AND SAMPLING TECHNIQUES USED IN SUPPORT OF A CLEANUP ACTION AT AN INACTIVE DRUM RECYCLING FACILITY**

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*took place in  
 1992*

**INTRODUCTION**

Based on the threat posed by unsecured hazardous substances at a former drum recycling operation, the U.S. Environmental Protection Agency (USEPA) Denver office conducted a Federal cleanup action under authority of the Comprehensive Environmental Resource Compensation and Liability Act (CERCLA). During removal activities the EPA's Environmental Response Team (ERT) and their support contractor, Roy F. Weston/REAC, provided a variety of air monitoring, sampling and on-site analytical capabilities during three different phases of the work.

Drum recycling occurred at the eight acre site for more than twenty years. The drums contained a wide variety of hazardous wastes, including oils, acids, solvents, paint wastes, polychlorinated biphenyls (PCBs), pesticides, and radioactive materials. Residual drum contents were dumped into a floor drain leading to a buried discharge line or onto the ground. The drums were then passed through an incinerator to remove any further residue and refurbished. A bead blaster utilizing lead pellets to remove drum paint was also used. Numerous drum piles, crushed automobiles, and scrap metal were scattered throughout the site. The site is situated in a mixed residential and industrial area, with private homes located adjacent and across the street.

The main objective of the air monitoring and sampling during three phases of work was to provide quality data immediately or within hours to effectively direct cleanup activities and ensure the safety of the nearby workers and citizens. As work proceeded, problem compounds with low odor thresholds were discovered, slowing the cleanup and creating more demand for field analytical techniques with sensitivity and selectivity for the target compounds of concern. An overview of each phase of site cleanup and associated air monitoring/sampling is presented. Selected equipment and techniques which provided rapid data on-site will be highlighted and the results briefly discussed.

## AIR MONITORING AND SAMPLING OVERVIEW

### Phase I-Drum Removal

During the Phase I initial removal of drums and scrap material strong rotten cabbage type odors were encountered. This led to a partial evacuation of the nearby neighborhood. Workers were unable to pinpoint the exact source among hundreds of drums. The U.S. EPA/ERT and Roy F. Weston/REAC conducted emergency air sampling for volatile organics (VOA), pesticides, and inorganic acids.

Air sampling stations were established along the perimeter of the site and in the exclusion zone adjacent to areas of activity. Ambient air sampling results showed low parts per billion by volume (ppbv) concentrations of benzene, toluene, ethyl benzene, xylenes (BTEXs) and chlorinated organics. All pesticides and inorganic acids analysis did not reveal contaminants above their respective method detection limits (MDL).

Exploratory trenching operations were performed adjacent to the drum processing area to a depth of approximately 2 feet. Grab six-liter evacuated stainless steel Summa canister samples were taken during the trenching operation. Samples were sent to an off-site analytical laboratory for VOA analysis by gas chromatography/mass spectrometry (GC/MS).

A limited soil gas survey was conducted at eight locations near the drum handling area. Each location (at a depth of three feet) was screened with a flame and photoionization detector. Based upon the highest screening results, a grab soil gas sample (six-liter Summa) was collected and shipped to an off-site laboratory for VOA analysis by GC/MS.

The trenching and soil gas Summa canister samples contained part per million by volume (ppmv) levels of BTEXs and styrene. The soil gas Summa canister also contained numerous sulfur compounds and chlorinated organics, including 38 ppmv diethyl disulfide, 4 ppmv diethyl sulfide, and 21 ppmv trichloroethylene. The results of the trenching and soil gas samples (Table 1) were used to generate a target compound list for Phase II.

### Phase II- Soil Excavation

Further site characterization activities were conducted by Ecology and Environment personnel. A geophysical survey throughout the site found no evidence of buried drums. Portable X-Ray Fluorescence (for metals) was used to identify lead as the most widespread soil contaminant. The greatest concern, however, were soils in the drum handling area, containing volatile organics and sulfur containing compounds. During removal of these soils there was the potential for emissions of extremely pungent odors and possibly hazardous levels of organic vapors.

U.S. EPA/ERT-REAC chose an array of air monitoring/sampling techniques for use during this phase of the work. Air monitoring/sampling locations were based specifically upon daily activities and meteorological conditions. Stationary/integrated sampling was conducted at a minimum of 4 feet off the ground around the perimeter of the site and in the areas of activity.

Stationary/integrated samples for VOCs were collected on charcoal tubes in duplicate. One set was analyzed on-site within hours with a transportable Viking GC/MS unit (see equipment). The other was sent to an off-site GC/MS analytical laboratory (REAC); these results were received within twenty-four hours. Table 2 compares the results from the off-site laboratory (REAC) with results from the on-site Viking GC/MS at two locations adjacent to the soil excavation zone on three consecutive days.

Results of air monitoring/sampling for VOCs identified the highest ambient organic concentrations emanating from soils adjacent to and under the drum handling/incinerator pad, where soil excavation proceeded to a depth of approximately six feet.

During one day of excavation Time Weighted Average (TWA) concentrations of VOCs were above background at all fixed sampling locations. Compounds were detected at low parts per billion levels at the site perimeter, with the highest of 71 ppbv 1,1,1-trichloroethane recorded adjacent to the pit.

Air sampling was conducted for methyl mercaptan at the same locations used for VOCs. A thirty-seven-millimeter glass fiber filter cassette impregnated with 5 percent (w/v) mercuric acetate solution was utilized for the sampling and sent off-site for analysis utilizing a GC with a flame photometric detector (FPD). Methyl mercaptan was not detected in the time-weighted sampling results above a detection limit of 0.009 ppmv.

Grab air samples were collected in 10-Liter Tedlar bags utilizing a vacuum box. Samples were taken adjacent to areas of excavation or in areas of concern and analyzed on-site by the Viking GC/MS. Table 3 highlights the grab samples that contained significant levels of contaminants.

A Trace Atmospheric Gas Analyzer (TAGA, see equipment) mobile unit was used to meet the needs for mobile real-time air monitoring on and off the site. The TAGA mainly patrolled the western site perimeter adjacent to the residences to identify fugitive emissions emanating from on-site areas of excavation and to act as an early warning system.

Mobile monitoring with the TAGA adjacent to the site revealed trace levels of VOCs, except for several temporary elevated excursions. The most pronounced compounds detected were styrene, trichloroethylene (TCE), and tetrachloroethylene (PCE). The highest concentrations of these compounds were obtained from sampling directly in the pit, including levels of TCE and PCE at 3000 and 2500 ppbv, respectively. The TAGA also tentatively identified butyl and ethyl mercaptan at low ppbv levels.

The results from Phase II facilitated the decision to use only on-site analysis along with emerging handheld portable instrumentation for Phase III.

### **Phase III- Solidification Activities**

Approximately 8000 cubic yards of contaminated soil was removed and stockpiled according to three different waste types; organics, lead, and radioactive. Since the bulk of the soil was lead contaminated, on-site solidification/stabilization was the selected remedy. Prior to treatment all contaminated soil was passed through a power screen to reduce particle size to less than two inches. The screened soil was then mixed with fly ash, water, and cement under controlled conditions and staged on-site prior to final off-site disposal.

Due to the potential for air releases during screening and solidification of the soil organics pile, further air monitoring/sampling was performed. Sampling for VOCs at stationary air sampling locations was again conducted around the perimeter of the site and in the exclusion zone adjacent to the power screen/processing area. All samples were analyzed on-site by the Viking GC/MS. Results for these air samples were similar to the results from Phase II. Table 4 depicts the highest time-weighted sample from Phase II (excavation) compared to the highest time-weighted sample from Phase III (screening).

Additionally, grab air samples in Tedlar bags were collected adjacent to the soil screening and analyzed by the Viking GC/MS, the Scintrex OVD 229 and the Photovac SnapShot GC.

Due to the offensive nature and persistence of mercaptan and sulfur odors on-site a Scintrex OVD 229 Odorant Vapor Detector (see equipment), a specialized gas chromatograph which responds only to sulfur containing compounds, was utilized for air monitoring on-site.

Mercaptan and sulfur odors were apparent during site activities (excavation and soil screening). The OVD 229 Odorant Vapor Detector did identify sulfur containing compounds including mercaptans. The results generated by the OVD 229 were used with caution because there were no analytical laboratory means of confirming the information. Furthermore the sulfur/mercaptan standards made on-site were unstable and reacted quickly in the presence of air and light and therefore did not store well in Tedlar gas sampling bags. The OVD 229 did not detect mercaptans at levels greater than the lowest Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs) of 0.5 ppmv for these compounds. The odor threshold for n-butyl mercaptan ranges from 0.1 to 1.0 ppb. The readily noticeable level is about 0.1 to 1 ppm. The odor threshold for ethyl mercaptan is 30 parts per trillion (ppt) in air.

Another portable air monitoring instrument tested at this site was the handheld Photovac Snapshot GC (see equipment) for near real-time analysis of selected volatile organics. The Photovac SnapShot was on loan from the manufacturer for field testing purposes. One of the field limitations of the instrument is an operating temperature range of 50 to 105 °F. Ambient temperatures during the three days of sampling/monitoring in Phase III were all below 50 °F. The temperatures seem to have a greater effect on the BTC8 module than the PCE/TCE as evident in the "Ambient Drift" error messages received. Tedlar bag samples were collected and analyzed in the U.S. EPA Command Post to compensate for the problems with temperatures.

The two bag samples analyzed by the Viking GC/MS and screened by the SnapShot had similar results. The SnapShot results for most cases were slightly higher. The Viking GC/MS identified PCE at levels of 76.01 ppbv for the sample collected 2 feet east of the screened pile and 18.63 ppbv at the sample collected 2 feet west of the screened pile. SnapShot screening results were PCE at 112 ppb and TCE was not detectable, respectively. The Viking GC/MS identified TCE at levels of 124.73 ppbv at the sample collected 2 feet east of the screened pile and 27.65 ppbv at the sample collected 2 feet west of the screened pile. SnapShot results were 322 ppb and 278 ppb, respectively.

## EQUIPMENT

### Trace Atmospheric Gas Analyzer (TAGA) Monitoring

The TAGA 6000E MS/MS mobile unit was used exclusively in Phase II. The TAGA is a direct air sampling instrument capable of real-time detection of trace levels of many organic compounds in ambient air. The technique of MS/MS is used to differentiate and quantitate organic compounds.

The TAGA mobile unit performed stationary and mobile real-time air monitoring on and off site in an effort to identify fugitive emissions emanating from the areas of excavation on site. The TAGA was fitted with an Atmospheric Pressure Chemical Ionization (APCI) source which employs benzene as a chemical ionization reagent to investigate low molecular weight polyaromatic hydrocarbons (PAHs) (e.g., styrene). The TAGA unit was also fitted with a Low Pressure Chemical Ionization (LPCI) source to analyze for benzene, toluene, xylenes, chlorobenzenes, and trichloroethylene. Background subtracted parent or daughter ion spectra were collected in either the parent ion only mode or the parent/daughter ion mode, depending on the compound being studied. The mode of monitoring was chosen based on the compounds selectivity/sensitivity characteristics. The preliminary results of on site and perimeter monitoring were reported rapidly to provide the U.S. EPA Work Assignment Manager and the OSC with data for the protection of the nearby public health and welfare.



### Viking GC/MS

The Viking GC/MS is a transportable, multicomponent system consisting of a GC, MS, and data system. The Viking was used to analyze samples (tubes and Tedlar bags) in Phases II and III. The MS is based on the Hewlett-Packard model 5971A Mass Selective Detector. The HP 5971A uses a monolithic, fused silica mass filter with four electrically conductive hyperbolic surfaces. The analyzer can scan the mass range between 10 and 650 atomic mass units (amu) at eight selectable scanning speeds up to 2000 amu per second with 0.1 amu resolution. The GC is able to house a variety of capillary columns with internal diameters of 0.30 millimeters or smaller and up to 105 meters long. It has the capability of heating the oven at a single programmable ramping rate of up to 20° Celsius per minute. It may be operated in the split or splitless mode and has a cryofocusing mode that allows the trapping of light volatiles at the head of the column to improve chromatography.

At the beginning of each day, the GC/MS system was tuned to verify that acceptable performance criteria could be achieved.

Before any analysis, the GC/MS was calibrated using standards contained in pressurized cylinders at approximately 1 part per million by volume (ppmv) in nitrogen. A single-point calibration was created by injecting a 50-milliliter volume of the 1-ppmv gas standard onto the thermal desorber and analyzing it in the GC/MS. For each compound in the calibration, the retention times and relative abundances of selected ions are stored on the hard disk of the GC/MS computer to be used for compound identification.

### Scintrex OVD 229 Odorant Vapor Detector

The Scintrex OVD 229 Odorant Vapor Detector (OVD 229) (Scintrex, Ltd., Concord, Ontario, Canada) is a field portable GC coupled with an electro-chemical cell (ECC) detector. The OVD 229 was used exclusively in Phase III. The various compounds present in vapor phase samples are separated in the GC column so that each compound elutes the GC column at a unique retention time (RT). Once the compounds elute from the GC column they enter the ECC. The ECC is designed to respond only to sulfur containing compounds. At present, the OVD 229 is configured to identify and quantitate nine compounds that are typically used by the natural gas industry as odorants in pipelines. The OVD 229 reports the analytical results in a hard copy printout listing the compounds by number (1-9), with the compound abbreviations next to the number, and the results in two different concentration units. All nine compounds are reported at all times. The number of compounds and names can not be changed on the OVD 229 systems currently available.

These nine mercaptans and sulfur compounds that the OVD 229 is currently configured are below, listed by compound numbers, compound identities and their abbreviations used by the OVD 229:

Compound 1,	hydrogen sulfide	(H <sub>2</sub> S)
Compound 2,	methyl mercaptan	(MM)
Compound 3,	ethyl mercaptan	(EM)
Compound 4,	dimethyl sulfide	(DMS)
Compound 5,	isopropyl mercaptan	(IPM)
Compound 6,	tertiary butyl mercaptan	(TPM)
Compound 7,	methyl ethyl sulfide	(MES)
Compound 8,	normal propyl mercaptan	(NPM)
Compound 9,	tetrahydrothiophene	(THT)

The OVD 229 determines if there is a match between the RTs of the samples and the RTs of the calibrated compounds. When a match occurs, the peaks are identified. The ratio of the sample peak heights to those of the calibrated standards yields the concentrations of each peak. Compounds that elute from the column and are detected by the ECC, but do not match the calibration RTs are not reported. The analog output of the ECC response, called chromatograms, shows that these peaks are present, but there are no results associated with them. The OVD 229 can be configured to sample in the manual or automatic mode in a preset sequenced event.

The OVD 229 was calibrated, in the field, for compounds 3 through 8 by using a single standard of each at approximately 200 ppbv. These were prepared daily in Tedlar bags. Results for compounds 1 and 9 were not reported. Screening for compound 2 was done but no field calibration was performed since a standard was not available. Default values for the response factor and RT were used to quantitate compound 2.

#### **Photovac SnapShot GC**

Air monitoring/sampling for benzene, toluene, total C8 aromatics, tetrachloroethylene, and trichloroethylene was also performed in Phase III using the Photovac handheld SnapShot GC. In the SnapShot, gas chromatography is used to detect and identify volatile compounds. The sample is moved from the point of injection through the column and then out through the detector. The sample is moved through the system by a continuous flow of carbon dioxide (CO<sub>2</sub>) carrier gas.

As the sample is carried through the column, sample components interact with the column packing or coating and are temporarily adsorbed and then subsequently desorbed. As each component enters the detector, a signal voltage is generated, processed and shown on the display.

The RT of each peak gives an indication of what the contaminant is, while the size (area or height) of the peak indicates how much is present. SnapShot does not display the actual peaks.

In each sample analysis, peak RTs are compared to retention times of compounds stored in the application module. If they match (within the peak recognition window of 5% stored in the application module), the peak is identified as the corresponding compound of interest.

The ratio of peak area to known compound concentration is the sensitivity (response to concentration ratio, measured in millivolts/ppm) for the compound. To calculate the peak's concentration, its integrated area is divided by the sensitivity stored in the application module. The application module calculates the sensitivity for each compound each time the instrument is calibrated.

The detector consists of a high frequency (HF) driver circuit and the electrodeless discharge lamp. The lamp generates photons which ionize specific molecules in the gas stream. Many of the chemicals considered pollutants, including most hydrocarbons, are ionized. The permanent gases (argon, carbon dioxide, nitrogen, oxygen, water vapor, etc.) require a relatively high energy for ionization, and are not ionized by the UV photons.

After the compounds have been ionized by the lamp, the ionized particles in the detector cell are subjected to a continuous electric field between electrodes. The ions move in the electric field, generating a current which is proportional to the concentration of the ionized molecules in the detector cell. An electrometer circuit converts the current to a voltage which is then fed to the microprocessor.

Two application modules benzene, toluene and total C8 aromatics (BTC8) and tetrachloroethylene and trichloroethylene (PCE/TCE) modules were used on site. The BTC8

module had detection limits of benzene at 0.1 ppm, toluene at 1.0 ppm, and total C8 aromatics at 1.0 ppm. The PCE/TCE module was reprogrammed at the manufacturer to give a lower detection limit of parts per billion (ppb) as opposed to the normal detection limits of PCE at 1.0 ppm and TCE at 5.0 ppm.

The SnapShot was calibrated in the field using standards at approximately 1.0 ppm of benzene, 20 ppm of toluene, 20 ppm of ethyl benzene, 20 ppm of m-xylene, 20 ppm of o-xylene in balance air for the BTC8 module and approximately 50 ppm of methylene chloride, 20 ppm of tetrachloroethylene, and 50 ppm of trichloroethylene in balance air for PCE/TCE module.

## SUMMARY

All Time Weighted Average (TWA) sampling results for all phases, whether along the perimeter of the site or in areas of activity, were below the Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).

The compounds most prevalent during all phases were 1,1-dichloroethane, 1,1,1-trichloroethane, trichloroethylene, tetrachloroethylene, BTEXs and styrene.

The highest concentrations of VOCs (time weighted) were identified adjacent to the activity areas (excavation Phase II and screening Phase III). Results for the perimeter locations were significantly lower.

In Phase II the on-site Viking GC/MS results were in good agreement with the off-site analytical laboratory GC/MS results as shown in Table 2. This agreement of data justified the sole use of the Viking GC/MS for the analysis of samples in Phase III of the investigation.

BTEXs were identified at concentrations levels of low ppbvs at stationary sampling stations throughout the site. Vehicular traffic (heavy equipment) or equipment with combustion engines often produce low ppbv levels of BTEXs as a by-product. Therefore, sampling locations adjacent to such equipment or activities that involve combustion engines may influence the results.

The use of on-site analytical equipment (TAGA, Viking GC/MS, OVD 229 and the SnapShot GC) for the determination of ambient contaminants allowed for the effective cleanup and assurance of public safety in a timely and cost effective manner.

Table 1  
 Summary of the Soil Gas and Trenching Summa Canister Results  
 Phase II  
 Concentrations in ppbv

Date Location Analysis	9/17/92 Soil Gas GC/MS	9/16/92 Trench GC/MS
Compound		
1,1-Dichloroethane	120	ND
1,1,1-Trichloroethane	43	167
Trichloroethylene	21307	176
Tetrachloroethylene	3477	1849
Benzene	180	199
Toluene	917	8233
Total Xylenes	1627	5146
Styrene	2340	12234

Table 2  
Phase II  
Off-site GC/MS Laboratory (REAC) versus On-site GC/MS (Viking)  
Concentrations in ppbv

Date Location Analysis	9/14/93 Location 8 REAC	9/14/93 Location 8 Viking	9/14/93 Location 9 REAC	9/14/93 Location 9 Viking
Compound				
1,1-Dichloroethane	ND	ND	ND	ND
1,1,1-Trichloroethane	1.6	0.21	1.9	1.9
Trichloroethylene	ND	ND	ND	1.1
Tetrachloroethylene	2.3	4.0	4.4	12.0
Benzene	ND	0.47	2.6	2.7
Toluene	1.6	2.3	2.6	5.0
Total Xylenes	0.63	1.49	0.61	2.0
Styrene	4.4	6.7	ND	1.0

Date Location Analysis	9/15/93 Location 8 REAC	9/15/93 Location 8 Viking	9/15/93 Location 9 REAC	9/15/93 Location 9 Viking
Compound				
1,1-Dichloroethane	ND	ND	ND	ND
1,1,1-Trichloroethane	ND	ND	ND	ND
Trichloroethylene	1.8	3.2	ND	1.4
Tetrachloroethylene	3.4	8.7	0.9	1.8
Benzene	ND	1.5	3.6	4.0
Toluene	2.5	4.3	6.2	6.2
Total Xylenes	1.7	5.0	1.3	2.8
Styrene	4.3	7.4	2.0	3.4

Table 2 (cont'd)  
Phase II  
Off-site GC/MS Laboratory (REAC) versus On-site GC/MS (Viking)  
Concentrations in ppbv

Date Location Analysis	9/16/93 Location 8 REAC	9/16/93 Location 8 Viking	9/16/93 Location 7 REAC	9/16/93 Location 7 Viking
Compound				
1,1-Dichloroethane	ND	ND	ND	ND
1,1,1-Trichloroethane	71	20	3.1	ND
Trichloroethylene	30	43	1.0	3.9
Tetrachloroethylene	9.0	19	ND	2.0
Benzene	2.5	2.8	ND	0.62
Toluene	5.2	9.7	ND	1.9
Total Xylenes	3.5	7.5	0.31	1.26
Styrene	ND	2.0	ND	0.26

Table 3  
Tedlar Bag Grab Air Samples During Excavation Activities  
Phase II  
Concentrations in ppbv

Date Location Analysis	9/10/93 Hole 1 Viking	9/15/93 South Pad Viking	9/16/93 Ambient Viking
Compound			
1,1-Dichloroethane	41	430	120
1,1,1-Trichloroethane	12	87	590
Trichloroethylene	94	ND	1200
Tetrachloroethylene	480	77	98
Benzene	6	5400	11
Toluene	250	110	ND
Total Xylenes	128	65	77
Styrene	260	510	10

Table 4  
Phase II (Soil Excavation) versus Phase III (Soil Screening)  
Exclusion Zone Highest Concentrations  
Concentrations in ppbv

Date Location Analysis	9/16/93 Location 8 REAC	2/21/94 Location 5 Viking
Compound		
1,1-Dichloroethane	ND	ND
1,1,1-Trichloroethane	71	63.51
Trichloroethylene	30	52.36
Tetrachloroethylene	9.0	34.40
Benzene	2.5	ND
Toluene	5.2	5.17
Total Xylenes	3.5	4.0
Styrene	ND	ND

# Generic Spill Modeling framework

## A System

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→ concentrated on modelling Framework

• modelers functions

Decision:

- which model
- How big a model
- what resolution

interpretation:

- How precise (Reliability)
- what is worst case
- how can we improve.

	A	w	G	Aw	Ag	wG
Gas	*A	w				
misc. Liq						
imm liq p>1						
imm liq p<1						
Solid p>1						
Solid p<1						

in total = 9 model necessary to model all situation

"Buoyancy"?



AIR SAMPLING AND MONITORING USING OPEN PATH FOURIER  
TRANSFORM INFRARED SPECTROPHOTOMETER (OP-FTIR) AND OP  
ULTRA VIOLET (OP-UV) TO DETERMINE SO<sub>2</sub> AND VOC RELEASE  
RATES AT A TEST EXCAVATION

by

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The U. S. Environmental Protection Agency's Environmental Response Team (ERT) was established in October 1978 to provide scientific support to Federal On-Scene Coordinators (OSC's), Remedial Project Managers (RPM's), Regional Response Teams (RRT's), Federal/State and Foreign governmental agencies in the area of hazardous waste sites, oil spills, and environmental emergencies.

The ERT assisted EPA Region IX in March of 1992 in determining the emission rate of sulfur dioxide (SO<sub>2</sub>) and volatile organics at a test excavation in Westminster, CA. This paper will describe the procedure and the results using OP-FTIR and OP-UV to determine the emission rates for these compounds.

#### INTRODUCTION

The site is located in the city of Westminster, Orange County, Ca. approximately 40 miles south of Los Angeles. The site is located in a residential neighborhood surrounded by light industrial/commercial areas. The waste is located in trenches along the backyards of the neighborhood and in a vacant lot.

From the 1930's through 1950's, tarry acid waste from unidentified petroleum refining or production processes were placed in unlined surface impoundments in the area. When the area was developed for housing in 1958-1961, the impoundments were excavated and redeposited in subsurface trenches along the backyard boundary lines of the houses in the neighborhood.

Usually, during hot summer temperatures, seeps of tarry material rise to the surface causing an increase in the potential for human exposure, both by direct contact

with highly corrosive material and via inhalation of various toxic substances, including aromatic hydrocarbons and sulfur dioxide. The fresh tar also emits a pungent odor commonly associated with various thiols and organic sulfide compounds.

U.S. EPA Region IX decided to perform a test excavation of the material that was in trenches in vacant lots in the area. The purpose of the test excavations were to determine what gases would be emitted during excavation of the material, if it was feasible to excavate the material, and to assess the effect the release would have on the nearby residents.

Remote Optical Sensing (ROS) with an Open-Path Fourier Transform Infrared (OP-FTIR) Spectrometer and an Open-Path Ultra-violet (OP-UV) Spectrometer was utilized, to determine the emission rate for  $\text{SO}_2$ , benzene, toluene, ethyl benzene, and xylene (BTEX) and tetrahydrothiophene (THT) during the test excavations.

#### THEORY

Remote optical sensing is generally set up to transmit a beam of radiation across a parcel of air to be measured. In a uni-static configuration, the transmitter and receiver are collocated and a retro-flector is used to reflect the transmitted radiation back to the receiver. The molecules in the beam's path absorb some of the radiation at certain wavelengths resulting in the reduction of the intensity of the beam at that wavelength. The ratio of the measured intensities,  $I/I_0$  ( $I_0$  is the intensity that would be measured in absence of molecular absorption), which is also defined as the transmittance,  $T$ , is related to the concentration,  $C$ , of the absorbing gas by the Beer-Lambert-Bouguer (BLB) law:

$$I(\nu)/I_0(\nu) = \exp(-A(\nu))$$

and  $A(\nu) = \alpha_m(\nu)CL$

where:

$A(\nu)$	=	is the absorbance,
$\alpha_m(\nu)$	=	is the instruments-independent molecular absorption coefficient associated with the collision-broadened absorption spectra of gases under standard atmospheric conditions,
$L$	=	is the path-length of the radiation through the gas

$I, I_0, A$ , and  $\alpha$  are functions of the radiation frequency,  $\nu$ , which is proportional to the reciprocal wavelength.

In the second equation, the absorbance,  $A(v)$  is proportional to the concentration-path product,  $CL$ . The proportionality constant is the molecular absorption coefficient,  $\alpha(v)$ , which is unique for each chemical and, thus is the source of the unique "fingerprint" of the absorption spectra of the different molecules. These absorption features also have temperature and pressure dependencies. The IR spectral region measured is between 3-13 microns and the UV spectral region is 0.24-0.68 microns.

Gaseous contaminant concentrations are generally reported in unit mass of contaminant per volume of gas, such as part million by volume (ppmv) or parts per billion by volume (ppbv). Path-integrated concentration, however, are typically reported in units of micrograms per square meter ( $\mu\text{g}/\text{m}^2$ ) or ppm-meters (ppm-m). With an open-path system, the total contaminant burden is measured within the cylinder defined by the finite cross-section of the light beam at each end and the length of the beam itself. The contaminant burden is then normalized to a path-length of one meter.

A ratio technique is used to estimate emission rates from either point sources or area sources. Use of ratio technique requires no assumptions about the nature of the plume dispersion. The ratio technique is conceptually very simple to implement. The approach is to release an appropriate tracer gas at a known concentration at a controlled flow rate from locations that adequately simulates the source geometry. Both sulfur hexafluoride ( $\text{SF}_6$ ) and carbon tetrafluoride ( $\text{CF}_4$ ) are good tracers. Assuming that the tracer and source plume are fully contained by the down wind beam, the following ratio applies:

$$C/Q = C_T/Q_T$$

where:

$C$	=	ground-level cross wind-integrated concentration of contaminate at distance $x$ , $\text{g}/\text{m}^2$ ,
$C_T$	=	ground-level cross wind-integrated concentration of tracer at distance $x$ , $\text{g}/\text{m}^2$ ,
$Q$	=	uniform emission rate of contaminant, $\text{g}/\text{s}$ ,
and		
$Q_T$	=	uniform emission rate of tracer, $\text{g}/\text{s}$ .

The equation simply states that the ratio of the path-integrated concentration of the contaminant to its emission rate is equal to the ratio of the path-

integrated concentration of the tracer to its emission rate. The equation is then solved for  $Q$ . Once  $Q$  is determined, air models can be used to estimate downwind concentrations and thus in effect of the excavation on the neighborhood.

## RESULTS

With the exception of  $SO_2$ , no concentration of target contaminants (BTEX) were observed above their respective quantitation limits (QLs) for the entire 10-day program. Table 1 presents the daily maximum concentration of  $SO_2$  attributable to the site, as generated by the open-path FTIR and UV spectrometers. All measurements are reported in ppm-m values. For OP-FTIR minimum detection levels (MDL's) are defined as twice the concentration residual from the least-square-fit matching subroutine and QL is defined as four times the concentration residual. The  $J$  value is defined as a concentration between the respective MDL and QL.

$SO_2$  concentrations were consistently observed only during soil-intrusive activities ( days 5,7,9, and 10) with the maximum values occurring on days 9 (OP-FTIR 24.4 ppm-m, OP-UV 35.7 ppm-m) and 10 (OP-FTIR 32.0 ppm-m, OP-UV 43.4 ppm-m).

Using the ratio technique the highest emission value for  $SO_2$  ( 1.67 grams per second) was obtained from the OP-UV results from day 10. This result was the input into version 2.1 of the Gaussian-Plume algorithms for Point, Area, and Line sources (PAL2). The information used to define the model run includes:

```
Source Type = Area
Emission Rate = 0.167 g/s-m2
Source Height = 2 meters
Source Size = 10 m2
Receptor Height = 1.5 m
```

The results of the PAL2 model using both worst case and typical meteorological parameters as inputs suggest that maximum  $SO_2$  exposures caused by excavation activities may exceed the Time Limited Value-Time Weighted Value (TLV-TWA 0.00524 g/m<sup>3</sup>), but will be below the Immediately Dangerous to Life and Health (IDLH 0.262 g/m<sup>3</sup>) at the receptor. The worst and typical daily conditions are 0.1188 g/m<sup>3</sup> and 0.02412 g/m<sup>3</sup>. A plot of center line concentration obtained from the worst conditions reveals that concentrations may exceed the TLV-TWA threshold as far as 400 meters downwind of the source. The center line plot using typical or variable meteorology conditions reveal that TLV-TWA levels will not be exceeded beyond 200 meters.

## CONCLUSION

The results from OP-FTIR/UV were helpful in determining release rates for SO<sub>2</sub> from the site during excavation. This information along with the air models will assist EPA and Public Health officials in assessing the possible impact areas and the effect on the community. Based on the results from the test excavations, it was determined that the material can be excavated safely.

These results indicate that either OP-FTIR or UV may be used during site work to assist personnel performing the cleanup in determining the impact the cleanup activities is having on the community on a real-time basis.

**TABLE 1**  
**Daily Maximum Concentration of**  
**SO<sub>2</sub> (ppm-m)**

DAY	OP-FTIR (ppm-m)	OP-UV (ppm-m)
2	ND (3.0) *	ND (2.0)
3	ND (3.0)	ND (2.0)
4	ND (3.0)	ND (2.0)
5	21.3	29.35
7	5.4	9.1
9	24.4	35.7
10	32.0	43.4

\* - MINIMUM DETECTION LIMIT (MDL)

Determination of Response Factors for The  
HN $\mu$  and MicroTip Photoionization Detectors

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The U. S. Environmental Protection Agency's (USEPA) Environmental Response Team (ERT) was established in October 1978 to provide scientific support to Federal On-Scene Coordinators (OSC's), Remedial Project Managers (RPM's), Regional Response Teams (RRT's), Federal/State and Foreign governmental agencies in the area of hazardous waste sites, oil spills, and environmental emergencies.

During many of these response activities, the ERT conducts air monitoring activities with various types of field instruments. To monitor for volatile organics, the ERT utilizes instruments which have a photoionization detector(PID). The ERT presently employs two types of PID's, the Photovac MicroTIP and the HN $\mu$  PID.

Since each of the instruments and the different models of these instruments may respond differently to various volatile organic compounds, a study was conducted by ERT's Response Engineering and Analytical Contractor to determine the response factors for each of the instruments and their different models.

#### OBJECTIVE

The objective of the study was to develop a response factor data base for the Photovac MicroTIP and the HN $\mu$  Systems Inc. PID's which are presently being used by the ERT. These response factors were also compared to those published by the manufacture for each of the instruments. The response factors were determined for 15 gases listed in Table 1.

#### METHODOLOGY

##### MicroTIP

The MicroTIP model HL-200 and model IS-3000, an intrinsically safe unit, PID's equipped 10.6 eV bulb were used for this study. The MicroTip PID sensor consists of a sealed ultra violet source that emits photons which are

capable of ionizing many trace species, particular organic compounds which have an ionization potential of 10.6 eV or less when using the 10.6 eV bulb. The MicroTip is a total reading instrument and it is not capable of distinguishing between individual pollutants. The reading displayed represents the total concentration of all photoionizable chemicals present in the sample.

The following procedure was used for cleaning, calibrating and zeroing the instrument for this study: Both instruments were disassembled, checked, and cleaned according to the manufacture's instructions prior to beginning the study. The 10.6 eV lamp was then cleaned and placed in to the MicroTip before measurements were conducted. The instrument was zeroed by filling a Tedlar® bag with ultra-zero air and calibrating the MicroTip's zero point to this sample. The MicroTip was calibrated by filling a second Tedlar® bag with a reference gas standard (97.4 ppm isobutylene). The MicroTip was then connected to the bag and a sample was drawn through the instrument. The MicroTip was then electronically calibrated to read the reference standard concentration. This calibration point was then verified by repeating this procedure twice more.

Once the instrument had been calibrated to the reference standard, the MicroTip was used to measure the other gas standards at various concentrations. This was performed using a Transducer Research Inc. model MP-1 Gas Calibrator, each gas standard was diluted with ultra-zero air to 12, 25, 50, 75, and 100 percent (%) of the original concentration (200 ppm). Each predetermined, diluted concentration was then read on the instrument and the results recorded. Each standard was measured for a total of three readings. The response factor for (relative to isobutylene) for each chemical was determined by comparing the MicroTip's readings, averaged over the three trial runs, to the actual standard concentration. The correlation, as a response factor (RF), was determined utilizing the following equation:

$$RF = \frac{\text{Concentration reading at the dilution \%}}{(\text{actual standard concentration})(\text{dilution \%})}$$

The response factor is a ratio of the observed concentration to the actual concentrations. The response factor determined during this study and those listed by the manufacture, if they are known are found in Table 2.

#### HN $\mu$ PID's

Two HN $\mu$  PID's, models HW-101 and PI-101, equipped with 10.2 eV bulbs was used for this study. These instruments also employ the principle of photoionization to measure trace gases.

The same procedures that were used for preparing the



MicroTip's were followed for the HN $\mu$  instruments. The HN $\mu$  instruments was zeroed according to the manufacture's zeroing procedures. Also, a five-point calibration was conducted utilizing five concentrations of isobutylene (9.5, 50, 97.4, 194, and 506 ppm). The instrument was then adjusted to read benzene directly by way of isobutylene.

Once the instrument was calibrated, the same procedure for determining response factors for the different gases using the TIP's was followed for the HN $\mu$  instruments.

The experimental response factors for the each of the gases are found in Table 3.

## DISCUSSION OF RESULTS

The percent difference between the experimental and published response factors for the MicroTip's ranged from 1 to 41 %. These differences can be attributed to a variety of scientific errors in this study. Each span gas utilized is accurate to plus or minus (+/-) 5%. The gas calibrator lists its accuracy as +/-1%. The manufacture states that the TIP has an accuracy of +/-10% and the accuracy of their response factors as +/- 10 ppm or +/-25% of the results, whichever is greater. Any other error could be attributed to the operation of the instrument or integrity of the Tedlar<sup>®</sup> bags.

The MicroTip response factors for the two models study were within experimental error. The percent difference ranged from 0 to 7% for the two models for the same compounds.

The percent difference between the experimental and the published response factors for the HN $\mu$  instrument model PI-101 varied from 0 to 38%. At present, there are no published response factors for the HW-101. The manufacture states that you can use the response factors for the PI-101 as a guide for the HW-101. The percent difference for the response factors for the two models ranged from 8 to 100%. The difference could be due to the different instruments or to the same scientific errors described previously for the MicroTIP.

## CONCLUSION

The response factors for the 13 compounds study was comparable to the data published by the manufacturers. Some of the response factors for the same compound for the HN $\mu$  and the MicroTip were different. Also, some the response factors were not the same for the identical compound for the different HN $\mu$  models.

Response factors may assist response personnel in obtaining more accurate results from the PID's when monitoring known contaminates.

The mention of trade name of commercial products does not constitute and endorsement or recommendation for their use by EPA.

**TABLE 1**  
**Gas Standards**

COMPOUND	CONCENTRATION (ppm)	IONIZATION POTENTIAL (eV)
1,2-Dichloroethylene	203	9.65
Acetone	192	9.69
Benzene	203	9.24
Chlorobenzene	193	9.07
Cyclohexane	210	9.88
Cyclohexanone	219	9.14
Diethylamine	220	8.01
Heptane	193	9.90
Isobutylene	194	9.90
Methyl Ethyl Ketone	221	9.53
o-Xylene	202	8.56
Styrene	195	8.40
Trichloroethylene	210	9.45
Toluene	219	8.82

**TABLE 2**  
**Response Factors For MicroTip**

Compound	RF HL-200	RF IS-3000	RF Manufact.
1,2-Dichloro-ethylene	1.15	1.39	N/A
Acetone	0.79	0.88	0.86
Benzene	2.13	2.12	1.78
Chlorobenzene	3.29	4.10	N/A
Cyclohexane	0.65	0.64	0.53
Cyclohexanone	0.65	0.67	1.11
Diethylamine	1.66	1.53	N/A
Heptane	0.26	0.31	N/A
Isobutylene	0.94	0.99	1.00
Methyl Ethyl Ketone	1.17	1.21	1.10
o-Xylene	1.17	1.30	N/A
Styrene	2.34	2.08	2.20
Toluene	1.63	2.16	1.91
Trichloro-ethylene	2.02	2.10	1.61

N/A - Not available

**TABLE 3**  
**Response Factor's For HN $\mu$  PID**

Compounds	RF HW-101	RF PI-101	RF Manufact.
1,2-Dichlor-ethylene	0.39	0.53	N/A
Acetone	0.73	0.39	0.63
Benzene	0.71	0.97	1.00
Chlorobenzene	0.52	1.43	N/A
Cyclohexane	0.38	0.29	N/A
Cyclohexanone	0.22	0.43	0.51
Diethylamine	0.66	0.72	0.99
Heptane	0.23	0.14	0.17
Isobutylene	0.58	0.53	0.53
Methyl Ethyl Ketone	0.68	0.53	0.57
Styrene	0.21	1.10	0.97
Trichloro-ethylene	0.66	0.87	0.87
Toluene	0.71	0.77	1.00

N/A - data not available

## **CAN OVERBOARD! ..... A GLOBAL SUMMARY OF MARINE CHEMICAL EMERGENCIES**

by

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*"He is truly wise who gains from another's mishap". Publius Syrus, Maxim 825 (c.43 B.C.)<sup>1</sup>*

### **INTRODUCTION**

Marine emergencies involving hazardous materials ("haz-mats") such as chemicals and other dangerous goods, have probably occurred in the seafaring world since the days of the ancient Phoenicians. A more recent example<sup>2</sup> occurred in 1872, when the brig MARY CELESTE, carrying 1,700 barrels of crude alcohol, was found mysteriously abandoned, but still under sail in the Atlantic, with some empty barrels in the hold, and evidence of a hasty crew departure. On another historical note, Canada's experience includes one of the worst marine accidents ever, in the tragic 1917 Halifax harbour disaster. This event<sup>3</sup> involved ship-laden high explosives and other chemicals, a vessel collision and fire, followed by a massive explosion which killed nearly 2,000 people, injured 9,000 and levelled large parts of the city.

Under similar circumstances, many of the accidents that are summarized in this paper might have happened in Canadian coastal waters or port areas, or in our larger lakes or rivers. Of course, some of them did, as Table 9 illustrates. To those who say it can't happen here, here's just a sample of evidence that it can, it has and it will !

### **PURPOSE**

There are many potential benefits, both operational and technical, to be gained from a comprehensive study of such case histories. One of the early reasons for beginning this spread-sheet information base, was to assemble and organize some historical and technical perspective for the haz-mat "spill community" on a segment of the haz-mat spill problem that, both on a global basis and within Canada, has been little-publicized and largely ignored, both by industries and by government agencies. A lot of attention and effort has been given over the years to marine oil spills, perhaps because oil spills happen more frequently and are more visible, and because the necessary countermeasures are simpler. Marine chemical spills can be considered to represent a larger, if less frequent challenge. However, this paper shows that on a global basis, they are not rare events, and that they deserve increased attention and priority.

Another function of the information base is to build a foundation for future analyses, to give a sense of the nature of the problems and to raise the priority for improved prevention methods and technical countermeasures that may be both feasible and needed for marine chemical accidents. A sample history or summary of world-wide marine chemical spills has not been easy to find, although one global survey was found, assembled in a non-annotated form for a US Coast Guard study<sup>4</sup>.

## **INFORMATION BASE AND SUMMARY TABLES**

This paper describes some early analysis of only part (perhaps 1/3rd) of an information base of collected marine chemical emergency case histories which span a 20+ year period. Some of the cases are comprehensive, but where excerpts are taken from monthly summary tables (many of HCB-based entries), or from one of the spill report data bases (NATES or DGAIS), there isn't much more information available. Regardless of extent, key elements of this information base are being summarized on a computerized spreadsheet, compiled on the Borland software Quattro Pro for Windows v.1.0. ("QPW 1.0").

In this paper, the definition of "marine emergencies" includes events which occur at marine terminals, where haz-mats are loaded or unloaded for vessels. Because only a portion of the case histories have been examined, with an admitted initial focus on events in Canada, and events occurring in the 1980's, the picture may not be completely representative of relative timing and locations of global marine chemical emergencies. In addition, because an attempt was made to capture events with a wide variety of different hazardous materials, a relative frequency of substances involved is not yet available. However, the current analysis serves as a starting "snapshot" of typical events that occur around the world.

From the computerized database, fourteen tables here give a global perspective of such emergencies. The first twelve tables are sorted by date into separate topic areas. The first eight tables cover examples of events involving haz-mats in Classes 1-8 of the international hazard classes for dangerous goods. (Note: class 9 substances usually have another prior class assigned, so appear in most of the first eight listings. Also, tables 1&2, 4&5, and 6&7 have each been combined on one page because of relatively fewer numbers of incidents). The next four tables look at other categories of interest, including:

- Table 9: for Canadian readers, a partial summary of marine incidents in Canadian or adjacent waters;
- Table 10: a table giving sample marine casualties involving either multiple numbers of different chemicals, or else, non-listed substances of possible interest or concern; and
- Table 11: a sample listing of major marine chemical emergencies, which many times required a significant emergency (fire and/or spill) response, and on most occasions, a significant salvage operation;
- Table 12: a sample listing of non-ship source chemical spills into water, from land- or air-based origins.

To complete the set of summary tables, two tables listing all of the marine casualty events currently entered in the data base, are sorted by location (Table 13) and by substance (Table 14). These summary tables include another 32 marine haz-mat emergency events which are not listed in any of the first 11 tables.

Table 12 represents additional information regarding water-borne events which don't start on the water. Although these events are not technically marine or vessel spills, they could conceivably require similar water-borne response countermeasures to the same release from a vessel in a harbour or river. In table 12, a sample listing from the information base focuses on such releases which have had impacts on river or port areas or on coastal waters or the atmosphere. These incidents are not summarized in Tables 13 or 14.

## **USES OF THE INFORMATION**

The collected and analyzed information serves as a reference source for lessons learned for spill prevention, preparedness, response, salvage or for countermeasures research and technology development. When completed, the computerized information base, together with its background paper files may highlight problem areas where shippers, carriers, governments or international organizations could consider future actions. Further tables could also be developed to determine trends in other categories, such as material behaviour, identification of cases where response or salvage operations were attempted, or other cases where applicability of existing countermeasures may have been technically feasible. Other possible applications of the info-base, when combined with analysis of the source information, include helping industries and government agencies to identify experienced contacts for further technical information on specific events, or lists of marine emergency response contractors and salvage firms experienced in dealing with marine chemical emergencies. The information could also help personnel of haz-mat Response teams, and those in marine haz-mat incident assessment or contingency planning roles to identify some possible additional risks/scenarios to consider.

To date, two typical uses have been made of the available information:

- A recent loss of sodium cyanide off the Chile coast resulted in a request from an international agency to request help in providing technical information and identification of previous case histories of this type. Our Environmental Technology Centre was able to respond to both requests. Our replies included provision by fax of many pages on properties, fate, behaviour and modelling information from the Emergencies Science Division, and a 4-page tabular listing of nine relevant case histories from the Emergencies Engineering Division, including pertinent operational details, countermeasures used and possible contacts.
- Copies of this paper are being distributed for information purposes to all members of a Canadian government-industry committee called the "Marine Chemical Spill Consultation Group" and to other individuals in industry and government agencies who are involved in related work. The consultation group has a specific focus on this problem area, has requested this study be made, and will likely use this information in planning some of its future work.

TABLE 1\* - "Explosives"

## SAMPLE MARINE CASUALTIES WITH BULK ("B") OR PKGD. ("P") CHEMICALS - CLASS 1 - EXPLOSIVES

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	10-Mar-87	Azores	ANTONIO ENES	Ammunition	P - 1	Four killed on Portuguese frigate when ammunition magazine exploded entering port; 20 injured, 1 missing.	HCB 06/87
2	01-Jul-87	France, Bay of Biscay	INDIAN GRACE	Explosives	P - 1	Fire in explosives hold, extinguished same day; experts gave "all-clear"; no casualties; cargo re-stowed.	HCB 10/87
3	18-Oct-87	Germany, off coast	COMETA	Fireworks	P - 1	Fire on ro-ro ship w/ fireworks; no injuries; fire in cargo space; reason unknown; ship beached to save it.	HCB 12/87
4	28-Oct-87	S. Pacific, Savaii Is.	ANGELAZZUL	Ammunition	P - 1	Vessel out of fuel & drifting w/ cargo of ammunition enroute Houston; cargo re-stowed to USCG standards.	HCB 12/87
5	23-Dec-88	Philippines, central	DONA CONCHITA	Fireworks	P - 1	Explosion caused many of 128 passengers to jump overboard; several casualties; illegal fireworks in hold (?)	HCB 12/87
6	12-May-89	N. Sea, UK Sector	BRITISH PIPER	Explosives	P - 1	Vessel lost 2 containers overboard; one box carried explosives, most of which was inerted by water.	HCB 08/89

TABLE 2\* - "Gases"

## SAMPLE MARINE CASUALTIES WITH BULK ("B") OR PKGD. ("P") CHEMICALS - CLASS 2: GASES

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	01-Jul-87	US, HI, Honolulu	LURLINE	Ammonia anhydrous	P - 2 & 9	Cylinder leak from ruptured gasket on gauge; 151 containers and 18 cars "contaminated" by the gas.	HCB 12/87
2	17-Jul-87	Dutch Antilles	PELICANO	Oxygen, pressurized liq.	P - 2 & 5	Container of cryogenic LOx broke free in storm; LOX escaped through valve; much damage to deck plating.	HCB 10/87
3	14-Dec-87	S. China Sea	JINYANG 103	Ammonia anhydrous	P - 2 & 9	Tank on fishing vessel exploded; 12 crew overcome; all taken to hospital in Singapore by police launch.	HCB 02/88
4	18-Mar-88	Sicily, Palermo	CAPO FALCONE	Propylene	B - 2	Gas carrier w/ 950 tonnes began to list, then sank in shallow waters; crew rescued; plans to raise vessel.	HCB 05/88
5	19-Mar-88	India, Port Okha	HESTIA	Butadienes, inhibited	B - 2	Gas carrier grounded approaching port with full cargo; 2 weeks later, ship refloated by jettison of 270 tonnes.	HCB 05/88

\*from "Can Overboard! - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCS Seminar, Vancouver: 07-Jun-94.



**TABLE 3\* - "Flammable Liquids"**

**SAMPLE MARINE CASUALTIES WITH BULK ("B") OR PACKAGED ("P") CHEMICALS - CLASS 3: FLAMMABLE LIQUIDS**

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	02-Jul-86	Chile, Talcahuano	GOLDEN ORCHID	Resin solution, flammable	B - 3	Ship to harbour w/ 2 holds plastic resin cargo blazing; despite 24 hrs of effort, fire extended to four holds	HCB 12/86
2	28-Jul-86	US, LA., Morgan City	barge SP - 4	Cyclohexane	B - 3 & 9	Tank, pushed by tug, hit submerged object on Intracoastal Waterway; 160 tonnes cargo leaked out.	HCB 12/86
3	26-Aug-86	US, LA, Kenner	barge SYM 7	Acrylonitrile	B - 3, 6 & 9	Lightning struck while loading at berth; fire destroyed 200 tonnes cargo; 30 in hospital and 1,500 evacuated.	HCB 12/86
4	17-Oct-86	Japan, Osaka Bay	ANSEI MARU	Benzene	B - 3 & 9	Explosion in coastal tanker's pump room after 1,000 tonnes of cargo discharged; two killed & three injured.	HCB 12/86
5	30-Jan-87	Portugal, Sines	MERCATOR	Naphtha	B - 3	Tanker w/ 18,000 tonnes naphtha grounded nr. Sines; 8 tanks open & cargo lost, w/ resultant pollution.	HCB 06/87
6	24-Sep-87	Philippines, Manila	KING FAMILY	Methyl methacrylate monomer	B - 3 & 9	Explosion during discharge to barges, (man smoking on barge?); 15 killed; tanker, 2 barges & tug damaged.	HCB 12/87
7	16-Oct-87	UK, Felixstowe	SILVERFALCON	Propanol residues	B - 3	Tug pulling tanker off jetty in hurricane; engines failed; tanker outer shell opened; double hull protected cargo	HCB 12/87
8	30-Oct-87	Japan, Lake Hamana	EIKUKU MARU # 55	Isopropanol	B - 3	Chem. tanker w/ Isopropanol hit coaster carrying steel products; latter partly fractured; no chemical spillage.	HCB 01/88
9	21-Nov-87	Japan, Inland Sea	NORDTRAMP	Naphtha	B - 3	Tanker w/ 54,000 tonnes naphtha in collision w/ coaster w/ steel products; tanker set adrift; no spillage.	HCB 01/88
10	23-Jun-88	Japan, nr. Shirokita	SAKURA	Styrene monomer	B - 3 & 9	Chem. tanker w/ 10,000 tonnes styrene, plus methanol & ethylene dichloride in collision; 235 t. styrene lost.	HCB 09/88
11	08-Sep-88	US, MS, Natchez	KATHIE G	Styrene monomer	B - 3 & 9	Barge pulled by tug grounded and spilled entire cargo of styrene: 80 km section of river closed to traffic.	HCB 11/88
12	17-Dec-88	Singapore	REGAL VOYAGER	Naphtha	B - 3	Cargo pumproom fire during discharge of 15,000 tonnes at terminal; 2nd fire when pumping restarted.	HCB 12/88
13	22-Dec-88	Algeria, Arzew	DELAWARE	Condensate	B - 3	2 explosions, in pumproom & forepeak of OBO vessel, while loading condensate; one crewman hospitalized.	HCB 03/89
14	23-Dec-88	Australia, Melbourne	STOLT TENACITY	Cyclohexanone	B - 3	Five tonnes of product spilled into bay during discharge operations; emergency responders spread foam.	HCB 03/89
15	20-Nov-89	Netherlands, Flushing	BRIGITTE	Benzene	B - 3 & 9	Loading explosion caused 16 tonnes benzene to escape; vessel arrested; much ship & terminal damage.	HCB 04/90

\*from "Can Overboard! - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCs Seminar, Vancouver: 07-Jun-94.

**TABLE 4\* - "Flammable Solids, Etc."**

**SAMPLE MARINE CASUALTIES WITH BULK ("B") OR PACKAGED ("P") CHEMICALS - CLASS 4: FLAMMABLE SOLIDS, PLUS SUBSTANCES LIABLE TO SPONTANEOUS COMBUSTION AND THOSE EMITTING FLAMMABLE GASES UPON CONTACT WITH WATER**

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	15-Dec-79	Spain, Barcelona	JAY AMBIKA	direct reduced iron	B - 4	Major cargo fire of chemically reactive product, creating difficult fire control and significant vessel damage.	HCB 04/80
2	19-Feb-86	US, CN, New Haven	KAPETAN ANTONI	swarf	B - 4	Spontaneous combustion in cargo of metal shavings; bulk carrier diverted for cargo discharge & fire repairs.	HCB 12/86
3	16-Jul-87	UK, England, Dartford	DUKE OF ANGLIA	Naphthalene	P - 4 & 9	12 crew in hospital after product leak from container on moored ship; firemen w/ protective suits fixed leak.	HCB 10/87
4	05-Mar-88	US, TX, Port Neches	MARINE FLORIDA	Sulphur, molten	B - 4	Cargo leaked into steam line, solidified sulphur found in heating spaces; substantial repairs required.	HCB 05/88
5	02-Sep-88	Bangladesh, Chit'gong	LETA	Cotton, wet	P - 4	Fire in baled raw cotton; vessel towed; burned 1 week despite firefighting effort; ship badly damaged.	HCB 11/88
6	31-Dec-88	S. China Sea	NORDSUND	yellow phosphorus	P - 4, 6, & 9	Enroute to Manila, fire in deck container carrying 72 drums phosphorus; 3 hrs to control blaze; no injuries	HCB 01/89
7	29-Apr-92	South China Sea	INCHON GLORY	Calcium carbide	P - 4 & 9	Collision w/ cruise ship (771 pass.); no casualties; 1000 drums product later removed from flooded hold.	HCB 06/92
8	19-Mar-90	Canada, PQ, La Baie	Unidentified ship	Aluminum dross	P - 4	Explosion of spent pot linings in containers, killed two loading crew & injured 8 others; 1 sq. km. evacuated.	DGAIS

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**TABLE 5\* - "Oxidizing Substances and Organic Peroxides"**

**SAMPLE MARINE CASUALTIES WITH BULK ("B") OR PKGD. ("P") CHEMICALS - CLASS 5: OXIDIZERS & ORGANIC PEROXIDES**

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	12-Apr-89	E. Africa, Djibouti	YIN HE	Ammonium persulphate	P - 5	With fire in container hold, vessel put into port & unloaded boxes on quayside; one w/ product burnt out.	HCB 06/89
2	27-Jul-89	Netherlands, Rotterdam	Unidentified ship	Calcium hypochlorite	P 5 & 9	700 evac'd from vessels & houses due to product evolving chlorine gas & oxygen from blazing container.	HCB 09/89
3	05-Sep-91	Baltic Sea	BORE XI	Hydrogen peroxide	B - 5 & 8	Engine room fire in Ro-Ro cargo ship carrying hydrogen peroxide; cargo later transferred to another vessel.	HCB 12/91

\*from "Can Overboard! - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCS Seminar, Vancouver: 07-Jun-94.

**TABLE 6\* - "Poisonous and Infectious Substances"****SAMPLE MARINE CASUALTIES WITH BULK ("B") OR PKGD. ("P") CHEMICALS - CLASS 6 - POISON. & INFECT. SUBSTANCES**

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	22-Jul-80	US, LA, nr. N. Orleans	TESTBANK	Chlorophenols, solid (PCP)	P - 6 & 9	Collision; lost cargo Incl. 11.4 tonnes pentachlorophenol near fishing/oyster areas; large search operation.	HCB 09/80
2	01-Jan-81	N.Sea, UK, nr Tees R.	ELK	Sodium cyanide	P - 6 & 9	Four drums punctured on Ro-Ro deck after fall fm. truck due to storm and list by other cargo shift; washed off.	HCB 02/81
3	05-May-86	Spain, Huelva	ETILICO	Acetone cyanohydrin	B - 6 & 9	Up to 3 tonnes of toxic cargo spilled into harbour; significant marine life damage, near nature reserve.	HCB 05/86
4	24-Sep-88	Singapore	MARKHAM BAY	Sodium cyanide	P - 6 & 9	In salvage of capsized vessel, found wet product had contaminated vessel & cargo; long clean-up operation.	HCB 12/88
5	18-Jul-89	Germany, NW coast	OOSTZEE	Epichlorohydrin	P - 6 & 9	Storm caused 38 of 210 drums product to leak in hold; port refusals and media coverage; crew check-ups.	HCB 10/89
6	15-Mar-90	English Channel	FATHULKHAIR	Potassium cyanide	P - 6 & 9	Six 0.5kg canisters of product on popular Sussex, UK beaches among 34 lost in storm; 24 km beach closed.	MPB 04/90,
7	01-Aug-90	Carrib. Sea, St. Martin	unidentified ship	Tetra-ethyl lead	P - 6 & 3	Tank with 10 tonnes fell overboard during inter-island voyage; salvage vessel to recover sealed tank.	HCB 10/90
8	09-Sep-92	Netherlands, Rotterdam	POL EAST	Organophosphorus pesticide	P - 6 & 9	Two leaking containers w/ 148 drums severely contaminated cargo& ship; tough salvage/cleaning job.	HCB 01/93

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**TABLE 7\* - "Radioactive Materials"****SAMPLE MARINE CASUALTIES WITH BULK ("B") OR PKGD. ("P") CHEMICALS - CLASS 7: RADIOACTIVE MATERIALS**

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	25-Aug-84	N. Sea, off Belgium	MONT LOUIS	Uranium hexafluoride	P - 7	Ro-Ro collision, sank in 15m. w/ 350 tonnes low-risk product in 30 cylinders; salvaged; much media/political.	HCB 09/84,
2	07-Apr-89	Norwegian Sea	Soviet submarine	radioactive fuel and weapons	P - 7	Nuclear MIKE-class sub. w/ nuclear weapons & fuel sank in 1,700 m. water; concern & monitoring re leaks.	MPB 11/93
3	17-Dec-91	France, Cherbourg	PACIFIC PINTAIL	Nuclear material	P - 7	Container fm carrier of Irrad'd nuclear fuel fell onto hatch cover; no damage to container or its contents.	HCB 02/92

\*from "Can Overboard! - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCS Seminar, Vancouver: 07-Jun-94.

TABLE 8\* - "Corrosive Substances"

## SAMPLE MARINE CASUALTIES WITH BULK ("B") OR PACKAGED ("P") CHEMICALS - CLASS 8: CORROSIVE SUBSTANCES

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	25-Dec-86	Sardinia	STAINLESS TRAD'	Sulphuric acid	B - 8 & 9	Ship sank in storm w/ 3,200 tonnes acid; 8 crew lost; some rescued suffered acid burns; inquiry launched.	HCB 03/87
2	07-Jan-87	France, Bay of Biscay	CHEM'L DISCOVE	Phosphoric acid	B - 8 & 9	Acid into heating system via hole in tank heating coil; system damaged & cargo contaminated by water.	HCB 03/87
3	11-Apr-87	US, WV, Ohio R.	unidentified barge	Caustic soda, solution	B - 8 & 9	Grounded barge capsized w/ 1400 tonnes, with leakage dissipated by fast-flowing water; no injuries.	HCB 07/87
4	01-Jul-87	S. Korea, nr. Busan	PARAVALOS	Phosphoric acid	B - 8 & 9	Ship w/ 45,000 tonnes acid grounded on rocky seabed off coast; listed 60 degrees; crew abandoned ship.	HCB 10/87
5	29-Nov-87	Japan, Niihama	SHINSEN MARU	Caustic soda, solution	B - 8 & 9	Chem. tanker w/ 150 tonnes caustic soda collided w/ empty cargo ship; tanker & caustic lost; 2 crew saved.	HCB 01/88
6	06-Dec-87	Pacific Ocean	FORT PRODUCER	Caustic soda, solution	B - 8 & 9	Storm caused rupture in tank bulkhead; caustic leaked & damaged ballast pumps, lines, double bottom linings.	HCB 02/88
7	21-Dec-87	US, OR. coast	ELAINE D	Sulphuric acid	B - 8 & 9	Tank barge damaged in storm; acid tank opened to sea; chemical reaction prompted further corrosion.	HCB 02/88
8	03-Feb-88	Japan, off coast	TENRYU MARU #5	Acetic acid	B - 8 & 9	Chemical tanker w/ 800 tonnes of acetic acid listed 40 degrees and subsequently sank; all 6 crew rescued.	HCB 03/88
9	15-Apr-88	Japan, Shima Bay	SHOWA MARU	Hydrochloric acid	B - 8 & 9	Grounded vessel listing; crew abandoned ship; 200 tonnes of acid aboard, but no further news in report.	HCB 06/88
10	22-Sep-88	Uruguay, Farallon Ch1	ELADIA ISABEL	Caustic soda, solution	P - 8 & 9	2 semi-trailers on Ro-Ro w/ 102 tonnes caustic, one trailer-tank fell on its side; lost 9 tonnes on deck/overbd.	HCB 03/91
11	05-Oct-88	US, FL, off coast	EDGE MOOR 1	Ferric chloride	B - 8 & 9	Tank barge w/ 10,440 tonnes aboard reported large holes in barge shell while enroute, but no pollution.	HCB 12/88
12	07-Oct-88	N. Sea, UK, Lowestoft	WESERTAL	Hexamethylenediamine	P - 8	Two tank containers lost fm. Ro-Ro; this chemical container floated 1 mo. & recovered; other not found.	HCB 12/88
13	27-Oct-88	Ivory Coast, Abidjan	LETO II	"corrosive products"	P - 8	Cargo ship into port due to storm damage & leaking drums of "corrosive chemicals" in hold; cleaned at port.	HCB 01/89
14	04-Apr-89	US, WV, Parkersburg	unidentified barge	Caustic soda, solution	B - 8 & 9	Tank barge w/ 1290 tonnes grounded, capsized; chem. lost through tank vents; cleanup took several weeks.	HCB 06/89
15	13-Apr-89	Lebanon, off Beirut	ISOLA AZZURA	Sulphuric acid	B - 8 & 9	Tanker w/ 4,000 tonnes acid hit in crew's quarter by artillery shell; no-one hurt; cargo discharged safely.	HCB 06/89

\*from "Can Overboard! - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCS Seminar, Vancouver: 07-Jun-94.

TABLE 9\* - "Events in Canadian or Adjacent Waters"

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## SAMPLE MARINE CASUALTIES IN CANADIAN OR ADJACENT WATERS WITH BULK ("B") OR PKGD. ("P") CHEMICALS - ALL CLASSES

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	02-Dec-78	Canada, NS, Halifax	LESLIE B.	Caustic soda, solid (flaked)	P - 8 & 9	Hull ice damage outbound caused water in hold to dissolve 500 tonnes in non-waterlight drums; pH > 12.	NATES
2	13-Dec-78	Canada, QC, Montreal	CAST BEAVER	Sulfuryl chloride	P - 8	5 day-leak of 1.7 tonnes from 5 barrels in container; neutralized w/ hydrated sodium carbonate in Montreal	NATES
3	24-Nov-79	Canada, Qn.Charl. Sd.	GREAT LAND	Pesticide, liq., flam., tox., nos	P - 3, 6 & 9	19 drums (4 t.) of bactericide X-CIDE lost w/ container off Ro-ro cargo vessel; one drum washed ashore.	NATES
4	18-Jul-80	Canada, Ft. Provid'nce	JOHNNY HOPE	Hydrochloric acid	P - 8	Approximately 4.6 tonnes of acid leaked into Mackenzie R. from tank container due to a weld/seam failure.	NATES
5	21-Sep-80	Canada, Cabot Strait	CAST OTTER	Calcium hypochlorite	P - 5 & 9	Container overboard w/ 17.4 tonnes mat'l in 45 kg. buckets; notice given to shipping and to public on radio.	NATES
6	16-Nov-80	Canada, Cape St. Jam.	WESTWARD	Methanol	P - 3 & 6	Loss of 7.8 tonnes of product from container due to storm damage, with runoff into Pacific Ocean.	NATES
7	23-Nov-80	Canada, NF, off coast	JALAKRISHNA	High explosives + other DGs	P - 1	50 cases class 1.1 explosives spilled on deck due to storm; ship also carrying Ammon. nitrate & T-Ethyl lead.	NATES
8	22-Dec-80	Canada, QC, Quebec	STOLT CASTLE	Styrene monomer - inhibited	B - 3 & 9	Approx. 10 tonnes spilled during loading transfer on deck and into water; some product recovery attempted.	NATES
9	29-Dec-80	Canada, QC, Montreal	CAST ORCA	Diethylamine	P - 3 & 9	16 of 38 drums (2.5 tonnes) leaking/empty in unlabelled container due to storm; ship's deck and quay cleaned.	NATES
10	29-Jan-81	Canada, QC, Pt Cartier	CAST ORCA	Thionyl chloride	P - 8	Leaking container lost 53 tonnes of product in Gulf of St. Lawrence; vessel cleanup in Port by contractor.	NATES
11	23-Sep-81	Canada, QC, Montreal	MANCHEST.VANG'	Sodium cyanide	P - 6 & 9	23 drums damaged by storm & seawater; mat'l spilled inside container; neutralized w/ hypochlorite solution.	NATES
12	29-Sep-81	Canada, ON, Sarnia	SILVER MAGPIE	Styrene monomer - inhibited	B - 3 & 9	Loading line overstressed by surge from passing vessel; 1.4 tonnes spilled onto ship and into St. Clair R.	NATES
13	19-Apr-83	Canada, QC, Montreal	STOLT SYDNESS	Styrene w/ linseed oil/carbonb	B - 3 & 9	Before unloading, pumped 11 tonnes shore tank waste to harbour, w/ paint damage and quay evacuation	NATES
14	10-Nov-83	Canada, NS, Halifax	WIEN	Phosphorus pentoxide, in wine	P - 8	Four damaged containers spilled 60 tonnes product into wine leaked from other containers in hold.	NATES
15	17-Apr-84	Canada, BC, Port Alice	B'rge SEASPAN 902	Ammonia, anhydrous	P - 2 & 9	Barge w/ 6 railcars vented 27 t. from ruptured seam under water; cause: burst internal product transfer line.	NATES

TABLE CONTINUED NEXT PAGE

TABLE 9\* - "Events in Canadian or Adjacent Waters", continued

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## SAMPLE MARINE CASUALTIES IN CANADIAN OR ADJACENT WATERS WITH BULK ("B") OR PKGD. ("P") CHEMICALS - ALL CLASSES

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
16	11-Feb-85	Canada, ON, Samia	Unidentified barge	Propylene oxide	P - 3 & 9	Tank car w/ 70 tonnes fell fm. rail ferry into Sm. St. Clair R; team surveyed, secured, floated, offloaded & lifted.	VANC
17	25-Feb-85	Canada, NS, Halifax	STUTTGART EXPR	2-Methyl-5-ethyl pyridine	P - 6	Small leak in vent valve of offloaded container; toxic, corrosive irritant; cautionary call to container owner.	NATES
18	14-Mar-85	Canada, BC, Gold R.	Unidentified barge	Sodium chlorate (45% sol'n)	B - 5	Tank overflowed during barge offload; 22 tonnes mat'l flowed via ditch to foreshore; co. flushed w/ water.	NATES
19	04-May-87	Canada, BC, Vanc'ver	SCANDINAVIA	Ethanol (40%)	P - 3	Shuttle offloading vessel dropped container of bottled whiskey; runoff drained to harbour	NATES
20	31-Mar-88	Canada, BC, Vanc'ver	IVER HERON	Methanol	B - 3 & 6	Loading 20 mln.while crew ignored open valve caused 10 tonne spill on deck; most flowed to harbour	NATES
21	02-Apr-88	Canada, BC, Victoria	Unidentified ship	Methanol	P - 3 & 6	Open valve on cross-over line flooded deck during bulk loading; Police, Fire and Environment called to scene	DGAIS
22	28-Jun-88	Canada, BC, Vanc'ver	Unidentified ship	Methylene chloride	P - 6	Forklift punctured a drum unloading container; six checked at hospital; Fire, Police & ER staff on scene.	DGAIS
23	02-Mar-89	Canada, PQ, Quebec	Unidentified ship	Toluene diisocyanate	P - 6	Entire 30 tonnes spilled during offloading, and solidified due to cold; cleanup (contract?) crew cost \$466,000.	DGAIS
24	14-May-89	Canada, QC, Montreal	Unidentified ship	Uranium hexafluoride, non-fiss.	P - 7 & 8	Spill from three damaged containers left 12 people exposed, not contaminated"; ER (contract?) cleanup.	DGAIS
25	18-Jul-89	Canada, NS, Halifax	Unidentified ship	Corrosive liquids, n.o.s.	P - 8 & 9	Drum of Chloroethyl phosphoric acid punctured & leaking in container; cleanup by ER (contract?) crew.	DGAIS
26	10-Sep-89	Canada, NS, Yarmouth	Unidentified ship	Formic acid	B - 8 & 9	Corroded valve caused leak of 650 l. acid on vessel at public wharf: ER (contract?) staff called to scene.	DGAIS
27	10-Dec-89	Canada, QC, Gulf St. L.	Unidentified ship	Aluminum phosphide	P - 4 & 6	33 sealed tins, each 1.5 kg. missing from ship upon arrival for repairs; believed washed overboard.	DGAIS
28	13-Feb-91	Canada, BC, Vanc'ver	Unidentified ship	Caustic soda, sol'n	B - 8 & 9	Railcar/bulk barge loading w/ 1,270 tonnes caustic overflowed < 1 tonne out inspection port; no injuries.	DGAIS
29	23-Jun-92	Canada, BC, Vanc'ver	Unidentified ship	Formic acid	P - 8 & 9	While unloading ship, drums found leaking in container; leak dyked, then ER (contract?) crew cleaned up.	DGAIS
30	01-Jul-93	Canada, BC, Vanc'ver	Unidentified ship	Ethylene dichloride	B - 3, 6 & 9	Overfilling ship's tank caused spill through vapour recovery line; Environment staff ensured co. cleanup.	DGAIS

\*from "Can Overboard! - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCs Seminar, Vancouver: 07-Jun-94.

**TABLE 10\* - "Multiple and Non-Listed Substances"**

**SAMPLE MARINE CHEMICAL INCIDENTS WITH NUMEROUS OR NON-LISTED SUBSTANCES, BULK ("B") OR PACKAGED ("P")**

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	19-Feb-75	Canada, BC, Malaspina	Barge FMC 100	Chlorine & caustic soda, so/n	P - 2, 8 & 9	Towed rail barge flipped; 4 cars w/ 340 tonnes chlorine into deep water; 570 tonnes caustic lost from barge.	NATES
2	07-Jul-83	Canada, Tuktoyaktuk	C/MAR SUPPLIER 8	Ethylene glycol	B - not listed	Tank overflow of 1 tonne while loading supply vessel, most of spill went into Tuk. harbour on Arctic coast	NATES
3	14-Jun-84	Papua New Guinea	B'rge CLOSEL L-43	Sod. cyanide & hyd. peroxide	P - 6&9, 5&8	Lost 270 tonnes sodium cyanide & 26 cont'rs hydrogen peroxide; search & warning; some found 20km away.	HC8 08/84
4	17-Jul-86	Strait of Malacca	GOLDEN CITY	Sod. hydrosulphite, formic acid	B - 4, 8 & 9	Fire engulfed 2 cargoes in adjacent holds; fire allegedly started after fire (sic) (acid?) contacted chemical.	HC8 01/87
5	19-Jan-87	Malta, Valleta	FIONE	"salt of chromite"	B - not listed	Maltese warned not to eat bagged sugar offloaded from FIONE due to residue of previous chemical cargo	HC8 06/87
6	01-Feb-87	Germany, Dormagen	not available	"chemical fertilizer"	B - not listed	42 tonnes went into Rhine when cargo vessel hit empty anchored tanker; 1 killed; ship sank w/ 550 t. fertilizer	HC8 06/87
7	06-Feb-87	Germany, Dusseldorf	VTG 208	Lighter fluid	B - not listed	Ten tonnes spilled into Rhine R. when cargo vessel hit anchored tanker w/ 1,000 tonnes lighter fluid aboard.	HC8 06/87
8	06-Mar-87	Belgium, Zeebrugge	Herald, Free E'prise	variety of chemicals, on trucks	P - various	Vessel capsized; 180+ died; chemicals incl'd lead compounds, cyanides, resin and Tol. di-isocyanate.	HC8 11/87
9	08-Oct-87	Guernsey, St. Peter	BREIZH-IZEL	"chemicals"	B - not listed	Ro-ro ferry in storm near Guernsey, lost a container of chemicals; firemen checked for cargo leaks in port.	HC8 12/87
10	18-Mar-88	Netherlands, Terneuze	LA QUINTA	"chemicals"	B - not listed	Chem. tanker in collision enroute Antwerp; prior to fix, vessel put to sea to "clean tanks" due to lack of facility	HC8 01/88
11	22-Apr-88	Canada, BC, Gillies Ba	Unidentified ship	LPG, n.o.s.	P - 2 (+)	Barge w/ LPGs and mixed other DGs caught fire near coast; Fire & E.R. personnel at scene; \$200K damage.	DGAIS
12	26-Sep-88	Irish Sea, UK, Wales	ARDLOUGH	Eth. acetate, dimeth. acetamide+	P - 3, 6 & 9 +	Ship sank in storm (crew rescued); 5 of 12 floating containers had chemicals; two came ashore in UK.	HC8 11/88, & 02/89
13	26-Apr-89	Canada, ON, Clarkson	Unidentified ship	Tallow (fatty acid)	B - not listed	Spill of 80 cu.m. of tallow occurred in Lake Ontario from break-bulk ship; Coast Guard staff were at scene.	DGAIS
14	28-Oct-89	English Channel	MUREE	variety of chemicals, containers	P - various	Ship sank in storm; lost paint drums & 8 containers, four w/ chemicals; later, packages washed ashore.	HC8 01/90
15	05-Jul-91	Canada, ON, Oshawa	Unidentified ship	Cement	B - not listed	Approx. 6.5 tonnes cement spilled when hose ruptured during offloading of bulk carrier at Lake Ontario port.	DGAIS

\*from "Can Overboard! - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCS Seminar, Vancouver: 07-Jun-94.

TABLE 11\* - "Major Events"

## SAMPLE MAJOR MARINE INCIDENTS WITH BULK ("B") OR PACKAGED ("P") CHEMICALS - ALL CLASSES

No.	Date	Location	Vessel	Substance	Cat./Class	Incident Details	Source
1	13-Jan-84	N.Sea, UK, ne coast	DANA OPTIMA	s.nitrophenol pesticide (s/t/nos)	P - 6 & 9	Ro-Ro lost 80 drums (16 t.) Dinoseb; fishing shut & 6wk futile search done; 53 drums found in later 12d. search. Search & recovery costs: \$1.9m excl. Dutch costs	AMSTER.
2	27-Jul-84	US, TX, Houst.ShipCh.	RIO NEUQUEN	Aluminum phosphide	P - 4 & 6	Offloaded container dropped & exploded, releasing volatile, tox. fumigant (evolves phosphine gas): 1 dead, 8 inj'd; tricky handling/disposal - ocean disposal OK'd	HCB 09/84
3	16-Nov-84	Adriatic S, Yugoslavia	BRIG. MONTANARI	Vinyl chloride, inhibited	B - 2	Ship sank w/ 1,300 tonnes in 4 cargo tanks, in 82m. sensitive waters nr. nat'l park/nature reserve; monitor/plan/salvage over 3-1/2 yrs yielded 700 tonnes: \$2.5m	MALTA
4	24-Aug-85	Somalia, Mogadishu	ARIADNE	Multi- chemicals	P - 3,5,6 & 8	Ship under salvage broke up & caught fire in port; 650 tonnes chemicals in 70 containers, incl. tetraethyl lead, pesticides, calcium carbide (+); 20 c. washed ashore	HCB 11/85
5	03-Mar-87	English Channel	HORNESTRAND	Seismic gelatin & detonators	P - 1	2-wk fire on ship w/ 400 tonnes seismic gelatin (Class 1.1 - mass explosion hazard) & hundreds of thousands of detonators; Wjismulter salvage operation a success	HCB 6/87
6	05-Dec-87	Spain, off nw coast	CASON	Multi- chemicals	P - 4,3,6,8,9,+	Fire, storm; 23 drowned; explosion in boxed DGs (?); many chems: sodium metal, ortho-cresol, aniline oil+; costly salvage & recovery conducted in winter cond'ns	HCB 01/88
7	22-Jan-88	France, off Ushant	BREA	Acids & insecticides	P - 8 & 6	Cargo ship lost deckload of 800 drums of hydrochloric, formic and propionic acids in bad weather; insecticides also lost; several drums washed ashore.	HCB 03/88
8	27-May-88	N.Sea, off Netherlands	ANNA BROERE	Acrylonitrile, dodecylbenzene+	B - 3, 6 & 9	After collision, Dutch-owned chem. tanker sank in only 32m. water. Due to nav'n & env'l hazards, Dutch gov't contracted Smit Tak to survey/secure/salvage - \$1.7m.	HCB 08/88+ MPB 08/88
9	13-Mar-89	English Channel	PERINTIS	Lindane, other pesticides (nos)	P - 6 & 9	Ship sank w/ 6 tonnes lindane, 1 t. permethrin & 0.5 t. cypermethrin; ROV wreck dive; floating lindane conf'r found in 2 days, lost in tow (1+mo.search - not found)	HCB 05/89
10	04-Jan-92	US, NJ + NC, ne coast	SANTA CLARA I	Ars.trioxide & mag.phosphide	P - 6, 4 & 2	Search for 441 drums arsenic trioxide overboard into 40m. sensitive waters; in same emergency, magnesium phosphide had contaminated hold; cost est'd \$4.3m.	HCB 03/92+ MSC 01/93

\*from "Can Overboard! - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCS Seminar, Vancouver: 07-Jun-94.



TABLE 12\* - "Land &amp; Air Sources"

## SAMPLE MARINE CHEMICAL INCIDENTS FROM LAND- &amp; AIR-BASED SOURCES - BULK ("B") OR PKGD. ("P"), ALL CLASSES

No.	Date	Location	Chem.Source	Substance	Cat./Class	Incident Details	Source
1	24-May-80	Canada, NB, Juniper	Derailment (bridge)	Methylene chloride + mixed	P - 2,3,5 & 9	Eight derailed containers into Miramichi R.; damaged/lost chemicals also incl. calc. hypochlorite & isopropanol	NATES
2	04-Mar-84	Canada, BC, Surrey	Plant Vandalism	Chlorophenols, liq. (PCP/TTCP)	B - 6 & 9	Approx. 45 tonnes to key fisheries river; 5 t. recovered, plus contaminated water & soil; most unrecoverable.	NATES
3	08-Aug-84	Canada, BC, Fraser Lk.	Truck (bridge)	Sodium cyanide	P - 6 & 9	Pallet of 8 drums fell & broke open on bridge; some fell in river; remainder picked up and surfaces rinsed.	NATES
4	13-Aug-85	Canada, ON, Sarnia	Truck Loading St'n	Perchloroethylene	B - 6	18 of 48 tonnes leaked from valve into swift St. Clair R.; product behaviour & cleanup techniques of interest.	HALIFAX
5	01-Nov-86	Switzerland, Rhine R	Warehouse	Pesticides(n.o.s.), mercury (+)	P - 6, 8, & 9	Fire runoff sent 30 tonnes of pesticides & chemicals into Rhine, series of downstream spills(?) followed.	HCB 12/86
6	13-Jan-87	UK, Essex	Tank Container	Benzyl cyanide	P -	Leak at Tilbury docks, likely from faulty valve as tank itself was undamaged; firemen sanded area down.	HCB 12/87
7	13-Jan-87	Finland, Kotka	Storage Tank	Chlorobenzene	P - 3 & 9	Storage tank valve leaked 450 tonnes of toxic, flammable product into ice-covered harbour; liquid sank.	HCB 06/87
8	28-May-87	UAE, Dubai, Pt.Rashid	Container Term'l	Org/phos.pesticide,sol.tox.nos	P - 6 & 9	Fire in one of 32 containers of Malathion; sun heating others; fought by experts w/ nitrogen, shade & water	HCB 02/88
9	12-Sep-87	UK, T&W, Sunderland	Chemical Plant	"toxic gas"	B -	Explosion at dockland plant sent cloud of toxic gas across port area; crews from two ships evacuated.	HCB 12/87
10	29-Oct-87	France, Nantes	Warehouse	Ammonium nitrate	P - 5	Warehouse fire w/ 500 tonnes ammonium nitrate; plume over city/port estimated 13 x 5 km; 25,000 evacuated.	HCB 12/87
11	17-Feb-88	US, OH, Toledo	Pipeline	Toluene	B - 3, 9 & 6	Pipeline leak sent 300 tonnes into Sandusky R; 3 injured, 4000+ evacuated; lower water supplies shut.	HCB 04/88
12	02-Nov-88	Canada, NS, Halifax	Container Term'l	Methyl isopropenyl ketone	P - 3	Two drums punctured (poor blocks/braces); Fire H-M team assessed and contractor cleaned/repacked.	NATES
13	18-Aug-89	Canada, BC, Surrey	Tanker truck	Wood preservative - TCMTB	P - 8 & 9	12 tonne spill at start of fishing led to 2-day closure; no fish contamination found, but high regional concern.	MPB 11/89
14	10-Dec-90	Canada, PQ, Montreal	Pipeline (loading)	Naphtha	B - 3	Missing plug on loading line led to 1 tonne into port waters, where it evaporate quickly; no damage evident.	NATES
15	14-Jul-91	US, CA, Sacramento R.	Derailment (trestle)	Herbicide - Metam Sodium	P - not listed	Tank contents of 19,500 US gal. killed all fish for 64 km of river & lake; much media, public & political concern.	HMI26/07/91

\*from "Can Overboard! - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCS Seminar, Vancouver: 07-Jun-94.

**TABLE 13\* - "All Sample Events, Sorted by Location" (Page 1 of 3)**  
**LOCATION SUMMARY(1974-93): GLOBAL MARINE CASUALTIES-ALL CLASSES**

No.	Date	Location	Vessel	Substance	Cat./Clas
1	16-Nov-84	Adriatic S, Yugoslavia	BRIG. MONTANARI	Vinyl chloride, inhibited	B - 2
2	22-Dec-88	Algeria, Arzew	DELAWARE	Condensate	B - 3
3	22-Jun-87	Antwerp, Belgium	ATHLON	Cotton, wet(?)	P - 4
4	23-Dec-88	Australia, Melbourne	STOLT TENACITY	Cyclohexanone	B - 3
5	10-Mar-87	Azores	ANTONIO ENES	Ammunition	P - 1
6	05-Sep-91	Baltic Sea	BORE XI	Hydrogen peroxide	B - 5 & 8
7	02-Sep-88	Bangladesh, Chitt'gong	LETA	Cotton, wet	P - 4
8	08-Jul-91	Basilan Strait	RUTH RIIS	Ammonium nitrate	B - 1
9	06-Mar-87	Belgium, Zeebrugge	Herald, Free E'prise	variety of chemicals, on trucks	P - various
10	22-Apr-88	Canada, BC, Gillies Bay	Unidentified ship	LPG, n.o.s.	P - 2 (+)
11	14-Mar-85	Canada, BC, Gold R.	Unidentified barge	Sodium chlorate (45% so'n)	B - 5
12	19-Feb-75	Canada, BC, Malaspina	Barge FMC 100	Chlorine & caustic soda, so'n	P - 2, 8 & 9
13	17-Apr-84	Canada, BC, Port Alice	B'rge SEASPAN 80	Ammonia, anhydrous	P - 2 & 9
14	13-Feb-91	Canada, BC, Vanc'ver	Unidentified ship	Caustic soda, so'n	B - 8 & 9
15	28-Jun-88	Canada, BC, Vanc'ver	Unidentified ship	Methylene chloride	P - 6
16	31-Mar-88	Canada, BC, Vanc'ver	IVER HERON	Methanol	B - 3 & 6
17	04-May-87	Canada, BC, Vanc'ver	SCANDINAVIA	Ethanol (40%)	P - 3
18	23-Jun-92	Canada, BC, Vanc'ver	Unidentified ship	Formic acid	P - 8 & 9
19	01-Jul-93	Canada, BC, Vanc'ver	Unidentified ship	Ethylene dichloride	B - 3, 6 & 9
20	02-Apr-88	Canada, BC, Victoria	Unidentified ship	Methanol	P - 3 & 6
21	21-Sep-80	Canada, Cabot Strait	CAST OTTER	Calcium hypochlorite	P - 5 & 9
22	16-Nov-80	Canada, Cape St. Jam.	WESTWARD	Methanol	P - 3 & 6
23	18-Jul-80	Canada, Ft. Provid'nce	JOHNNY HOPE	Hydrochloric acid	P - 8
24	31-Oct-78	Canada, NB, Saint John	OCEAN FAITH	Naphtha	B - 3
25	26-Feb-85	Canada, NB, Saint John	MARIA ANGELICO	Phosphoric Acid	P - 8
26	23-Nov-80	Canada, NF, off coast	JALAKRISHNA	High explosives + other DGs	P - 1
27	02-Dec-78	Canada, NS, Halifax	LESLIE B.	Caustic soda, solid (flaked)	P - 8 & 9
28	10-Nov-83	Canada, NS, Halifax	WIEN	Phosphorus pentoxide, in wine	P - 8
29	25-Feb-85	Canada, NS, Halifax	STUTTGART EXP	2-Methyl-5-ethyl pyridine	P - 6
30	18-Jul-89	Canada, NS, Halifax	Unidentified ship	Corrosive liquids, n.o.s.	P - 8 & 9
31	10-Sep-89	Canada, NS, Yarmouth	Unidentified ship	Formic acid	B - 8 & 9
32	26-Apr-89	Canada, ON, Clarkson	Unidentified ship	Tallow (fatty acid)	B - not listed
33	05-Jul-91	Canada, ON, Oshawa	Unidentified ship	Cement	B - not listed
34	29-Sep-81	Canada, ON, Sarnia	SILVER MAGPIE	Styrene monomer - inhibited	B - 3 & 9
35	11-Feb-85	Canada, ON, Sarnia	Unidentified barge	Propylene oxide	P - 3 & 9
36	26-Jul-89	Canada, ON, Snell Lock	LAKE ANNE	Xylene	B - 3 & 9
37	19-Mar-90	Canada, PQ, La Baie	Unidentified ship	Aluminum dross	P - 4
38	18-Mar-87	Canada, PQ, Montreal	STOLT CASTLE	Naphtha, w/ sunflower oil	P - 3
39	02-Mar-89	Canada, PQ, Quebec	Unidentified ship	Toluene diisocyanate	P - 6
40	20-Mar-87	Canada, PQ, Quebec	STOLT CASTLE	Naphtha w/ tank wash residue	P - 3
41	10-Dec-89	Canada, QC, Gulf St L.	Unidentified ship	Aluminum phosphide	P - 4 & 6
42	13-Dec-78	Canada, QC, Montreal	CAST BEAVER	Sulfuryl chloride	P - 8
43	14-May-89	Canada, QC, Montreal	Unidentified ship	Uranium hexafluoride, non-fiss.	P - 7 & 8
44	19-Apr-83	Canada, QC, Montreal	STOLT SYDNESS	Styrene w/ linseed oil/carbonb	B - 3 & 9
45	23-Sep-81	Canada, QC, Montreal	MANCHEST. VANG'	Sodium cyanide	P - 6 & 9
46	29-Dec-80	Canada, QC, Montreal	CAST ORCA	Diethylamine	P - 3 & 9
47	29-Jan-81	Canada, QC, Pt Cartier	CAST ORCA	Thionyl chloride	P - 8
48	22-Dec-80	Canada, QC, Quebec	STOLT CASTLE	Styrene monomer - inhibited	B - 3 & 9
49	24-Nov-79	Canada, Qn. Charl. Sd.	GREAT LAND	Pesticide, liq., flam., tox., nos	P - 3, 6 & 9
50	07-Jul-83	Canada, Tuktoyaktuk	C'MAR SUPPLIER	Ethylene glycol	B - not listed

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**TABLE 13\* - "All Sample Events, Sorted by Location", continued (Page 2 of 3)**  
**LOCATION SUMMARY(1974-93): GLOBAL MARINE CASUALTIES-ALL CLASSES**

No.	Date	Location	Vessel	Substance	Cat./Clas
51	01-Aug-90	Carrib. Sea, St. Martin	unidentified ship	Tetra-ethyl lead	P - 6 & 3
52	02-Jul-86	Chile, Talcahuano	GOLDEN ORCHID	Resin solution, flammable	B - 3
53	17-Jul-87	Dutch Antilles	PELICANO	Oxygen, pressurized liq.	P - 2 & 5
54	12-Apr-89	E. Africa, Djibouti	YIN HE	Ammonium persulphate	P - 5
55	28-Oct-89	English Channel	MUREE	variety of chemicals, containers	P - various
56	13-Mar-89	English Channel	PERINTIS	Lindane, other pesticides (nos)	P - 6 & 9
57	03-Mar-87	English Channel	HORNESTRAND	Seismic gelatin & detonators	P - 1
58	15-Mar-90	English Channel	FATHULKHAIR	Potassium cyanide	P - 6 & 9
59	07-Jan-87	France, Bay of Biscay	CHEM'L DISCOVE	Phosphoric acid	B - 6 & 9
60	01-Jul-87	France, Bay of Biscay	INDIAN GRACE	Explosives	P - 1
61	17-Dec-91	France, Cherbourg	PACIFIC PINTAIL	Nuclear material	P - 7
62	11-Feb-92	France, off Brest	AZILAL	Acetic acid	P - 8
63	20-Oct-89	France, off Ushant	EAL RUBY	Hydrochloric + other acids	P - 8
64	22-Jan-88	France, off Ushant	BREA	Acids & insecticides	P - 6 & 6
65	01-Feb-87	Germany, Dormagen	not available	"chemical fertilizer"	B - not listed
66	06-Feb-87	Germany, Dusseldorf	VTG 208	Lighter fluid	B - not listed
67	18-Jul-89	Germany, NW coast	OOSTZEE	Epichlorohydrin	P - 6 & 9
68	18-Oct-87	Germany, off coast	COMETA	Fireworks	P - 1
69	08-Oct-87	Guernsey, St. Peter	BREIZH-IZEL	"chemicals"	B - not listed
70	14-Jan-92	Gulf of Thailand	NAVKUN 4	Vinyl chloride monomer	B - 2
71	25-Jul-91	Hong Kong	WAN XIANG	Hydrogen peroxide	P - 5
72	19-Mar-88	India, Port Okha	HESTIA	Butadienes, inhibited	B - 2
73	11-May-89	Indian Ocean	TROPIGAS FAR E.	Vinyl chloride monomer	B - 2
74	26-Sep-88	Irish Sea, UK, Wales	ARDLOUGH	Eth. acetate, dimeth. acetamide	P - 3, 6 & 9 +
75	27-Oct-88	Ivory Coast, Abijian	LETO II	"corrosive products"	P - 8
76	21-Nov-87	Japan, Inland Sea	NORDTRAMP	Naphtha	B - 3
77	30-Oct-87	Japan, Lake Hamana	EIKUKU MARU # 5	Isopropanol	B - 3
78	29-Nov-87	Japan, Niihama	SHINSEN MARU	Caustic soda, solution	B - 6 & 9
79	17-Oct-86	Japan, Osaka Bay	ANSEI MARU	Benzene	B - 3 & 9
80	15-Apr-88	Japan, Shima Bay	SHOWA MARU	Hydrochloric acid	B - 6 & 9
81	23-Jun-88	Japan, nr. Shirokita	SAKURA	Styrene monomer	B - 3 & 9
82	31-Oct-89	Japan, off Shikoku	INCHON PIONEER	Isopropyl alcohol	B - 3
83	03-Feb-88	Japan, off coast	TENRYU MARU #5	Acetic acid	B - 6 & 9
84	13-Apr-89	Lebanon, off Beirut	ISOLA AZZURA	Sulphuric acid	B - 6 & 9
85	19-Jan-87	Malta, Valletta	FIONE	"salt of chromite"	B - not listed
86	12-May-89	N. Sea, UK Sector	BRITISH PIPER	Explosives	P - 1
87	07-Oct-88	N. Sea, UK, Lowestoft	WESERTAL	Hexamethylenediamine	P - 8
88	26-Aug-84	N. Sea, off Belgium	MONT LOUIS	Uranium hexafluoride	P - 7
89	13-Jan-84	N. Sea, UK, nr coast	DANA OPTIMA	s.nitrophenol pesticide (s/t/nos)	P - 6 & 9
90	01-Jan-81	N. Sea, UK, nr. Tees R.	ELK	Sodium cyanide	P - 6 & 9
91	27-May-88	N. Sea, off Netherlands	ANNA BROERE	Acrylonitrile, dodecylbenzene+	B - 3, 6 & 9
92	20-Nov-89	Netherlands, Flushing	BRIGITTE	Benzene	B - 3 & 9
93	27-Jul-89	Netherlands, Rotterdam	Unidentified ship	Calcium hypochlorite	P 5 & 9
94	09-Sep-92	Netherlands, Rotterdam	POL EAST	Organophosphorus pesticide	P - 6 & 9
95	18-Mar-88	Netherlands, Terneuzen	LA QUINTA	"chemicals"	B - not listed
96	11-Dec-90	North Sea	LOVERVAL	Pyridine	P - 3 & 6
97	07-Apr-89	Norwegian Sea	Soviet submarine	radioactive fuel and weapons	P - 7
98	06-Dec-87	Pacific Ocean	FORT PRODUCER	Caustic soda, solution	B - 6 & 9
99	14-Jun-84	Papua New Guinea	B'rge CLOSEL L-43	Sod. cyanide & hyd. peroxide	P - 6&9, 5&8
100	14-Jun-84	Papua, New Guinea	B'rge CLOSEL L-43	Sod. cyanide & hyd. peroxide	P - 6&9, 5&8

----- TABLE CONTINUED NEXT PAGE -----

**TABLE 13\* - "All Sample Events, Sorted by Location", continued (Page 3 of 3)**  
**LOCATION SUMMARY(1974-93): GLOBAL MARINE CASUALTIES-ALL CLASSES**

No.	Date	Location	Vessel	Substance	Cat./Clas
101	22-Mar-88	Persian Gulf, off Dubai	HAVGLIMT	Ammonia, anhydrous	B - 2 & 9
102	24-Sep-87	Philippines, Manila	KING FAMILY	Methyl methacrylate monomer	B - 3 & 9
103	23-Dec-88	Philippines, central	DONA CONCHITA	Fireworks	P - 1
104	30-Jan-87	Portugal, Sines	MERCATOR	Naphtha	B - 3
105	03-Jul-92	Red Sea	ORIENTAL KNIGH	Yellow phosphorus	P - 4
106	31-Dec-88	S. China Sea	NORDSUND	yellow phosphorus	P - 4, 6, & 9
107	14-Dec-87	S. China Sea	JINYANG 103	Ammonia anhydrous	P - 2 & 9
108	01-Jul-87	S. Korea, nr. Busan	PARAVALOS	Phosphoric acid	B - 8 & 9
109	10-May-92	S. Korea, off Busan	STAINL'S PRINCE	Propylene glycol	B - not listed
110	25-Jan-92	S. Korea, off Makpo	CAPT. VENIAMIS	Calcium nitrate	B - 5
111	28-Oct-87	S. Pacific, Savaii Is.	ANGELAZZUL	Ammunition	P - 1
112	25-Dec-86	Sardinia	STAINLESS TRAD'	Sulphuric acid	B - 8 & 9
113	18-Mar-88	Sicily, Palermo	CAPO FALCONE	Propylene	B - 2
114	24-Sep-88	Singapore	MARKHAM BAY	Sodium cyanide	P - 6 & 9
115	17-Dec-88	Singapore	REGAL VOYAGER	Naphtha	B - 3
116	24-Aug-85	Somalia, Mogadishu	ARIADNE	Multi- chemicals	P - 3,5,6 & 8
117	29-Apr-92	South China Sea	INCHON GLORY	Calcium carbide	P - 4 & 9
118	15-Dec-79	Spain, Barcelona	JAY AMBIKA	direct reduced iron	B - 4
119	19-Jul-91	Spain, Corunna	BALDER PHENIX	Propylene	B - 2
120	05-May-86	Spain, Huelva	ETILICO	Acetone cyanohydrin	B - 6 & 9
121	05-Dec-87	Spain, off nw coast	CASON	Multi- chemicals	P - 4,3,6,8,9
122	17-Jul-86	Strait of Malacca	GOLDEN CITY	Sod. hydrosulphite, formic acid	B - 4, 8 & 9
123	28-Jul-92	Trois Riv., PQ, Canada	Unidentified ship	Lithium hypochlorite, dry	P - 5
124	07-Mar-87	U.S. - Gulf Region	GOLDEN QUEEN	Benzene (as cleaning agent)	P - 3
125	16-Jul-87	UK, England, Dartford	DUKE OF ANGLIA	Naphthalene	P - 4 & 9
126	16-Oct-87	UK, Felixstowe	SILVERFALCON	Propanol residues	B - 3
127	19-Jan-91	UK, Humberside	IVYBANK	Nuclear waste+copra expeller	B - 7 & 4
128	30-Dec-88	UK, nr. Liverpool	DEEPPDALE H	caustic soda	B - 8
129	03-May-91	UK, off Norfolk	NORDIC PRIDE	Ethyl acrylate+ 2 other chems.	P - 3 & 6
130	19-Feb-86	US, CN, New Haven	KAPETAN ANTONI	swarf	B - 4
131	24-Jan-92	US, Chesapeake Bay	EVER GRACE	Allyl alcohol	P - 3, 6 & 9
132	05-Oct-88	US, FL, off coast	EDGE MOOR 1	Ferric chloride	B - 8 & 9
133	01-Jul-87	US, HI, Honolulu	LURLINE	Ammonia anhydrous	P - 2 & 9
134	20-Apr-89	US, HI, Molokai Is.	KAMALU	Mixed flammables, insecticide	P - 3,2,6 & 9
135	26-Aug-86	US, LA, Kenner	barge SYM 7	Acrylonitrile	B - 3, 6 & 9
136	25-Jan-92	US, LA, Morgan C.	unidentified barge	Styrene monomer	B - 3 & 9
137	22-Jul-80	US, LA, nr. N. Orleans	TESTBANK	Chlorophenols, solid (PCP)	P - 6 & 9
138	28-Jul-86	US, LA, Morgan City	barge SP - 4	Cyclohexane	B - 3 & 9
139	08-Sep-88	US, MS, Natchez	KATHIE G	Styrene monomer	B - 3 & 9
140	07-Sep-91	US, NC, Wilmington	RECIFE	Sodium hypochlorite	P - not listed
141	04-Jan-92	US, NJ + NC, ne coast	SANTA CLARA I	Ars.trioxide & mag.phosphide	P - 6, 4 & 2
142	21-Dec-87	US, OR, coast	ELAINE D	Sulphuric acid	B - 8 & 9
143	17-Mar-90	US, PA, Philadelphia	JO ROGN	Cumene	B - 3
144	22-Dec-92	US, TX, Houst. Ship Ch.	barge DUVAL 2	Sulphur, molten	B - 4
145	27-Jul-84	US, TX, Houst.ShipCh.	RIO NEUQUEN	Aluminum phosphide	P - 4 & 6
146	05-Mar-88	US, TX, Port Neches	MARINE FLORIDA	Sulphur, molten	B - 4
147	11-Apr-87	US, WV, Ohio R.	unidentified barge	Caustic soda, solution	B - 8 & 9
148	04-Apr-89	US, WV, Parkersburg	unidentified barge	Caustic soda, solution	B - 8 & 9
149	01-Sep-88	USSR, Black Sea	NOBLE SKY	Ammonia, anhydrous	B - 2 & 9
150	22-Sep-88	Uruguay, Farallon Ch'l	ELADIA ISABEL	Caustic soda, solution	P - 8 & 9

\*from "Can Overboard - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCS Seminar, Vancouver: 07Jun94

**TABLE 14\* - "All Sample Events, Sorted by Substance" (Page 1 of 3)**  
**SUBST. SUMMARY (1974-93): GLOBAL MARINE CASUALTIES - ALL CLASSES**

No.	Date	Location	Vessel	Substance	Cat./Clas
1	01-Feb-87	Germany, Dornagen	not available	"chemical fertilizer"	B - not listed
2	18-Mar-88	Netherlands, Terneuzen	LA QUINTA	"chemicals"	B - not listed
3	08-Oct-87	Guernsey, St. Peter	BREIZH-IZEL	"chemicals"	B - not listed
4	27-Oct-88	Ivory Coast, Abijan	LETO II	"corrosive products"	P - 8
5	19-Jan-87	Malta, Valleta	FIONE	"salt of chromite"	B - not listed
6	25-Feb-85	Canada, NS, Halifax	STUTTGART EXP	2-Methyl-5-ethyl pyridine	P - 6
7	03-Feb-88	Japan, off coast	TENRYU MARU #5	Acetic acid	B - 8 & 9
8	11-Feb-92	France, off Brest	AZILAL	Acetic acid	P - 8
9	05-May-86	Spain, Huelva	ETILICO	Acetone cyanohydrin	B - 6 & 9
10	22-Jan-88	France, off Ushant	BREA	Acids & insecticides	P - 8 & 6
11	26-Aug-86	US, LA, Kenner	barge SYM 7	Acrylonitrile	B - 3, 6 & 9
12	27-May-88	N. Sea, off Netherlands	ANNA BROERE	Acrylonitrile, dodecylbenzene+	B - 3, 6 & 9
13	24-Jan-92	US, Chesapeake Bay	EVER GRACE	Allyl alcohol	P - 3, 6 & 9
14	19-Mar-90	Canada, PQ, La Baie	Unidentified ship	Aluminum dross	P - 4
15	10-Dec-89	Canada, QC, Gulf St L.	Unidentified ship	Aluminum phosphide	P - 4 & 6
16	27-Jul-84	US, TX, Houst. ShipCh.	RIO NEUQUEN	Aluminum phosphide	P - 4 & 6
17	14-Dec-87	S. China Sea	JINYANG 103	Ammonia anhydrous	P - 2 & 9
18	01-Jul-87	US, HI, Honolulu	LURLINE	Ammonia anhydrous	P - 2 & 9
19	17-Apr-84	Canada, BC, Port Alice	B'rge SEASPAR 90	Ammonia, anhydrous	P - 2 & 9
20	22-Mar-88	Persian Gulf, off Dubai	HAVGLIMT	Ammonia, anhydrous	B - 2 & 9
21	01-Sep-88	USSR, Black Sea	NOBLE SKY	Ammonia, anhydrous	B - 2 & 9
22	12-Apr-89	E. Africa, Djibouti	YIN HE	Ammonium persulphate	P - 5
23	08-Jul-91	Basilan Strait	RUTH RIIS	Ammonium nitrate	B - 1
24	10-Mar-87	Azores	ANTONIO ENES	Ammunition	P - 1
25	28-Oct-87	S. Pacific, Savail Is.	ANGELAZZUL	Ammunition	P - 1
26	04-Jan-92	US, NJ + NC, ne coast	SANTA CLARA I	Ars trioxide & mag. phosphide	P - 6, 4 & 2
27	17-Oct-86	Japan, Osaka Bay	ANSEI MARU	Benzene	B - 3 & 9
28	20-Nov-89	Netherlands, Flushing	BRIGITTE	Benzene	B - 3 & 9
29	07-Mar-87	U.S. - Gulf Region	GOLDEN QUEEN	Benzene (as cleaning agent)	P - 3
30	19-Mar-88	India, Port Okha	HESTIA	Butadienes, inhibited	B - 2
31	29-Apr-92	South China Sea	INCHON GLORY	Calcium carbide	P - 4 & 9
32	21-Sep-80	Canada, Cabot Strait	CAST OTTER	Calcium hypochlorite	P - 5 & 9
33	27-Jul-89	Netherlands, Rotterdam	Unidentified ship	Calcium hypochlorite	P 5 & 9
34	25-Jan-92	S. Korea, off Makpo	CAPT. VENIAMIS	Calcium nitrate	B - 5
35	13-Feb-91	Canada, BC, Vanc'ver	Unidentified ship	Caustic soda, sol'n	B - 8 & 9
36	02-Dec-78	Canada, NS, Halifax	LESLIE B.	Caustic soda, solid (flaked)	P - 8 & 9
37	04-Apr-89	US, WV, Parkersburg	unidentified barge	Caustic soda, solution	B - 8 & 9
38	29-Nov-87	Japan, Niihama	SHINSEN MARU	Caustic soda, solution	B - 8 & 9
39	11-Apr-87	US, WV, Ohio R.	unidentified barge	Caustic soda, solution	B - 8 & 9
40	22-Sep-88	Uruguay, Farallon Ch'I	ELADIA ISABEL	Caustic soda, solution	P - 8 & 9
41	06-Dec-87	Pacific Ocean	FORT PRODUCER	Caustic soda, solution	B - 8 & 9
42	05-Jul-91	Canada, ON, Oshawa	Unidentified ship	Cement	B - not listed
43	19-Feb-75	Canada, BC, Malaspina	Barge FMC 100	Chlorine & caustic soda, sol'n	P - 2, 8 & 9
44	22-Jul-80	US, LA, nr. N. Orleans	TESTBANK	Chlorophenols, solid (PCP)	P - 6 & 9
45	22-Dec-88	Algeria, Arzew	DELAWARE	Condensate	B - 3
46	18-Jul-89	Canada, NS, Halifax	Unidentified ship	Corrosive liquids, n.o.s.	P - 8 & 9
47	02-Sep-88	Bangladesh, Chit'gong	LETA	Cotton, wet	P - 4
48	22-Jun-87	Antwerp, Belgium	ATHLON	Cotton, wet(?)	P - 4
49	17-Mar-90	US, PA, Philadelphia	JO ROGN	Cumene	B - 3
50	28-Jul-86	US, LA., Morgan City	barge SP - 4	Cyclohexane	B - 3 & 9

----- TABLE CONTINUED NEXT PAGE -----

**TABLE 14\* - "All Sample Events, Sorted by Substance", continued (Page 2 of 3)**  
**SUBST. SUMMARY (1974-93): GLOBAL MARINE CASUALTIES - ALL CLASSES**

No.	Date	Location	Vessel	Substance	Cat./Clas
51	23-Dec-88	Australia, Melbourne	STOLT TENACITY	Cyclohexanone	B - 3
52	29-Dec-80	Canada, QC, Montreal	CAST ORCA	Diethylamine	P - 3 & 9
53	18-Jul-89	Germany, NW coast	OOSTZEE	Epichlorohydrin	P - 6 & 9
54	26-Sep-88	Irish Sea, UK, Wales	ARDLOUGH	Eth. acetate, dimeth. acetamide	P - 3, 6 & 9 +
55	04-May-87	Canada, BC, Vanc'ver	SCANDINAVIA	Ethanol (40%)	P - 3
56	03-May-91	UK, off Norfolk	NORDIC PRIDE	Ethyl acrylate+ 2 other chems.	P - 3 & 6
57	01-Jul-93	Canada, BC, Vanc'ver	Unidentified ship	Ethylene dichloride	B - 3, 6 & 9
58	07-Jul-83	Canada, Tuktoyaktuk	C'MAR SUPPLIER	Ethylene glycol	B - not listed
59	12-May-89	N. Sea, UK Sector	BRITISH PIPER	Explosives	P - 1
60	01-Jul-87	France, Bay of Biscay	INDIAN GRACE	Explosives	P - 1
61	05-Oct-88	US, FL, off coast	EDGE MOOR 1	Ferric chloride	B - 8 & 9
62	18-Oct-87	Germany, off coast	COMETA	Fireworks	P - 1
63	23-Dec-88	Philippines, central	DONA CONCHITA	Fireworks	P - 1
64	23-Jun-92	Canada, BC, Vanc'ver	Unidentified ship	Formic acid	P - 8 & 9
65	10-Sep-89	Canada, NS, Yarmouth	Unidentified ship	Formic acid	B - 8 & 9
66	07-Oct-88	N. Sea, UK, Lowestoft	WESERTAL	Hexamethylenediamine	P - 8
67	23-Nov-80	Canada, NF, off coast	JALAKRISHNA	High explosives + other DGs	P - 1
68	20-Oct-89	France, off Ushant	EAL RUBY	Hydrochloric + other acids	P - 8
69	18-Jul-80	Canada, Ft. Prov'd'nce	JOHNNY HOPE	Hydrochloric acid	P - 8
70	15-Apr-88	Japan, Shima Bay	SHOWA MARU	Hydrochloric acid	B - 8 & 9
71	25-Jul-91	Hong Kong	WAN XIANG	Hydrogen peroxide	P - 5
72	05-Sep-91	Baltic Sea	BORE XI	Hydrogen peroxide	B - 5 & 8
73	30-Oct-87	Japan, Lake Hamana	EIKUKU MARU # 5	Isopropanol	B - 3
74	31-Oct-89	Japan, off Shikoku	INCHON PIONEER	Isopropyl alcohol	B - 3
75	22-Apr-88	Canada, BC, Gillies Bay	Unidentified ship	LPG, n.o.s.	P - 2 (+)
76	06-Feb-87	Germany, Dusseldorf	VTG 208	Lighter fluid	B - not listed
77	13-Mar-89	English Channel	PERINTIS	Lindane, other pesticides (nos)	P - 6 & 9
78	28-Jul-92	Trois Riv., PQ, Canada	Unidentified ship	Lithium hypochlorite, dry	P - 5
79	16-Nov-80	Canada, Cape St. Jam.	WESTWARD	Methanol	P - 3 & 6
80	02-Apr-88	Canada, BC, Victoria	Unidentified ship	Methanol	P - 3 & 6
81	31-Mar-88	Canada, BC, Vanc'ver	IVER HERON	Methanol	B - 3 & 6
82	24-Sep-87	Philippines, Manila	KING FAMILY	Methyl methacrylate monomer	B - 3 & 9
83	28-Jun-88	Canada, BC, Vanc'ver	Unidentified ship	Methylene chloride	P - 6
84	20-Apr-89	US, HI, Molokai Is.	KAMALU	Mixed flammables, insecticide	P - 3, 2, 6 & 9
85	24-Aug-85	Somalia, Mogadishu	ARIADNE	Multi- chemicals	P - 3, 5, 6 & 8
86	05-Dec-87	Spain, off nw coast	CASON	Multi- chemicals	P - 4, 3, 6, 8, 9
87	17-Dec-88	Singapore	REGAL VOYAGER	Naphtha	B - 3
88	21-Nov-87	Japan, Inland Sea	NORDTRAMP	Naphtha	B - 3
89	31-Oct-78	Canada, NB, Saint John	OCEAN FAITH	Naphtha	B - 3
90	30-Jan-87	Portugal, Sines	MERCATOR	Naphtha	B - 3
91	20-Mar-87	Canada, PQ, Quebec	STOLT CASTLE	Naphtha w/ tank wash residue	P - 3
92	18-Mar-87	Canada, PQ, Montreal	STOLT CASTLE	Naphtha, w/ sunflower oil	P - 3
93	16-Jul-87	UK, England, Dartford	DUKE OF ANGLIA	Naphthalene	P - 4 & 9
94	17-Dec-91	France, Cherbourg	PACIFIC PINTAIL	Nuclear material	P - 7
95	19-Jan-91	UK, Humberside	IVYBANK	Nuclear waste+copra expeller	B - 7 & 4
96	09-Sep-92	Netherlands, Rotterdam	POL EAST	Organophosphorus pesticide	P - 6 & 9
97	17-Jul-87	Dutch Antilles	PELICANO	Oxygen, pressurized liq.	P - 2 & 5
98	24-Nov-79	Canada, Qn. Charl. Sd.	GREAT LAND	Pesticide, liq., flam., tox., nos	P - 3, 6 & 9
99	26-Feb-85	Canada, NB, Saint John	MARIA ANGELICO	Phosphoric Acid	P - 8
100	01-Jul-87	S. Korea, nr. Busan	PARAVALOS	Phosphoric acid	B - 8 & 9

----- TABLE CONTINUED NEXT PAGE -----

**TABLE 14\* - "All Sample Events, Sorted by Substance", continued (Page 3 of 3)**  
**SUBST. SUMMARY (1974-93): GLOBAL MARINE CASUALTIES - ALL CLASSES**

No.	Date	Location	Vessel	Substance	Cat./Clas
101	07-Jan-87	France, Bay of Biscay	CHEM'L DISCOVE	Phosphoric acid	B - 8 & 9
102	10-Nov-83	Canada, NS, Halifax	WIEN	Phosphorus pentoxide, in wine	P - 8
103	15-Mar-90	English Channel	FATHULKHAIR	Potassium cyanide	P - 6 & 9
104	16-Oct-87	UK, Felixstowe	SILVERFALCON	Propanol residues	B - 3
105	19-Jul-91	Spain, Corunna	BALDER PHENIX	Propylene	B - 2
106	18-Mar-88	Sicily, Palermo	CAPO FALCONE	Propylene	B - 2
107	10-May-92	S. Korea, off Busan	STAINL'S PRINCE	Propylene glycol	B - not listed
108	11-Feb-85	Canada, ON, Sarnia	Unidentified barge	Propylene oxide	P - 3 & 9
109	11-Dec-90	North Sea	LOVERVAL	Pyridine	P - 3 & 6
110	02-Jul-86	Chile, Talcahuano	GOLDEN ORCHID	Resin solution, flammable	B - 3
111	03-Mar-87	English Channel	HORNESTRAND	Seismic gelatin & detonators	P - 1
112	14-Jun-84	Papua, New Guinea	B'rge CLOSEL L-43	Sod. cyanide & hyd. peroxide	P - 6&9, 5&8
113	14-Jun-84	Papua New Guinea	B'rge CLOSEL L-43	Sod. cyanide & hyd. peroxide	P - 6&9, 5&8
114	17-Jul-86	Strait of Malacca	GOLDEN CITY	Sod. hydrosulphite, formic acid	B - 4, 8 & 9
115	14-Mar-85	Canada, BC, Gold R.	Unidentified barge	Sodium chlorate (45% so/n)	B - 5
116	24-Sep-88	Singapore	MARKHAM BAY	Sodium cyanide	P - 6 & 9
117	23-Sep-81	Canada, QC, Montreal	MANCHEST.VANG'	Sodium cyanide	P - 6 & 9
118	01-Jan-81	N.Sea, UK, nr. Tees R.	ELK	Sodium cyanide	P - 6 & 9
119	07-Sep-91	US, NC, Wilmington	RECIFE	Sodium hypochlorite	P - not listed
120	25-Jan-92	US, LA, Morgan C.	unidentified barge	Styrene monomer	B - 3 & 9
121	08-Sep-88	US, MS, Natchez	KATHIE G	Styrene monomer	B - 3 & 9
122	23-Jun-88	Japan, nr. Shirokita	SAKURA	Styrene monomer	B - 3 & 9
123	22-Dec-80	Canada, QC, Quebec	STOLT CASTLE	Styrene monomer - inhibited	B - 3 & 9
124	29-Sep-81	Canada, ON, Sarnia	SILVER MAGPIE	Styrene monomer - inhibited	B - 3 & 9
125	19-Apr-83	Canada, QC, Montreal	STOLT SYDNESS	Styrene w/ linseed oil/carbonb	B - 3 & 9
126	13-Dec-78	Canada, QC, Montreal	CAST BEAVER	Sulphuryl chloride	P - 8
127	22-Dec-92	US, TX, Houst. Ship Ch	barge DUVAL 2	Sulphur, molten	B - 4
128	05-Mar-88	US, TX, Port Neches	MARINE FLORIDA	Sulphur, molten	B - 4
129	25-Dec-86	Sardinia	STAINLESS TRAD'	Sulphuric acid	B - 8 & 9
130	21-Dec-87	US, OR, coast	ELAINE D	Sulphuric acid	B - 8 & 9
131	13-Apr-89	Lebanon, off Beirut	ISOLA AZZURA	Sulphuric acid	B - 8 & 9
132	26-Apr-89	Canada, ON, Clarkson	Unidentified ship	Tallow (fatty acid)	B - not listed
133	01-Aug-90	Carrib. Sea, St. Martin	unidentified ship	Tetra-ethyl lead	P - 6 & 3
134	29-Jan-81	Canada, QC, Pt Cartier	CAST ORCA	Thionyl chloride	P - 8
135	02-Mar-89	Canada, PQ, Quebec	Unidentified ship	Toluene diisocyanate	P - 6
136	25-Aug-84	N. Sea, off Belgium	MONT LOUIS	Uranium hexafluoride	P - 7
137	14-May-89	Canada, QC, Montreal	Unidentified ship	Uranium hexafluoride, non-fiss.	P - 7 & 8
138	11-May-89	Indian Ocean	TROPIGAS FAR E.	Vinyl chloride monomer	B - 2
139	14-Jan-92	Gulf of Thailand	NAVKUN 4	Vinyl chloride monomer	B - 2
140	16-Nov-84	Adriatic S, Yugoslavia	BRIG. MONTANAR	Vinyl chloride, inhibited	B - 2
141	26-Jul-89	Canada, ON, Snell Lock	LAKE ANNE	Xylene	B - 3 & 9
142	03-Jul-92	Red Sea	ORIENTAL KNIGH	Yellow phosphorus	P - 4
143	30-Dec-88	UK, nr. Liverpool	DEEPPDALE H	caustic soda	B - 8
144	15-Dec-79	Spain, Barcelona	JAY AMBIKA	direct reduced iron	B - 4
145	07-Apr-89	Norwegian Sea	Soviet submarine	radioactive fuel and weapons	P - 7
146	13-Jan-84	N.Sea, UK, ne coast	DANA OPTIMA	s.nitrophenol pesticide (s/nos)	P - 6 & 9
147	19-Feb-86	US, CN, New Haven	KAPETAN ANTONI	swarf	B - 4
148	28-Oct-89	English Channel	MUREE	variety of chemicals, containers	P - various
149	06-Mar-87	Belgium, Zeebrugge	Herald, Free E'prise	variety of chemicals, on trucks	P - various
150	31-Dec-88	S. China Sea	NORDSUND	yellow phosphorus	P - 4, 6, & 9

\*from "Can Overboard! - A Global Summary of Marine Chemical Emergencies" by B.H. Mansfield, TSOCS Seminar, Vancouver: 07/Jun94

## **PRELIMINARY ANALYSIS**

From the tables presented here on a portion of the information base, and from three other summary tables like 13 and 14, sorted by date, vessel or category/class, some interim conclusions can be drawn:

- There is a wide range of chemicals and other dangerous goods which need to be considered as potential marine haz-mat emergencies;
- There have been significant numbers of Canadian incidents;
- There are relatively greater numbers of events involving Class 3 and 8 (flammable liquids and corrosive) substances;
- On a global basis, at least 1-2 major incidents can be expected yearly;
- There does not appear to be a specific vessel with many events;
- The emergencies examined to date are about equally divided between the "bulk" and "packaged" categories;
- With full data, substance, location and date trends can be determined;
- Land- or air-based case histories provide additional useful information.

## **ACKNOWLEDGEMENTS**

My thanks go to several groups for documentation of the background information from which this study continues to draw:

- To all the unfortunate people who report their marine accident details;
- To dedicated workers in government agencies who document the reports and provide response support and advice, or who seek the causes, and the preventive and countermeasures cures;
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2. Watson, P., "A Possible Solution", Hazardous Cargo Bulletin, Vol.2, No.3, p.22, 1981.
3. Spencer, L., "Explosive Lessons", Hazardous Cargo Bulletin, Vol.1, pp. - , 1980
4. Volpe National Transportation Systems Center, U.S. Dept. of Transportation, Report on the Maritime Transport of Hazardous and Noxious Substances, prepared for U.S. Coast Guard, Haz-Mat Branch, Nov. '91

**SOURCE ACRONYMS AND REFERENCES:**

<b>HCB</b>	-	HAZARDOUS CARGO BULLETIN, published monthly by Intapress Publishing Ltd., London, UK (cited in SOURCE column of tables as "HBC mm/yy")
<b>MPB</b>	-	MARINE POLLUTION BULLETIN, published monthly by Pergamon Press Ltd., Oxford, UK & Tarrytown, NY, USA (cited in SOURCE column of tables as "MPB mm/yy")
<b>HMI</b>	-	HAZARDOUS MATERIALS INTELLIGENCE REPORT, published weekly by World Information Systems, Cambridge, MA, USA
<b>MSC</b>	-	Proceedings of the MARINE SAFETY COUNCIL, published bimonthly by the US Dept. of Transportation, United States Coast Guard, Washington, DC, USA
<b>DGAIS</b>	-	DANGEROUS GOODS ACCIDENT INFORMATION SYSTEM, a computer program operated by the Transport of Dangerous Goods Directorate, Transport Canada, Ottawa, Canada
<b>NATES</b>	-	NATIONAL ANALYSIS OF TRENDS IN EMERGENCIES SYSTEM, a computer program held by the Environmental Emergencies Branch, Environment Canada, Ottawa, Cda.
<b>AMSTER.</b>	-	Bockholts, P. and Heidebrink, I., (Ed.) <u>Proceedings of "Chemical Spills and Emergency Management at Sea" conference, Amsterdam, Nov. 1988.</u> - Kluwer Academic Publishers, pp 325-343
<b>MALTA</b>	-	IMO/UNEP: <u>Proceedings of the Workshop on Combatting Accidental Pollution of the Mediterranean Sea by Harmful Substances, Malta, May 1989.</u> REMPEC, June 1990, pp 53-58
<b>VANC.</b>	-	CCPA/DOT/DOE/EPC: <u>Proceedings: "Dangerous Goods Emergency Response '86" Conference, Vancouver, Sept. 1986,</u> CCPA, Sept 1986, pp 269-281
<b>HALIFAX</b>	-	CCPA/DOT/DOE/EPC: <u>Proceedings: "Dangerous Goods Emergency Response '89" Conference, Halifax, May. 1989,</u> CCPA, May 1989, pp 297-301



## OVERVIEW OF HUMAN HEALTH RISK ASSESSMENT METHODOLOGY FOR CHEMICAL SPILLS

by

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### Introduction

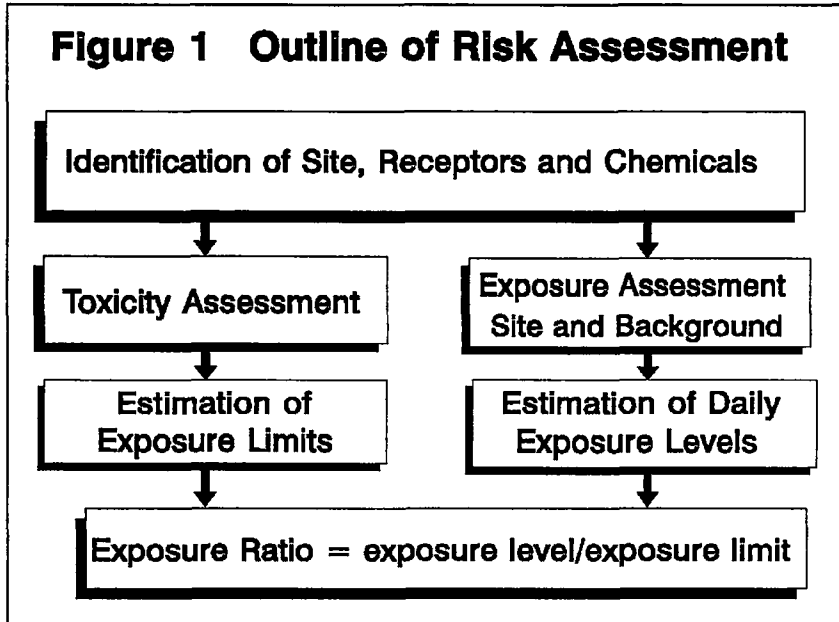
There are two basic processes for determining whether a chemical spill poses a threat to human health: (i) compare the resulting chemical concentrations to already-derived health criteria or cleanup guidelines that have been developed for the chemicals involved in the spill (*e.g.*, CCME, 1991); or (ii) conduct a site-specific human health risk assessment. Although the first process may be the most time and cost efficient method for initially determining whether a problem exists, the pre-existing guidelines are often derived using a series of conservative assumptions such that exceedance of these guidelines does not necessarily indicate a significant health risk to humans. Moreover, the guidelines invariably do not consider the site-specific conditions of the spill-impacted area that can have a significant bearing on the level of risk presented. As a result, site-specific human health risk assessment can be a valuable tool for determining whether or not clean-up is required for chemical spills which result in chemical concentrations in the environment greater than those specified in the guidelines. This paper discusses the basic methodology involved in the risk assessment of a chemical spill. A case study using the basic methodology described in this paper is presented in a subsequent paper in the proceedings by Willes and Treissman entitled "Case History - Development of Site-Specific Soil Clean-up Criteria Based on a Human Health Risk Assessment of a Former Wood Preserving Site".

### Basic Methodology

The methods used to predict the possible adverse effects to humans from exposure to chemicals originating from a chemical spill should be based on risk assessment procedures recommended by the regulatory agency(ies) with immediate jurisdiction over the affected area. Risk assessment procedures used by most regulatory agencies are based on the fundamental dose-response principle of toxicology. That is, the response of a receptor to chemical exposure increases in proportion to the chemical concentration in critical target tissues where adverse effects may occur (*e.g.*, the liver). The concentrations of chemicals in the target tissues depend upon the degree of exposure, which is proportional to the chemical concentrations in the environment where the receptor resides. The methods provided in this paper are consistent with the procedures used by regulatory agencies such as Health Canada, the U.S. Environmental Protection Agency and many provinces in Canada. However, since specific regulatory bodies on occasion may request variations in the approaches normally employed, proponents involved in spill clean-up are advised to consult with the appropriate regulatory authorities before conducting a risk assessment.

The four basic steps of the risk assessment procedure (see Figure 1) are:

- i) identification of the spill-affected area, receptors and chemicals;

**Figure 1 Outline of Risk Assessment**

- ii) estimation of the potential exposures received by the receptors of interest as a result of the chemical spill;
- iii) identification and assessment of potential hazards, and the recommendation of upper limits of exposure (*i.e.*, maximum exposure without measurable risks to health) for the chemicals of concern; and,
- iv) assessment of potential human health risks based on the comparison between the estimated exposures and the recommended exposure limits for the chemicals of concern.

These steps are described in greater detail in the sections that follow. It should be noted that quantitative risk assessment procedures may utilize deterministic analysis techniques or probabilistic (stochastic) analysis techniques. For deterministic analysis techniques, single point estimates are used to estimate model parameters, whereas, probabilistic analysis techniques use frequency distributions, rather than worst-case deterministic or point estimates, to represent receptor, site, and chemical parameters used in the numerical risk assessment model. Although there are advantages and disadvantages to each technique, probabilistic analysis techniques avoid the unrealistic risk estimates that can result from the combination of a myriad of upper-bound or worst-case assumptions for the various model parameters used in deterministic techniques. The risk assessor is advised to consult with the regulatory body with immediate jurisdiction over the risk assessment for advice on which technique is favoured.

### Step 1 - Identification of Site, Chemicals and Receptors

The first step of a risk assessment involves characterization of the spill-affected area and identification of the receptors and chemicals of potential concern. Using information on historical and on-going activities within and bordering the spill area, the risk assessor can get an early appreciation of the possible problem(s) with the site. Conducting a visit to the area and interviewing any users of the site may provide additional information.

An important site-specific variable in exposure assessment is the identification of the concentration of the chemical(s) of potential concern in the area affected by the spill. This is usually determined from site investigations which would already have been completed. However, additional on-site monitoring may be required in some cases. For each chemical of potential concern, point estimates (for deterministic procedures) or distributions (for probabilistic procedures) of the concentrations need to be defined for each environmental compartment of interest. If the number of chemicals identified at the site is large, chemical screening may be conducted such that the risk assessment is focused at the chemical's of greatest concern.

The types of people and their particular habits and characteristics are major factors in determining the rates of exposures to chemicals, and consequently the risks, from a chemical spill. Examples of receptors to consider could include persons living within or near the spill area at present or in the future or workers involved in clean-up and/or monitoring efforts. Important receptor characteristics or parameters to be considered in the risk assessment include body weight, volume of air inhaled per unit time, time spent indoors and outdoors on and off the site, ingestion/inhalation of soil and dust, ingestion of water, ingestion of locally grown produce and fish from local waters, *etc.* The numerical values for the various receptor parameters are subject to individual variability. In addition, some of the parameters may be positively or negatively correlated with each other (*e.g.*, body weight and amount of air breathed). The risk assessor should make every effort to ensure that all receptors within sensitive stages of the life cycle (*e.g.*, infants and the elderly) as well as receptors that are sensitive due to compromised health (*e.g.*, those with asthma, cardiovascular problems) or special needs (*e.g.*, expectant mothers) are considered in the assessment, if appropriate (*i.e.*, there is reasonable evidence that such receptors could be affected by the spill). This ensures that the results of the risk assessment are sufficiently stringent to ensure the protection of the health of these groups. Sensitive receptor groups can be evaluated in two ways: (i) define a receptor group containing only such types of individuals; or, (ii) ensure that the characteristics of sensitive individuals are encompassed in the frequency distributions of the parameters used in the assessment (*i.e.*, the sensitive individuals would be represented by the extremes of the frequency distribution of the parameter values used in a probabilistic assessment).

### Step 2 - Exposure Assessment

As indicated above, the assessment of potential occurrences of adverse effects from chemicals is based on the dose-response concept common to the responses of biological systems to chemicals, be they drugs, naturally occurring substances or undesirable chemicals in the environment (Doull *et al.*, 1980). Since it is not usually practical to measure concentrations of chemicals at the actual target site where the adverse response occurs within tissues and cells, these concentrations are estimated based on either the dose of the chemical that actually enters the receptor or, more indirectly, by the concentrations in various environmental media that act as pathways for exposure of the receptor.

The degree of exposure of receptors to chemicals from the environment therefore depends on the interactions of a number of parameters, including:

- The concentrations of chemicals in various compartments of the environment;
- The various exposure pathways for the transfer of the chemicals from the different environmental compartments to the receptors
- The behavioral and lifestyle characteristics of the receptors in the environment that determine the actual exposures through interactions of the receptor with the various pathways; and,
- The various physical, chemical and biological factors that determine the ability of the receptor to take the chemicals into the body from the exposure pathways.

- \* It should be emphasized that the physical/chemical characteristics of chemicals (e.g., water solubility, volatility, tendency to bind to particles, etc.) determine their behaviour in the environment. Therefore, knowledge of the physical/chemical characteristics of the chemicals involved is critical to selecting appropriate exposure pathways and to the estimation of the magnitude of exposure to chemicals through these pathways.

When conducting an exposure assessment, it is important to consider particular microenvironments (Lioy *et al.*, 1992; Schwab *et al.*, 1992; Whitmyre *et al.*, 1992). Microenvironments are defined as smaller regions within the spill-affected area characterized by specific ranges of environmental concentrations and physical features that would promote specific types of activities by potential users of the site. Analysis of microenvironments may identify areas where unacceptable exposures could occur that would be missed entirely using data averaging techniques to describe the site. The use of microenvironments therefore, improves the realism in exposure assessments.

It is also essential to evaluate all significant exposure pathways. If the exposure assessment fails to consider one or more significant pathways of concern, exposure may be significantly under-estimated, resulting in an under-estimation of the potential risks from the chemical spill.

Chemicals acting systemically must be absorbed into the body to cause adverse health effects, while chemicals acting locally do not require absorption; therefore, the data requirements for these two types of chemical exposure are different. For chemicals which act systemically, exposure should be expressed as the dose rate (U.S. EPA, 1992). The units of dose rate are usually " $\mu\text{g}/\text{kg}$  body weight/day". This unit describes the daily amount of chemical which is absorbed into the body relative to body weight. For example, if a 70 kg person absorbs 70  $\mu\text{g}$  of a chemical on a daily basis, the dose rate to that chemical would be 1  $\mu\text{g}/\text{kg}$  body weight/day. Any equation which is scientifically valid and can be shown to be an accurate method may be used for estimating dose rate.

For chemicals which act locally, the possible adverse effects which may occur from exposure to these chemicals are related to the concentration, time and frequency of exposure but are not usually related to the amount of chemical absorbed. As a result, it is not necessary to report exposure rate to locally-acting chemicals in terms of " $\mu\text{g}/\text{kg}$  body weight/day". Instead, it is more appropriate to express the exposure rate as the duration and frequency of contact as well as the concentration of the chemical in the media that is contacting the human

receptor. This information can then be used for comparison against some standard such as a maximum allowable concentration (MAC).

#### Background Exposure Assessment

Most of the chemicals considered in risk assessments are present within the environment independent of a spill incident, either from natural sources or due to other sources related to human activities (U.S. EPA, 1989). As a result, a risk assessment (and, therefore, an exposure assessment) also should be conducted based on the degree of exposure of the receptors to the selected chemicals independent of the spill (U.S. EPA, 1989). This background assessment provides a reference point for comparison of potential health risks related to exposures to the concentrations of the selected chemicals arising from the spill under investigation.

For the background exposure assessment, the same exposure pathways and receptors as used in the assessment of the spill-affected area should be examined. However, if additional routes of exposure exist from background sources that are not present at the spill site (*e.g.*, supermarket food, drinking water from a distant source), these should also be considered. Ambient concentrations of the chemicals of concern in local air, water, soil and food items should be estimated from off-site monitoring or the published literature, where available. Site-specific values (*i.e.*, ambient air concentrations of specified chemicals in the local area) should be used where available. In situations where site specific data are lacking, background concentrations in various media should be estimated from other similar areas in Canada, where possible.

Background exposure may be considered in two separate exposure assessment scenarios for each receptor. In the first case, exposure from the spill plus exposure from background sources of chemicals should be estimated. In the second case, exposure from background sources only should be estimated. This latter estimate describes the exposure a receptor would receive if the spill never occurred. These two separate assessments allow for the comparison of exposures received by persons potentially affected by the spill (*i.e.*, who reside within or near the spill-affected area) *versus* receptors who are removed from the spill site. This allows for an incremental comparison of exposures and risks.

#### **Step 3 - Toxicity Assessment**

In addition to the potential exposure determined for each receptor, the likelihood of adverse effects (*i.e.*, risk) occurring from exposure to a particular chemical also depends on its hazardous nature or toxicological characteristics. In general, data on the toxicological characteristics of a chemical are obtained from previous experiences involving exposure of receptors to the chemical, either from a variety of environmental sources or studies conducted under controlled laboratory conditions (Doull *et al.*, 1980). Exposure limits that would not result in adverse effects are developed for each chemical, based on the dose-response relationships demonstrated by these toxicological data.

The degree of exposure necessary to elicit an adverse response varies with the chemical and with the specific adverse effect involved. For example, a chemical may irritate the skin and respiratory system at certain rates of short-term exposure, damage the liver or kidneys following long-term exposure, or affect the immune system under other exposure conditions. Therefore, the assessment of potential risks of adverse effects due to chemical exposure requires the evaluation of rates of exposure that would be experienced under the

environmental conditions under investigation. For example, data on the adverse effects from exposure rates many times greater than those that could occur as a consequence of a chemical spill must be interpreted with caution when attempting to predict potential health effects and risks associated with the spill incident.

Exposure limits for chemicals are established to indicate a degree of exposure that will not result in adverse effects. They are usually expressed in terms of weight of chemical per unit body weight per unit time (e.g.,  $\mu\text{g}$  chemical/kg body weight/day) and are called allowable daily intakes (ADI), reference doses (RfD), tolerable daily intakes (TDI), risk specific doses (RsD), and other terms, depending on the regulatory jurisdiction involved and on the toxic properties of the individual chemical. The procedures followed in the development of exposure limits involve:

- selection of the most sensitive indicator of adverse effects, usually in the most sensitive receptor applicable to the situation under assessment; and,
- estimation of a degree of exposure that would not be anticipated to elicit adverse effects based on the toxicological characteristics of the chemical (i.e., dose-response profile).

Ideally, the best data for estimating exposure limits would be obtained from studies where the receptors of concern were exposed to the specific chemicals of interest. However, this requirement is often difficult to meet for humans due to ethical and moral considerations that preclude planned studies with chemicals of high toxic potency and no known benefits. Data collected from accidental exposures are usually complicated by exposures to mixtures of chemicals, inadequate information on the exact levels of exposure experienced, and lack of control of life-style variables within the exposed group. Therefore, exposure limits are usually established from toxicological data collected from various test systems, often using animals which have been exposed to the chemical of concern in a controlled laboratory environment. However, there are uncertainties associated with the extrapolation of such data from test animals to the receptors being assessed (e.g., rats to humans) and to real world situations where exposure levels are low and mixtures of chemicals are involved. Such data extrapolation between species requires the application of considerable scientific expertise and experience.

There are two basic but quite distinct methods for estimating exposure limits, with each approach yielding a different type of limit. Exposure limits vary according to whether a chemical is assumed to act as a genotoxic, non-threshold carcinogen (i.e., where zero risk is only accomplished by zero exposure), or, the chemical has an exposure threshold below which no observable adverse effects are expected (i.e., a No-Observable-Adverse-Effect-Level or NOAEL). A reference dose (RfD) is assigned as an exposure limit for chemicals which have demonstrated a dose-response threshold, do not cause cancer, or for chemicals which cause cancer only through secondary processes not involving alterations of genetic material. An RfD is calculated by applying a series of safety factors to the highest experimentally determined dose at which exposures to the most sensitive animal species were not associated with adverse effects (i.e., NOAEL). When the RfD is based on the NOAEL obtained from laboratory studies on animals, as is most often the case, the following safety factors are usually applied (i.e.,  $\text{RfD} = \text{NOAEL} \div \text{safety factor(s)}$ ):

- a ten-fold factor to account for interspecies differences between the test animal and humans;



- a ten-fold factor to account for sensitive human populations; and,
- a factor (usually 10-fold, but may be larger or smaller based on professional judgement) to account for any deficiencies in the adequacy or overall quality of the supporting toxicological database.

A risk specific dose (RsD) is assigned as an exposure limit for chemicals assumed to act as genotoxic, non-threshold carcinogens which cause tumours by modifying genetic material (e.g., mutations of DNA). A cancer potency factor ( $Q_1^*$ ) is determined for suspected carcinogens, based on dose-response extrapolation using a linearized multistage mathematical model (Crump and Howe, 1984). The  $Q_1^*$  is then used to calculate the RsD at a specified and acceptable risk level (for example, a risk level for developing cancer of one in one hundred thousand (1/100,000)). The risk level approach is adopted based on the assumption that "absolutely no chance of adverse effects" would only be observed when there is zero exposure. Therefore, an RsD based on a risk level of one in one hundred thousand would be determined as follows:  $RsD = 1 \times 10^{-5} / Q_1^*$ .

There are three basic options for determining exposure limits for use in the risk assessment:

- Option 1: Obtain the exposure limit directly from the appropriate regulatory authority (e.g., Health Canada, Environment Canada or appropriate Provincial Ministry).
- Option 2: Obtain the exposure limit from a computer database (in consultation with appropriate regulatory authority) (e.g., U.S. EPA's Integrated Risk Information System [IRIS]).
- Option 3: Develop the exposure limit through review and evaluation of the scientific literature (in consultation with appropriate regulatory authority).

The most straight forward approach is to use an exposure limit recommended by the appropriate regulatory body. However, the regulatory body may not have an exposure limit available for a particular chemical of concern in the risk assessment. Risk assessors may then consider the use (or modification) of exposure limits developed and published by other regulatory agencies or an authoritative group since such exposure limits have usually received extensive peer review. When regulatory-sanctioned exposure limits are not available, or are out-of-date based on new information, exposure limits can be developed through evaluation of toxicology literature using the same procedures as would be used in regulatory settings. In all cases, the exposure limits should be carefully reviewed by qualified scientists before the toxicity assessment is considered complete. In some cases, toxicological information is not available for some of the chemicals of concern. In such instances, structure-activity relationships may be applied, with caution, to enable the use of data from structurally similar chemicals to derive "surrogate" exposure limits. The rationale for the choice or development of exposure limits must be explained and the entire process must be thoroughly documented to allow for regulatory and public review.

#### Step 4 - Risk Characterization

The final step in a health risk assessment consists of a comparison between the exposure limits for the chemicals of interest and the predicted exposures from all pathways and routes associated with the chemical spill.

Depending on how the chemical acts and the specific requirements of the regulator, the risk estimates can be expressed as: (a) Exposure Ratio values (for both threshold and non-threshold response chemicals); (b) Hazard Quotients (only for threshold response chemicals); or (c) Unit Risk Values (only for non-threshold response chemicals). Essentially, the methods for calculating each type of risk estimate are mathematically identical; however, the approaches may have different implications for communication of risks. The specific regulator involved may have different preferences for the techniques used to express risk estimates. Therefore, proponents are advised to consult the appropriate regulatory bodies for direction on which approach is preferred. For the purposes of this paper, the Exposure Ratio value approach will be discussed.

Exposure Ratio values are calculated by dividing the predicted exposure by the exposure limit as shown in the following equation.

$$ER = \frac{\text{predicted exposure}}{\text{exposure limit}}$$

The potential risks from combined exposures to mixtures of chemicals with similar mechanisms of action from the spill area and background sources can be assessed by calculating a combined Exposure Ratio value for the chemicals as a group (e.g., naphthalene group, benzo[a]pyrene group, etc.).

Exposure Ratio value estimates are used to express the potential risks from exposures to the selected chemicals in order to facilitate the comparisons of risks between chemicals and different exposure scenarios (e.g., background versus the spill site), and to facilitate the estimation of risks from exposures to mixtures of chemicals that act on similar biological systems (e.g., all chemicals that cause liver toxicity, or kidney toxicity, or respiratory tract cancers).

The evaluation of Exposure Ratio value estimates can be applied with greatest confidence to situations where comparisons are made between two different exposure scenarios. This approach has proven to be particularly effective in communicating risks to the general public. For example, risk value estimates for chemical exposures resulting from a specific type of activity (e.g., dusts from a specific site) can be compared with Exposure Ratio value estimates resulting from exposures from normal ambient background concentrations of chemicals in dusts, or with risk value estimates from some other site. From such comparisons, the relative or incremental risks between the two or more different scenarios can be assessed with reasonable confidence, since the same methodologies are used in addressing each situation. Most of the uncertainties in such comparative risk assessments are related to the accuracies in estimating the concentrations in various environmental media that affect the different exposure pathways. Since the assumptions used in the estimation of exposure limits, in various exposure modifying factors and in different receptor characteristics, are common across scenarios that are being compared, any uncertainties in these parameters tend to cancel between the different scenarios.

For a threshold-response chemical, an Exposure Ratio value that is less than one indicates that the estimated exposure is less than the degree of exposure that is considered acceptable. Accordingly, risk value estimates for threshold-response chemicals that are less than one represent exposure scenarios that do not pose a significant health risk to exposed individuals. Risk value estimates that are greater than one represent scenarios that may present cause for concern. These values represent scenarios that are predicted to result in rates of exposure that exceed rates of exposure considered acceptable (*i.e.*, exposures that are greater than the exposure limit). Since there are many conservative factors used to derive exposure limits there is a considerable margin of safety between the exposure limit and rates of exposure that would produce overt, measurable adverse health effects. Nonetheless, a risk value estimate that is greater than one represents a health concern that should be closely evaluated to identify the reason for the elevated exposure ratio value, and possible sources of the occurrence of and exposure to the chemical identified.

For a non-threshold response chemical, an Exposure Ratio value that is less than one indicates that the rate of exposure is less than that attributed to a specified lifetime risk of cancer (*e.g.*, 1 per 100,000, or 1 per 1,000,000). Accordingly, risk value estimates for non-threshold response chemicals that are less than one (for Exposure Ratio value approach) or less than an acceptable level of risk (for Unit Risk value approach) represent exposure scenarios that do not pose a significant health risk to exposed individuals. Risk value estimates that are greater than one (for Exposure Ratio value approach) or greater than an acceptable level of risk (for Unit Risk value approach) represent scenarios that may be of cause for concern.

## Conclusion

This paper has described the basic methodology for completing an assessment of the potential human health risks presented by a chemical spill. The approach recommended involves a step-wise process in which the potential chemical exposures received by individuals due to their presence at or near the spill area are ultimately compared to exposure limits for the chemicals of concern. As part of the assessment, various assumptions inherent to the process, including the extrapolation of test data from animal studies to the human receptors under the conditions existing at the spill site are recognized and attempts made to understand and address the uncertainties involved. This can be accomplished through use of background assessments, with or without application of rigorous probabilistic analysis techniques. Once the risks have been estimated and described, risk management decisions related to clean-up criteria, site remediation, future site uses, *etc.* can be made with some authority to ensure that the chemicals associated with the spill do not adversely affect human health.

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**A CASE STUDY OF INDOOR AIR QUALITY  
INVESTIGATION AT ENVIRONMENTAL RESPONSE TEAM OFFICES**

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**ABSTRACT**

The U.S. Environmental Protection Agency's Environmental Response Team (ERT) conducted an Indoor Air Quality investigation in their offices located at Edison, N.J. Indoor air monitoring was conducted for preselected volatile organic compounds (VOC's) in consultation with health and safety professionals. A cost-effective Gas Chromatography/Mass Spectrometry (GC/MS) method for the preselected VOC's was developed. Low ppb levels of volatile organic compounds were detected at the ERT offices, including 4-Phenylcyclohexene (4-PC), one of the off-gas components of the carpets. The purpose of this paper is to report the analytical method used and indoor air quality monitoring studies conducted in the ERT offices.

**INTRODUCTION**

Complaints about poor indoor air quality and discomfort are often expressed when new carpeting is installed in a building. These complaints are usually traced directly or indirectly to the emission<sup>1,2,3,4</sup> of VOC's and 4-Phenylcyclohexene (4-PC) off-gassing from the carpet or glue.

In 1988, ERT had decided to move into newly renovated offices. During this time, much attention was focused on indoor air quality<sup>5</sup> at USEPA's Headquarters building at Waterside Mall in Washington, DC. Considerable attention was generated when numerous employees complained of health problems following the installation of new carpeting in the spring of 1988. Employees at the ERT office were very concerned that similar problems would occur in their own building, especially since the renovations that were going to take place included using the same carpet installed at the Headquarters building.

In response to the heightened awareness of indoor air quality concerns stemming from the Waterside Mall incident, ERT management decided to monitor their office building for VOC's. During the past five years, air samples were collected in the ERT offices. The sampling locations were selected in consultation with the health and safety officer and management. The indoor air samples for VOC's and 4-PC were collected on 600 mg charcoal tubes for a period of ten hours and analyzed by GC/MS quantitatively for selected compounds and semi-quantitatively for non-targeted compounds. During the course of this program, the EPA/ERT developed sampling and analytical methodologies for measuring indoor air contaminants.

### **SAMPLING**

During the past five years, indoor/outdoor air samples for VOC's and 4-PC were collected on 600mg two-stage charcoal tubes (400mg front and 200mg back activated charcoal separated with a foam plug) with Gillian monitoring pumps. A flow rate of 2L/min (for a total of 1200L sample) was used throughout the study in order to achieve lower detection limits. The charcoal front and back section of the tubes were desorbed with 2 mL carbon disulfide separately. The extracts were analyzed using a HP5996 GC/MS system.

### **ANALYTICAL METHOD**

The proposed method<sup>6,7,8</sup> uses full-scan GC/MS and a fused-silica capillary column for analyzing VOC's and 4-PC in air samples collected on charcoal tubes. The method was evaluated on charcoal tubes spiked with known quantities of compounds (Table 1) of interest, and air samples collected from office and outdoor environments. The method detection limits for the compounds tested were determined to be better than 0.2 ppbv at 99% confidence level. The accuracy and reproducibility was better than 80% and 10%, respectively. Quality assurance/quality control procedures were found to be essential criteria for obtaining reliable analytical data.

The analytical system consisted of an HP 5996 GC/MS equipped with a HP 7673 auto sampler and controlled by a HP-1000 RTE-6/VM computer data system equipped with the National Institute of Standard and Technology PBM Mass Spectral Library. The GC was equipped with a split/splitless injector port and a variable constant differential flow controller which maintains uniform column flow rate throughout the temperature program operation. A 30m x 0.32mm ID RTx-5 fused-silica capillary column with a 0.50 film thickness was used to separate the compounds tested. The sample extracts were analyzed by full-scan GC/MS with the MS operating in the EI mode (70ev), and scanned from 35-360 AMU at 5 scans per second. Two microliters of extract were injected in the GC. The GC was temperature programmed from 30°C (for 3 min) to 150° C at 4° C/min, and then ramped

to 220° C at 8° C/min.

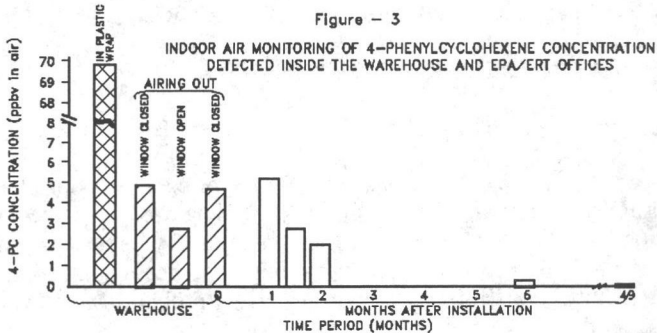
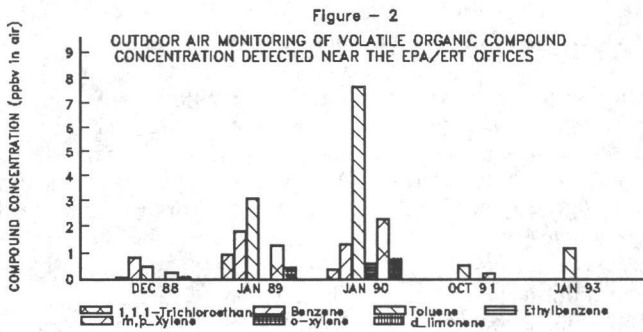
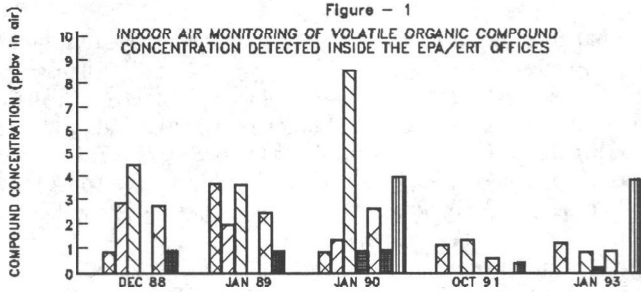
## RESULTS AND DISCUSSIONS

The analytical results of the indoor air quality survey are summarized in Figure 1, Figure 2, and Figure 3. Figures 1 and 2 illustrate the concentration of several VOCs (including benzene, toluene, ethylbenzene, m,p-xylene, 1,1,1-trichloroethane and d-limonene) in the indoor air in the ERT offices (Figure 1) and, simultaneously, in the outdoor air (Figure 2). This study shows the presence of low parts per billion by volume (ppbv) level of VOC's. Generally, VOC concentrations are higher in the offices when compared to outdoor concentrations though the levels of the aromatic compounds: benzene, toluene, ethylbenzene and xylenes, tend to correlate with outside concentrations. Relative concentrations for these analytes for the first sampling period (December 1988), are much higher which may indicate enhanced initial concentrations due to the renovations. Trichloroethane concentrations are relatively constant for the indoor samples for the five-year sampling period. High concentrations of d-limonene measured since 1990 may relate to pine oil-based cleaning material used by building maintenance.

Particular attention was given to the monitoring of 4-PC in air, illustrated in Figure 3. The carpet was aired out by unrolling it in a warehouse before installation. The concentration in the warehouse was 4.9 ppbv during the first week. The concentration dropped to 2.8 ppbv when windows were opened. In the second week of airing out the carpet with the windows closed, the 4-PC concentration went up to 4.7 ppbv. After the fourth week of airing out, the carpet was installed in the ERT offices in Edison, NJ. The concentration in the offices after installation averaged 5.2 ppbv in air. The concentration decreased to 2.8 ppbv two weeks later, and 1.9 ppbv after an additional two weeks. The new carpet odor was not detected six months after installation, during which time the 4-PC concentration in the air dropped to 0.31 ppbv. The concentration dropped to 0.026 ppbv after 49 months.

## CONCLUSION AND RECOMMENDATIONS

1. Low ppbv levels of VOC's were detected in the ERT offices.
2. By conducting this indoor air quality monitoring and taking steps to ensure the health of the employees (including airing out the carpet prior to installation, improving the ventilation by enhancing natural ventilation after installation), and through open communication with the members of ERT, any indoor air quality problems were avoided.
3. The GC/MS detection is the preferred method, because it is capable of unambiguous identification, confirmation and quantitation of most VOC'S at low ppbv levels.





4. Future efforts will be directed towards the effect of humidity on charcoal adsorption; extending the compounds list; use of other solvents including supercritical extraction (SFE) to desorb VOC's from charcoal tubes; and providing standard procedures for using charcoal-based methods for specific application.

## ACKNOWLEDGEMENTS

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**Table 1. Target Compound List for Charcoal Tube VOCs**

<b>Compound</b>	<b>Compound</b>
1,1,1-Trichloroethane	Cumene
Cyclohexane	Mesitylene
Carbon Tetrachloride	Alpha-methylstyrene
Benzene	1,3-Dichlorobenzene
Cyclohexene	1,4-Dichlorobenzene
n-Heptane	1,2-Dichlorobenzene
1,2-Dichloropropane	Benzyl Chloride
Trichloroethene	alpha-Terpinene
1,4-Dioxane	D-Limonene
Methylcyclohexane	4-tert-Butyltoluene
Methylisobutylketone	1,2,4-Trichlorobenzene
Toluene	Naphthalene
n-Octane	4-Phenylcyclohexene
Tetrachloroethene	n-Decene
Chlorobenzene	n-Decane
Ethylbenzene	n-Undecene
para-Xylene	n-Undecane
Bromoform	n-Nonanal
Styrene	n-Dodecane
ortho-Xylene	n-Tridecane
n-Nonene	n-Tetradecane
n-Nonane	n-Pentadecane
1,1,2,2-Tetrachloroethane	n-Hexadecane

## CASE HISTORY - DEVELOPMENT OF SITE-SPECIFIC SOIL CLEAN-UP CRITERIA BASED ON A HUMAN HEALTH RISK ASSESSMENT OF A FORMER WOOD PRESERVING SITE.

by

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### INTRODUCTION

The Alberta Environment Help End Landfill Pollution (HELP) Project has identified and investigated a number of wood preserving sites throughout the province. CanTox Inc. conducted a site-specific human health risk assessment for each of these sites. The following is a case study of one of these sites, describing how site-specific human health risk assessment was used to determine soil clean-up criteria, based on exposure to pentachlorophenol (PCP) contamination.

The human health risk assessment had four objectives: i) to quantitate the potential human health risk associated with exposures to selected chemicals identified on the wood preservative site; ii) to quantitate the potential health risks associated with exposures, assuming site remediation by removal of specific concentration ranges of chemicals in soils on the site, iii) to quantitate the potential health risks associated with ambient/background exposures to the same chemicals to provide a relative perspective to the results from i) and ii); and, vi) to recommend soil remediation criteria based on the predicted human health risk associated with the site "as is", with the two remediation scenarios, and with the background exposure scenario.

### METHODS

The basic risk assessment methodology followed for this case study was described earlier in the session in the paper by Davies and Wilson entitled "Overview of Human Health Risk Assessment Methodology for Chemical Spills". The risk assessment involved the comparison between the predicted exposure rate of selected receptors to chemicals from the site with the exposure limits (maximum recommended exposure rates) for the specific chemicals. This comparison was performed by calculating exposure ratios (ER), where  $ER = \text{predicted exposure} \div \text{exposure limit}$ . Probabilistic procedures based on a Monte Carlo analysis were used incorporating probabilistic frequency distribution relationships for various sites, receptors, and exposure and exposure limit characteristics. The Monte Carlo analysis was conducted using Crystal Ball<sup>®</sup> for Windows software, which sequentially selects values for the exposure/risk assessment model parameter from their frequency distribution functions. A total of 10,000 model iterations were executed, and the resulting ER values presented as an ER frequency distribution forecast. The ER frequency distribution forecast was presented graphically, and described in terms of the 50<sup>th</sup>, 95<sup>th</sup>, 99<sup>th</sup> and 99.9<sup>th</sup> percentiles (representing ER estimates for 50%, 5%, 1% and 0.1% of a population).

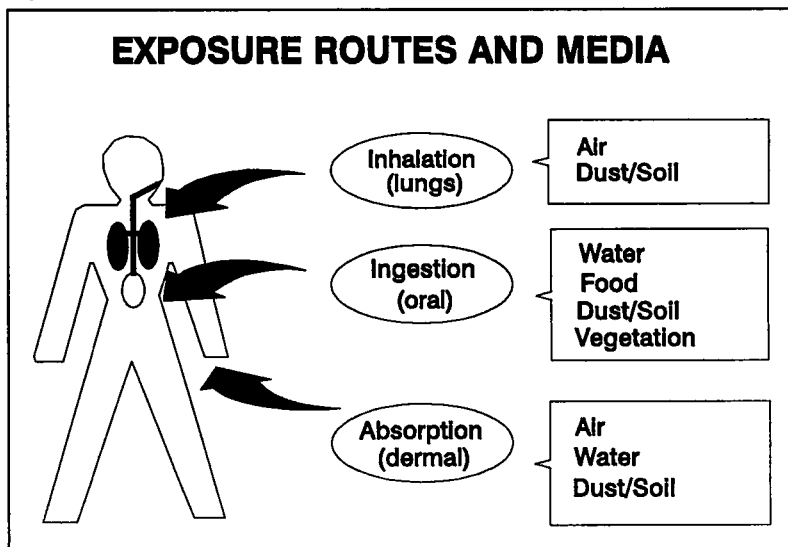
The chemicals of concern were identified based on chemical concentrations measured on the site, the extent of contamination, and on the relative toxicity of each chemical. A final list of chemicals was selected for the health risk assessment based on comparisons between the soil and ground water concentrations reported at the site, those recommended by the

Canadian Council of Ministers of the Environment (CCME, 1991), and through comparisons with known background concentrations of the chemicals. The chemicals selected for the human health risk assessment were pentachlorophenol, naphthalene, benzo[a]pyrene, and chlorinated dioxins and furans.

The receptors considered for this assessment were a child (2 to 5 years old), an adolescent (6 to 18 years old), and an adult (19 to 70 years old) living in a residence beside the site. It was assumed that the child and adolescent receptors moved away from the site at 5 and 18 years of age, respectively, and that the adult did not move near the site until 19 years of age. However, the composite receptor used to assess lifetime risks to carcinogens represented a combination of all three receptors and was considered to live beside the site for a 70-year lifetime.

The human exposure pathways assessed (Figure 1) included: i) inhalation, ingestion, and dermal absorption of chemicals associated with soil/dust from the site; ii) ingestion of chemicals associated with soil/dust blown from the site and deposited onto fruits and vegetables grown near the site; iii) ingestion of chemicals in drinking water from a ground water well; iv) inhalation and dermal absorption of chemicals during showering with well water; v) ingestion of beef and dairy products from cattle pastured and consuming water near the site; vi) ingestion of chemicals through consumption of fish from a pond close to the site; and, vii) ingestion and dermal absorption of water-borne chemicals while swimming in the pond. An agricultural food chain model was used to predict the concentrations of chemicals in beef and dairy products when the livestock grazed beside the site.

**Figure 1 Primary Exposure Pathways**



Four different exposure scenarios related to the site were considered in the human health risk assessment: an "as is" scenario, background scenario, and two clean-up scenarios. For the "as is" scenario it was assumed the site remained in its present condition (no remediation)

into the future. For site clean-up scenario #1, it was assumed that all the PCP concentrations that are currently greater than 1000 ppm were removed and replaced with soil from the lowest contaminated areas of the site (*e.g.*, < 0.05 ppm PCP, and appropriate concentrations of other chemicals typical of that part of the site). For site clean-up scenario #2, it was assumed that the PCP concentrations in on-site soils that were > 100 ppm were removed and replaced with soil from the lowest contaminated areas of the site. The background scenario provided the risk associated with exposures to the background concentrations of chemicals typical to the site under assessment, independent of those observed on the site (*i.e.*, as if the site did not exist).

The receptor types and characteristics considered for each scenario were identical, with the exception of soil, air, and water chemical concentrations. This relative risk assessment approach provided a reference point for comparisons of potential health risks between exposures to the concentrations of chemicals from background (naturally occurring) versus the site, using the same assumptions applied in the assessment of the other scenarios for receptor characteristics and exposure limits. This method of relative or incremental risk assessment is critical, providing a realistic perspective of the potential for occurrence of adverse effects from the site while considering the large number of conservative assumptions that are required in the risk assessment process.

For all four scenarios, the site where the wood treatment was conducted (described as the "on-site" area) was divided into three areas: i) the specific areas where the wood preserving activity occurred; ii) the area where PCP was stored; and, iii) the remainder of the site with lower concentrations of PCP. These divisions were based on the assumption that greater activity was expected in the areas on the site where operational structures still exist (*e.g.*, children would be more likely to play in these areas) and based on the distribution of chemical concentrations on the site. In this manner, any potential "hot spots" which could result in greater risks associated with exposures from the site were identified and accounted for. The probabilistic analysis was based on frequency distributions for the amount of time the receptors spend on these various sub-divisions of the site (see Table 1). It was assumed that each receptor spent specific periods of time outdoors on specific areas of the site (on-site exposure), beside the site (near-site exposure), and away from the site (background exposure) during the summer and winter (based on typical Alberta seasons), as well as time indoors at home (near-site exposure). The proportions of time each receptor spent in each location, including microenvironments (smaller regions) on the site are summarized in Tables 1 and 2.

**Table 1**      **Receptor Times (hours per day) Spent Indoors and Outdoors during Summer and Winter Seasons**

	Summer Hours		Winter Hours	
	Indoors	Outdoor	Indoors	Outdoors
<b>Child</b>	18	6	22	2
<b>Adolescent</b>	15	9	20	4
<b>Adult</b>	18	6	22	2

**Table 2**      **Percentage of Indoor and Outdoor Time Receptors Spent in Various Environments**

Type of Environment <sup>(1)</sup>	Percentage of Indoor and Outdoor Time in Various Environments per Receptor		
	Child	Adolescent	Adult
<u><b>Time Indoors</b></u>			
- in residence (near site)	90	67	90
- away from site <sup>(2)</sup>	10	33	10
<u><b>Time Outdoors</b></u>			
- near-Site <sup>(3)</sup>	17	11	33
- away from site <sup>(3)</sup>	33	55	33
- on-site <sup>(4)</sup>	50	34	34
<u><b>On-Site Time in Microenvironments</b></u>			
- wood treatment area	50	33	25
- PCP storage area	17	17	25
- remainder of site	33	50	50

<sup>(1)</sup> Description of the environmental locations where receptors spend varying amounts of time.

<sup>(2)</sup> Indoor and outdoor background represent time spent in locations not influenced by the site.

<sup>(3)</sup> The environment in the immediate vicinity of the site, outdoors, near the residence, that would be affected by dusts and vapours from the site.

<sup>(4)</sup> Since there are no closed structures on-site, all on-site time was outdoors. The time spent on various locations on the site was divided into small areas (microenvironments) based on physical features of the site that would promote various activities. For example, young children would be more likely to play on the areas of the site where there are pipes, tanks, culverts, *etc.* than on open areas of the site, whereas adolescents would spend more time on open areas of the site playing various sports, *etc.*

In addition to the dose or degree of exposure, the likelihood (*i.e.*, risk) of the occurrence of adverse effects from chemicals depends on the hazardous nature or toxicological characteristics of the chemical(s). The dose-response principle is central to the risk assessment methodology used and is comparable to the dose-response principles commonly used in pharmaceutical therapy. Data on the toxicological characteristics of the chemical are obtained from previous experiences involving exposure of organisms to the chemical either from a variety of environmental sources or studies on the effects of chemical exposures of the organisms under controlled laboratory conditions (Doull *et al.*, 1980; FDA, 1982). From these toxicological data, exposure limits that would not result in adverse effects are developed for each chemical. In the final analysis, exposure limits for chemicals are based on a consensus opinion and peer review by a number of experienced scientists with expertise in a wide range of scientific disciplines (*e.g.*, chemistry, physics, environmental sciences, biology, medicine, toxicology, pathology).

The level of exposure necessary to elicit an adverse response varies with the chemical and with the specific adverse effect involved. For example, a chemical may irritate the skin and

respiratory system at certain levels of short-term exposure, damage the liver or kidneys at other durations or levels of exposure, and affect the immune system under other exposure situations. Therefore, the assessment of potential risks of adverse effects due to chemical exposure requires the evaluation of usual levels of exposure that would be experienced under the environmental conditions of concern. Data on the adverse effects from exposure levels many times higher than those that could occur under practical conditions must be interpreted with caution when attempting to predict potential effects under "real world" exposure conditions.

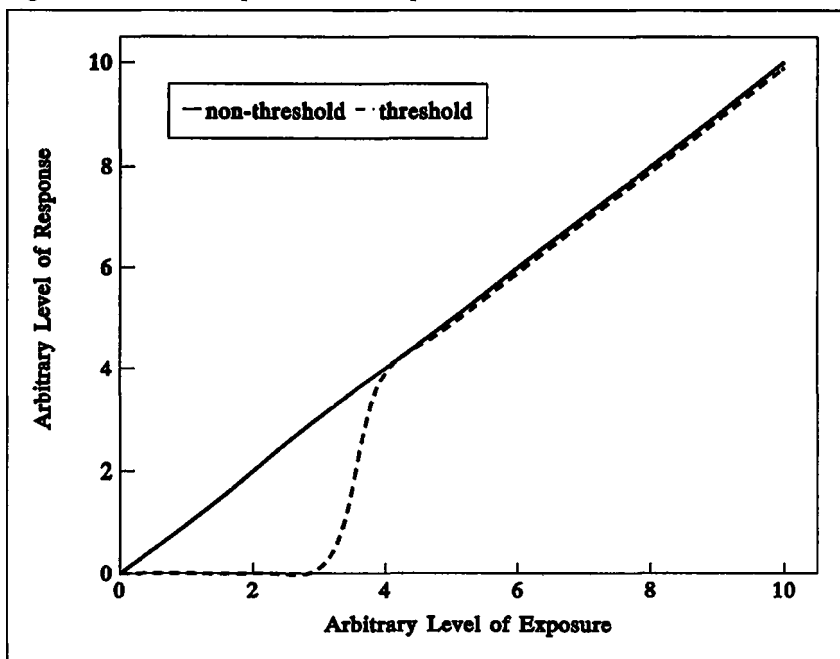
Exposure limits for chemicals are established to indicate an upper level of intake that would not result in adverse effects. They are usually expressed in terms of weight of chemical per unit body weight per unit time (*e.g.*, g/kg body weight/day) and are called allowable daily intakes (ADI), reference doses (RfD), permissible daily intakes (PDI), risk specific doses (RsD), and other terms, depending on the agencies involved and on the toxic properties of the individual chemical. The procedures followed in the development of exposure limits involve: i) selection of the most sensitive indicator of adverse effects, usually in the most sensitive organism applicable to the situation under assessment and the information available; and, ii) estimation of a level of exposure that would ensure that the adverse effects would not occur.

Two basic and quite different methods are commonly recognized by regulatory agencies for the estimation of exposure limits for chemicals (FDA, 1982; EPA, 1989). These are the non-observable-adverse-effect-level (NOAEL) - safety factor approach and the mathematical model-unit risk estimation approach. The use of the NOAEL-safety factor approach results in the establishment of a reference dose (RfD) for the chemical, below which no adverse effect would be expected. The use of the mathematical model-unit risk estimation approach results in the establishment of a risk-specific dose (RsD) which specifies the dose or exposure level of the chemical that would result in some specified level of risk of observing adverse health effects. The RsD approach is based on the assumption that the level where "absolutely no chance of adverse effects" would only be observed when the exposure level or dose was zero.

The NOAEL-safety factor approach is used where the available data demonstrate a threshold-type (*i.e.*, highly nonlinear) of dose-response relationship (Figure 2). Such a dose-response relationship suggests that there is a level of exposure below which no effects are observed and where the risks of adverse effects are zero for practical purposes. The generally accepted procedure for determining exposure limits for this type of chemical is to estimate the threshold exposure level or dose (NOAEL), then apply an extrapolation or safety factor to the NOAEL to estimate the exposure limit. The magnitude of the safety factor selected depends on the level of confidence in the available data, the nature of the toxic effect elicited, and the species from which the data are derived. As a general rule, the NOAEL is reduced by a factor of 10 (divided by 10) to account for potential differences in response between the test organisms and humans, and an additional 10-fold reduction in the NOAEL is applied to adjust for members of the population that are more sensitive to chemicals than average. This results in a total safety factor of 100-fold. Additional extrapolation factors of 2-fold to 10-fold, and sometimes larger, can be applied depending on the quality of the toxicological data available, the weight of the scientific evidence of the supporting data (FDA, 1982), or the severity of the effect.

The mathematical model-unit risk approach (EPA, 1989) is used for chemicals that show a non-threshold-type dose-response relationship (Figure 2) and where there is evidence of

Figure 2 Dose-Response Relationships



damage to genetic material. The dose-response curves for such chemicals are considered not to show an exposure threshold because the lesions produced are self-replicating since the damage to genetic material (*e.g.*, the mutation) can be passed on from one cell generation to the next during normal cell division. This means that once DNA damage has occurred, the presence of the chemical is no longer required for the expression of the adverse effects. Since there is a finite possibility of one molecule of a genotoxic chemical causing a mutation that results in a self-replicating lesion, there would not be an exposure threshold below which no risk of adverse effects would occur. It should be emphasized, however, that the assumption of the absence of an exposure threshold in such circumstances results in a conservative hazard assessment. Mathematical models are used for such chemicals to estimate an exposure level commensurate with risks acceptable to the individuals or groups involved (*e.g.*, the dose associated with a risk of one-in-a-hundred-thousand or one-in-a-million).

The final step in health hazard/exposure assessment consists of a comparison between the predicted exposures from all pathways and routes and the exposure limits (*i.e.*, the exposure level that would not produce adverse effects) for the chemicals. This comparison has been called the Exposure Ratio (ER) and is calculated by dividing the predicted exposure by the exposure limit, both adjusted appropriately for bioavailability, as indicated in the following equation.

$$ER = \frac{\text{adjusted exposure}}{\text{adjusted exposure limit}}$$



The potential risks from combined exposures to mixtures of compounds with similar mechanisms of action from the site and background sources were assessed by calculating a combined ER value for the chemicals as a group (*i.e.*, naphthalene group, benzo[a]pyrene group, and chlorinated dioxins/furans).

Stochastic assessment techniques (*e.g.*, Monte Carlo analysis) were used throughout the risk assessment. Therefore, the results of the risk assessment provided a frequency distribution diagram of the various exposure ratio (ER) values for different chemicals, receptors, and site scenarios.

The evaluation of ER values can be applied with greatest confidence to situations where comparisons are made between two different exposure scenarios. For example, ER values for chemical exposures resulting from a specific type of activity (*e.g.*, dusts from a specific site) can be compared with ER values resulting from exposures from normal ambient background concentrations of chemicals, or with ER values from some other site. From such comparisons, the relative or incremental risks between the two or more different scenarios can be assessed with reasonable confidence since the same methodologies are used in addressing each situation. Most of the uncertainties in such comparative risk assessments are related to the accuracies in estimating the concentrations in various environmental media that affect the different exposure pathways. Since the assumptions used in the estimation of exposure limits, in various exposure modifying factors and in different receptor characteristics, are common across scenarios that are being compared, any uncertainties in these parameters tend to cancel between the different scenarios.

The application of stochastic Monte Carlo analysis enabled the evaluation of the effects of variability in critical exposure and hazard assessment parameters (*e.g.*, body weight, respiration rate, food consumption, chemical concentrations, exposure limits) on the characterization of potential health risks associated with exposures to chemicals from the site. Suitable ranges of various empirical model parameters were incorporated into the risk characterization, rather than selecting single upper-bound or worst-case point estimates to the model parameters. Stochastic methods have been shown to provide a clearer understanding of the uncertainty in the characterization of potential health risks, and improve the reliability and understanding of potential risks associated with upper-bound and worst-case exposure/hazard scenarios (Thompson *et al.*, 1992; Whitmyre *et al.*, 1992a,b).

The results of the stochastic Monte Carlo analysis using the Crystal Ball® software were presented as Exposure Ratio (ER) frequency distribution forecasts, and as tabular data on the 50<sup>th</sup>, 95<sup>th</sup>, 99<sup>th</sup> and 99.9<sup>th</sup> percentiles of the ER values for the receptors. The risk characterization was based on several exposure scenarios to sources of chemicals from the site, and from background sources independent of the site. For this risk assessment the ER frequency distribution forecasts and summary statistics were based on 10,000 iterations of the Monte Carlo model.

The interpretation of the ER values estimated using a stochastic approach was based on an assessment of the ER frequency distribution forecasts and summary statistics for the site "as is" (no remediation), following clean-up scenarios #1 and #2, and for background exposure independent of the site. Action (additional remediation) was not required from a human health risk perspective if the following criteria were met: i) the ER values were less than 1.0 for 1% or 0.1% of the population potentially exposed from the site, or, ii) where background exposures resulted in ER values greater than 1.0, the ER values from the site were less than those predicted from the background assessment for 1% or 0.1% of the

receptor exposures. These criteria are considered conservative based on the extremes of the frequency distribution forecasts used, and because of the numerous conservative assumptions adopted in the selection of model parameters.

Considering the inherent conservatism, an ER distribution which is less than 1.0 indicates that the predicted exposure rates are below the exposure limit distribution and no adverse health effects would be expected. An ER distribution or a portion of an ER distribution greater than 1.0 indicates that the estimated exposure levels are higher than the recommended exposure limit distribution and may indicate potential hazards to health. However, the exposure limits used have substantial margins of safety, and any potential adverse health effects would only occur at exposures substantially greater than the exposure limit. In addition, it is important to remember that predicted ER distribution represents the potential risk distribution forecast (*e.g.*, if 99% of the predicted ER distribution is less than 1.0, this indicates that 99% of the exposure predicted would be less than the exposure limit).

By comparing ER distributions for exposures resulting from the source in question with those resulting from normal background concentrations of compounds of concern (where no adverse effects would be expected), comparative risk assessment procedures, such as those outlined above, are valuable in putting the overall exposure/hazard or risk assessment in perspective. It is highly unlikely that the potential health hazards from the site were underestimated by the procedures followed in this risk assessment.

## **SUMMARY OF RESULTS AND CONCLUSIONS**

The areas of the site that most affected human exposures to chemicals, and therefore had the greatest potential to cause human health risks, were identified. The stochastic procedures based on probabilistic Monte Carlo analyses that were used in the health risk assessment provided exposure ratio (ER) frequency distribution forecasts for exposures to receptor populations to chemicals from background sources independent of the site, from the site "as is" (no remediation), and following two sequential clean-up scenarios. The probabilistic analyses enabled the development of exposure/receptor behaviour scenarios that specifically recognized site characteristics and the distribution of chemicals on the site.

Preliminary risk assessment indicated that the female receptor had the greatest ER values from the predicted exposures to chemicals from the site "as is" (no remediation). Therefore, the evaluation of clean-up scenarios #1 and #2 were based on the predicted ER frequency distribution forecasts for the female receptor only.

The results of the "as is" (no remediation) assessment indicated that the predicted exposures to PAHs in the benzo[a]pyrene and naphthalene groups and exposures to chlorinated dioxins/furans resulted in ER forecasts less than one, or ER forecasts less than or similar to those associated with background exposures. Therefore, no adverse health effects would be expected from exposures to PAHs or chlorinated dioxins/furans from the site "as is". However, the characterization of the potential health risks from exposures of the specified receptors to PCP from the site indicated that site remediation may be warranted.

If the clean-up scenario #1 were implemented (reduction of soil concentrations to <0.05 ppm for areas with "as is" soil PCP concentrations >1000 ppm), the ER forecasts for PCP predicted were less than 1.0 for 99% of three receptor populations included in the risk characterization. For 0.1% of the adult female and the composite receptors, the ER forecasts predicted were 1.0 and 1.2, respectively. Due to the conservative nature of the stochastic

risk assessment, adverse health effects would not be expected in such populations. Implementation of site clean-up scenario #2 (reduction of soil concentrations to <0.05 ppm for areas with "as is" soil PCP concentrations > 100 ppm), indicated that adverse health risks would not be expected for 99.9% of three receptor populations included in the risk characterization.

Reduction of the site areas with the highest PCP concentrations through site remediation would also result in simultaneous reductions in the concentrations of the other chemical, and consequent reduction in the potential exposures and health risks from other chemicals on the site. Therefore, the results of the human health risk assessment indicated that no measurable health effects would be associated with the recommended soil criteria for clean-up scenario #1.

The two clean-up scenarios were included in the risk assessment in order to identify the maximum concentrations of chemicals on the site that would result in insignificant health risks and/or would result in risks similar to or lower than those associated with background/ambient exposures to the same chemicals independent of the wood preservative activities. The health risk information based on these scenarios could then be used by decision-makers, in conjunction with other factors (e.g., costs, socio-political considerations, alternate site uses), to decide the clean-up requirements and future uses of the site.

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## RISK AND HAZARD ASSESSMENTS IN THE CHEMICAL INDUSTRY

by

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Risk assessment (or analysis) and hazard assessment (or analysis) are often used interchangeably, when in fact, they closely inter-relate. The term "risk assessment" implies a more comprehensive study than "hazard assessment", and a risk assessment or analysis study will include a hazard assessment phase (refer to figure one). Risk assessment is the process of evaluating the probability that an event will occur, and interpreting the resulting data to determine acceptability of said event; mathematically,  $\text{Risk} = \text{Probability} \times \text{Consequence}$ . Hazard assessment identifies the sources and causes of potential accidents and the extent of their damage to property, people and the environment. This discussion will first present the concept of hazard assessment, and then show how it is incorporated into a risk assessment to satisfy environmental safety requirements.

Several methodologies for conducting hazard assessments were developed over the years; some are qualitative and some are quantitative. Qualitative methodologies are usually used in hazards identification. Some examples are safety or process reviews and checklist analyses.

Quantitative hazard assessment methods are used to numerically rank hazards and their consequences at a facility. Some examples of these are the "What If" Analysis, Failure Modes, Effects and Criticality Analysis (FMECA) and the Hazard and Operability (HAZOP) Study. There are also two well known logic methods, the Fault Tree Analysis (FTA) and the Event Tree Analysis (ETA).

These assessment methods while serving a similar purpose, give different kinds of results in varying degrees of specificity (refer to Table 1). A checklist analysis gives a general evaluation of a facility's overall safety status, and the information obtained is dependent on the level of detail of the questions on the checklist used. A HAZOP study, on the other hand, is a formal structured technique used to assess the safety of a particular piece of equipment on process, by matching guide words with operation parameters to determine the consequence of a specific failure. The result of this study is a table of potential failures and causes.

Regardless of the hazard assessment method used, the probability of a mishap can be analyzed to determine whether the consequences from said mishap are deemed unacceptable to the facility, regulators or the public. Risk assessment

is a tool which can be used by management when making decisions regarding choices of equipment and operating procedures. This kind of decision making has become essential in the chemical industry because of stringent regulations. The resulting data from a risk assessment study on two types of pressure release devices ,for example, used on a piece of equipment which stores a toxic gas, will indicate which device is better at controlling releases safely while maintaining air quality standards.

Method/model	Primary purpose	Resulting data
<b>Safety Review (Process Review)</b>	A walk-through inspection of an existing facility with the main aim of improving the overall safety and performance of the plant.	Qualitative descriptions of potential process safety problems with corresponding recommendations for corrective actions.
<b>Hazard and Operability (HAZOP) Study</b>	Identified process deviations that could lead to undesirable consequences threatening plant safety and the environment.	Identification of hazards and operating problems, assessment of their significance and corresponding existing safety measures and recommendations for changes, usually laid out in tabulated form.
<b>Fault Tree Analysis (FTA)</b>	Provides a method for graphically modeling the various basic reasons for a particular system failure (top event). They may include equipment malfunction, external factors, and human error.	A logic model for system failures using Boolean logic gates (such as AND, OR) to illustrate how various factors can combine to create a system failure on "top event."

Table 1

The risk associated with a particular operation is calculated by determining the consequence(s) of any possible accident and computing the probabilities of occurrence or frequency of the same. These values are obtained from: (a) equipment and instrument failure rate or repair rate data; and (b) human error probabilities and recovery probabilities. Both sets of data should be facility specific, taken from records maintained on operations at the facility.

For a new facility, generic failure and repair rates may be obtained from trade organizations such as IEEE, since the facility does not yet have a history of these events. For any facility, the evaluation of human error and recovery probabilities are more difficult in many ways. A fair estimate may be derived by dividing the number of errors by the number of opportunities

for errors under certain facility conditions.

Data from risk assessment calculations are usually represented graphically. Depending on the goal of the study (whether extent of human injury or damage to the environment or property), values for accident frequency are plotted against accident severity or consequence. Two common representation methods are risk contours and f/n curves. Risk contours allow for comparison of average risks to individuals from several activities or events. The f/n curve clearly illustrates the relationship between accident frequency and severity, the higher the frequency the fewer the fatalities.

Depending on the chosen method of study, risk and hazard assessments may require teams of professional and/or technical personnel with various degrees of expertise. For example, a HAZOP study should be done by a multi-disciplinary team (of technicians, plant operators and engineers) using a structured brain storming approach, whereas the FMECA can be performed by one experienced analyst. Risk assessment calculations are done by expert professionals in the field of study.

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## **The Development of A Mobile Decontamination Unit for Emergency Response**

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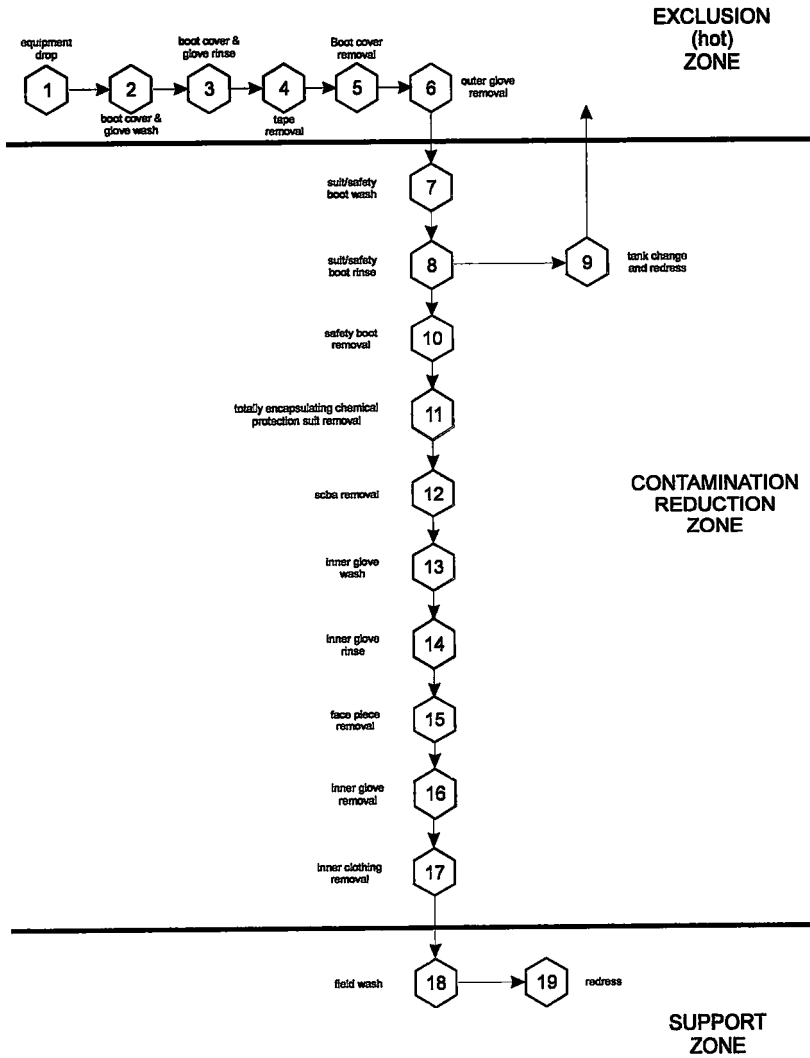
### **ABSTRACT**

*This paper describes the design of a new generation mobile decontamination unit. The basic requirements of decontamination are reviewed. These include hot-zone decontamination, final scrub-down, suit removal, and final cleanup. The new unit will include facilities for decontamination, changing and suiting up. The vehicle is to be constructed on a forty-eight-foot trailer and will be self contained including a power supply. Contaminated water will be collected in isolated tanks for future disposal.*

A decontamination program must minimize response personnel's contact with contaminants during the removal of personal protective equipment, prevent spreading of contaminants to off-site areas and prevent continual exposure. Most emergency responders utilize a decontamination line whereby the degree of contamination decreases as you move through the line. This decon line can consist of up to nineteen different stations. Figure 1 shows the layout of a typical nineteen station decon line.

Before one can select the appropriate decontamination procedure, one must evaluate many variables: type of contaminant, amount of contaminant, hazards and risks associated with the contaminant, type and level of personal protective equipment, work function and location of contamination. Once the hazards and risks of the material are analyzed, the number of decontamination stations may be reduced. However, at many spills, the identity of the spilled material(s) is not known until after the first entry. In this situation, a nineteen-station decontamination line would have to be in place before the first entry team entered the hot zone.

The decontamination equipment and supplies should be selected based on availability and whether they can be decontaminated for reuse or easily disposed. Table 1 lists the recommended equipment/supplies for decontaminating personnel and protective clothing. Most of the equipment is inexpensive and readily obtained at a hardware or department store. It is recommended that emergency responders have all the necessary decon equipment in their response inventory.



**Figure 1: Standard Decontamination Line Layout**

Several manufacturers have portable decontamination showers that are easily assembled. The showers usually consist of PVC poles that snap together to form the shower structure. Some units come with a self-contained bottom liner made of 6 mil polyethylene. The shower may have a single shower head configuration or have crisscrossing spray. Depending on the degree of decontamination required, these showers can be used in conjunction with the decon line or as the sole means of decontamination.

There are several difficulties with the traditional decontamination line. If the spill is in a remote area, a hardware or department store may not be found. Depending on the season, not all the necessary equipment will be available. For example, children's wading pools are very difficult to find during the dead of winter. The decon line requires dedicated personnel at each station to assist the site entry team with decontamination. The decon team should be dressed in the equivalent level of protection as the response team. There are some circumstances when the decon team can wear one less level of protection. This means that response agencies would have to maintain a large protective clothing inventory.

In choosing the wash/rinse solutions, several factors have to be considered: solubility of the contaminant(s), compatibility of solution with the contaminant(s) and the equipment, accessibility of the solution, the effectiveness of the solution, storage, handling and disposal requirements of the solution and the hazards associated with the cleaning solution. Water is easily obtained and can be stored on site without added safety controls. In addition to being the most readily available it generates no toxic fumes or contaminants of its own and has a minimal effect on the physical properties of most protective clothing materials. As a result, a water and decon solution are used most frequently, regardless of the solubility of the contaminant. One must be careful when selecting the decon solution. Several different agents have been suggested for use as the decon cleaner: sodium carbonate, trisodium phosphate, spic & span, calcium or sodium hypochlorite, hydrochloric acid, laundry detergent and dishwashing soap. Many of these agents can damage the protective clothing. One should avoid anything that contains abrasives. The most recommended decon solution is simply dishwashing soap and water.

Hazardous material spills often occur in unpopulated areas where a continuous supply of water is not available. In these incidences water has to be transported in. Depending on the magnitude of the spill, the water will have to be stored in pails, drums or pumper trucks. The cost of having water brought to the site can be phenomenal if the area is quite

Table 1: Recommended Equipment and Supplies for Decontamination Lines

Plastic drop sheets for placing contaminated tools/equipment and outer protective clothing
Large plastic garbage cans (lined) or drums for storing contaminated clothing which must be discarded
Soft-bristled, long-handled brushes for washing off contaminants
Buckets or garden sprayers for rinsing
Large galvanized tubs, stock tanks or children's wading pools to hold wash and rinse solution. These containers must be large enough to place a booted-foot in, and should not have a drain unless the drain is connected to a containment tank
Wash and rinse solutions
An appropriate means of containing and collecting contaminated wash/rinse solutions spilled during decon
Paper towels (or cloth) for drying clothing and equipment
Shower facilities for full body wash

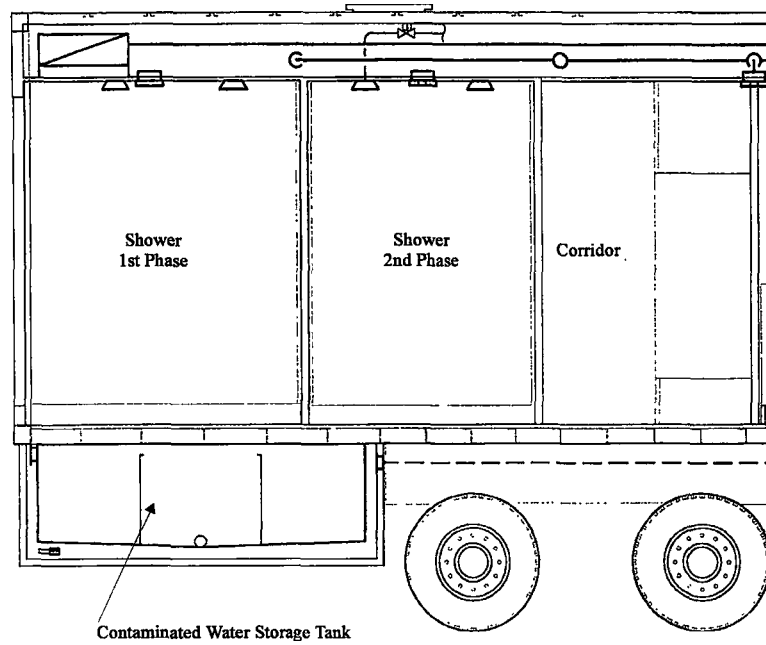
remote. The transporting in of water becomes an even greater problem when the spill occurs during the winter. Winter spills mean that the responder must find a way to heat the water or be forced to decontaminate using cold water.

The decon line is exposed to outside environments that means that personnel are also exposed. If it is precipitating, the ground could get quite slippery making slips and falls a concern. In extreme cold conditions, personnel could become ill because of removing their clothing outdoors. A shift in wind direction could also put personnel at risk. A risk of ground contamination also exists. As one moves from one decon station to the next, the water can get splashed around. This is especially true during the suit and safety boot wash and rinse stages. It is not always easy to contain or collect spilled water. This results in the spread of contamination. Although the amount of contaminated water lost would be expected to be small, the risk still exists.

The ideal situation would be to have a self-contained decontamination station. A station that is not exposed to outside environmental conditions and has its own source of water and electricity. In some cases, a building or facility exists outside of the hot zone and it can be used to set up the decon station. Many fire departments perform the bulk of their decontamination back at the station. They will quickly hose down on site and return to the station. As a result, personnel remain in potentially contaminated clothing for extended periods, innocent bystanders are put at risk and the contaminants are spread to the transport vehicle.

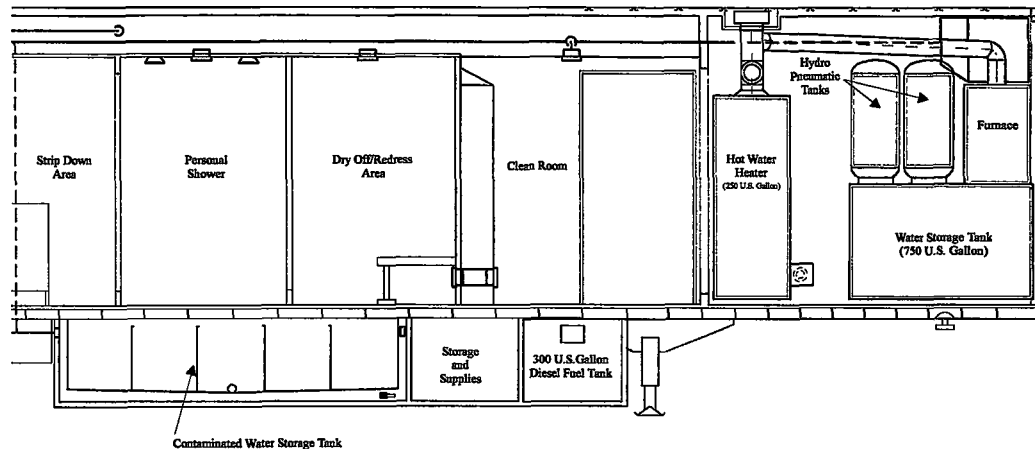
Mobile De-Con Systems Limited of Mississauga has designed a mobile decon unit (patents are pending) that would greatly assist emergency responders. The unit is a forty-eight-foot trailer that is fully self-contained. It has three distinct sections, decontamination area, clean room and mechanical room. The decontamination area is a graduating system, where a person can proceed from gross contamination through a series of showers to systematically reduce the contamination level. As the responder enters the unit, he/she immediately enters the first phase shower. It is in this shower that the outer protective clothing is decontaminated. From there one enters the second phase shower where the inner clothing is decontaminated. Figure 2 shows the side view layout of the first and second phase showers. Once the responder has finished the second shower he/she moves into the personal shower phase. To accommodate mixed sexes, two personal showers exist. Each one consists of a strip down area, a shower and a dry off/redress area. Figure 3 shows the side view of the personal shower area, the clean room and the mechanical room.

The principal behind the three shower system is simple. Outer clothing has the greatest chance of becoming contaminated. The first shower will remove the gross contamination. The chance of contamination in subsequent layers of clothing is minimal unless you get fully immersed in the hazardous product. To ensure that inner clothing is not contaminated, one can proceed through the second shower. The third shower is a personal shower. Each shower has an infrared sensor allowing for hands-free operation. Each shower head will provide a sixty second wash. The shower area is virtually barrier free to allow easy access from one stage to the next. On one side of the first two showers there is a corridor with disposal and/or storage bins for the removal of protective clothing



48 foot trailer

**Figure 2: Side View of Mobile Decontamination Unit  
1st and 2nd Phase Showers**



**Figure 3: Side View of Mobile Decontamination Unit  
Personal Shower Area, Clean Room and Mechanical Room**

and the storage of self-contained breathing apparatuses. Figure 4 shows the floor plan for the decontamination area. There is an emergency exit between the second phase shower and the personal shower. Besides providing an alternate means of escape, this door allows for a barrier free egress for emergency decon personnel who have brought an injured person through on a stretcher.

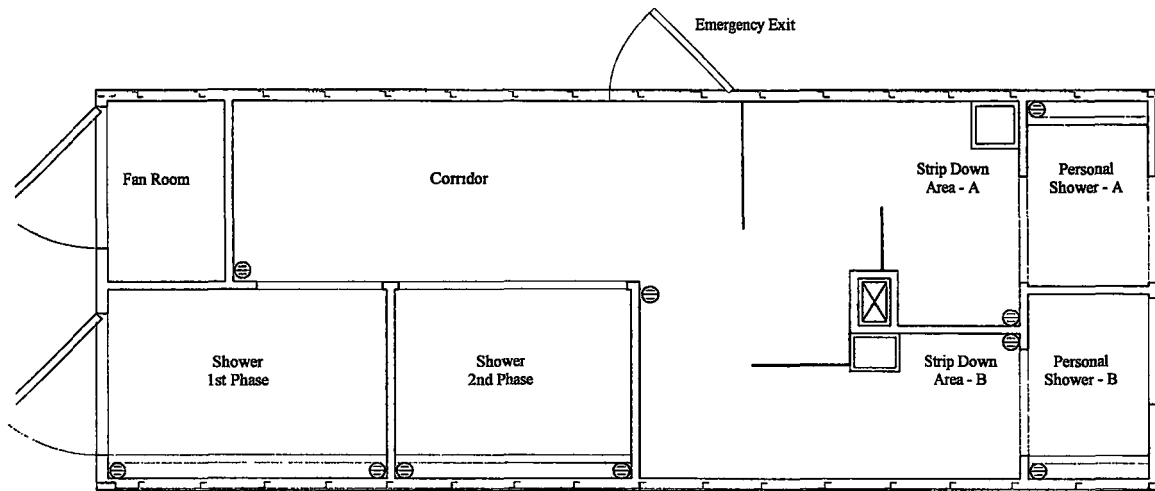
From the decontamination area, one enters into a clean area. This area can be used for a variety of functions. It can serve as a debriefing room, a protective equipment storage room or as a dressing room for site entry.

To prevent spread of contamination, the decontamination area is maintained at negative pressure and the clean room under positive pressure. The shower area is vented through a HEPA (high efficiency particulate) filter before being released to the atmosphere. The positive/negative pressure feature is unique to this unit.

The front portion of the unit is the mechanical room. In this area the water tanks, water heaters, diesel generator and furnace are housed. Access to this area is obtained either from the clean room or from the front of the unit. See Figure 5 for the layout of the mechanical room. The mechanical system has the ability to heat water from a cold water source. The water storage tank and water heater have a 750 U.S. gallon and 250 U.S. gallon storage capacity, respectively. The water system is tempered to allow for different water temperatures in each of the shower areas. The system has the capability of decontaminating up to thirty people per hour providing there is a continual water supply. If there is no water supply on site, for example a fire hydrant, the storage tank can be refilled using water tanker trucks.

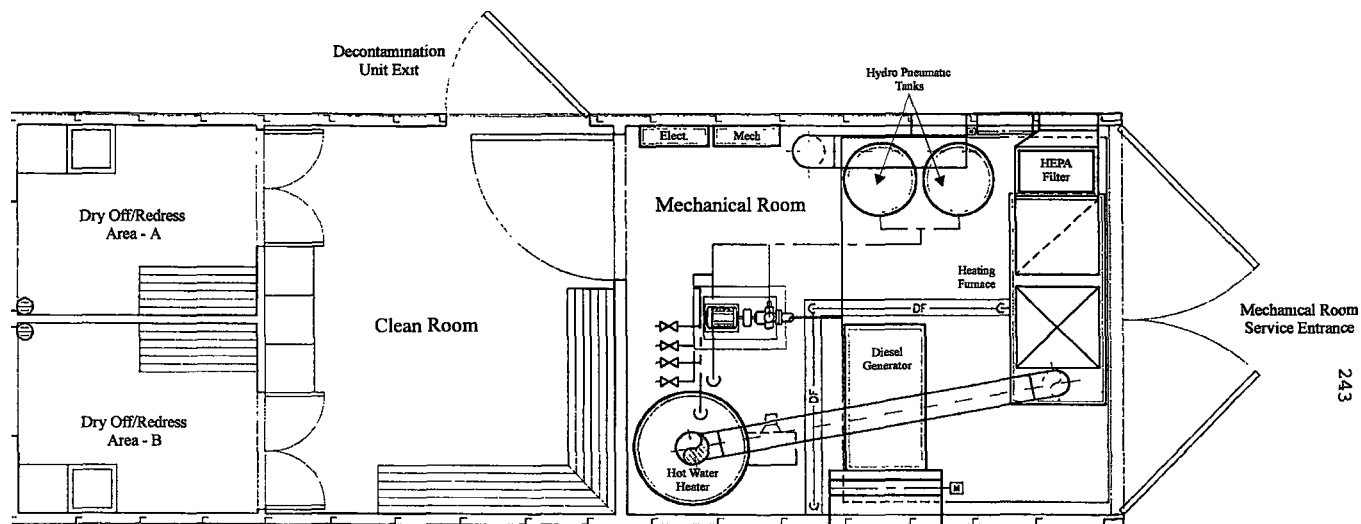
Other features on the unit will include two waste water storage tanks and a land connection. The first tank will contain the water from the first shower area. This tank would be expected to contain the highest level of contaminants. The second tank will hold water from the second phase and personal showers. The chance of this water being contaminated is minimal. The waste water tanks can be accessed from the exterior in order to take water samples to determine the degree of contamination. If the water is contaminated, it can be emptied by a licensed waste carrier. If the water is found not to be contaminated, it can be drained on site. The land connection will allow one to operate directly from electricity if available. If an electrical source does not exist, the unit can be operated by a diesel generator. A diesel fuel storage tank is attached below the unit. If the generator, furnace and water heater are all operating, the unit will function for 2.4 days before the diesel tank would have to be refilled. During summer operations, when the furnace would not be required, the unit will operate for 3.3 days.

Due to the design of the mobile decon unit, the number of decon personnel can be reduced. It would be ideal to have one additional person assisting with the wash down of the suit and with its removal. However, since the first two showers are large enough to accommodate two people, the entry team can decon in pairs and assist one another. If this procedure is used, one would not be required to have extra decon personnel. This would reduce the emergency responder's need to maintain a large protective clothing inventory.



**Figure 4: Floor Plan - Decontamination Area**





**Figure 5: Floor Plan  
Clean Room and Mechanical Room**

The advantages of this unit are numerous. The self-contained water system solves the problem of storing and heating water at remote spill sites. The number of people for the decon team is reduced thus decreasing the amount of personal protective clothing one must keep on hand. The amount of equipment and supplies needed to decontaminate is greatly reduced. All that are required are the unit, a tractor and a driver. Personnel are no longer exposed to the environment. Spread of airborne contaminants is reduced. The risk of uncontained contaminated runoff is eliminated. The exposure risk to innocent bystanders is eliminated as no one leaves the site without being decontaminated.

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