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## Groundwater Plume Development from a Complex Organic Mixture

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### ABSTRACT

Creosote is a complex mixture of polycyclic aromatic hydrocarbons (PAHs), heterocyclic compounds and phenolic compounds. The fate of plumes originating from mixtures of this type is complicated since the solubility and environmental persistence of the constituent compounds can vary greatly. The purpose of the present study is to evaluate the applicability of Raoult's law as a dissolution model for creosote at a field research site. In the laboratory component of this work, batch tests were conducted to evaluate the ideality of creosote. Batch results were then used to calculate expected initial concentrations of creosote compounds at a field site where a volume of soil containing coal tar creosote was emplaced below the water table. Transfer of organic compound mass from creosote to groundwater was characterized with intensive sampling of the developing plume and the dissolving source.

Results indicated that Raoult's law provides a reasonable prediction of batch test concentrations for 4 of the 10 compounds evaluated. A dissolution model based on Raoult's law and the concentrations from the batch test also provided a reasonable prediction of dissolution from the field source for three of four compounds evaluated. It was noted that throughout the source, concentrations of the more soluble compounds (m-xylene and naphthalene) became more variable with time while the degree of variability remained constant for the less soluble compounds (dibenzofuran and phenanthrene). The evolving ratios between compounds were predictable with the Raoult's law model. However it was necessary to extend the model well past the duration of the field experiment in order to fit all the data. This was taken as an indication that creosote was heterogeneously distributed in the original source. The increase in variability of the more soluble compounds with time has implications for evaluating mass flux from complex organic sources at contaminated industrial sites.

## INTRODUCTION

Many products and wastes derived from coal and oil contain varying amounts of PAHs, heterocyclic compounds and phenolic compounds. Examples of these types of materials include coal tar, creosote and petroleum sludges. They are often complex in composition, with constituents that vary widely in aqueous solubility. As a result, a complex groundwater plume may evolve if these types of mixtures are allowed to enter the environment. Typically, it is difficult to predict the resulting groundwater composition since the complete composition of the parent material is often not known. Also, even if the parent material is fully characterized the equilibrium solubilities of the constituent compounds may not be predictable by the simplifying assumption of ideal behaviour. Since many of these compounds are aerobically biodegradable (Meuller et.al. 1989) a first step in evaluating the environmental risk associated with a contamination occurrence may involve investigation of the expected degree natural attenuation (Salanitro, 1993). In order to do this, it is necessary to evaluate the mass flux of contaminants to groundwater.

The research discussed in this paper is part of the Coal Tar Organics in Groundwater Program at the Waterloo Centre for Groundwater Research and is ongoing. The objective of the overall program is to conduct research on the environmental behaviour of mixtures of coal tar organics, specifically, PAHs, heterocyclic compounds and phenolic compounds. In this paper we present results from a laboratory batch dissolution test and from an emplaced creosote source at a field site. Creosote was selected as the source material because it is comprised of a wide range of PAHs, heterocyclic and phenolic compounds that are found in other coal- and oil-derived mixtures. In the following, we compare laboratory and field dissolution results with predictions according to Raoult's law and provide preliminary conclusions. The purpose of this comparison is to evaluate the validity of applying Raoult' law as a dissolution model for creosote at field research site and other sites where groundwater is affected by similar mixtures. For the research site, this work will be used to estimate the mass flux of creosote compounds to groundwater so that the rate and processes of natural attenuation can be evaluated.

## BACKGROUND

### Creosote Properties and Environmental Significance

Creosote is used as an industrial wood preservative and is a thin oily liquid that may vary from yellow-green to black in colour. Since it has a density slightly greater than that of water and is composed of hydrophobic compounds it is classified as a dense nonaqueous phase liquid (DNAPL). In general, creosote may consists of up to 200 chemicals (Meuller et.al., 1989): approximately 85% PAHs, 10% phenolic compounds and 5% oxygen-, sulphur-, and nitrogen-heterocyclic compounds. The solubility of the components varies by several orders of magnitude.

In Canada, it is reported that creosote contamination of soils, groundwater and surface waters is known to be occurring at 24 past or present creosote-handling sites (Environment Canada, 1993). There are currently 27 creosote wood treatment facilities in operation in the country. It is estimated that almost 1400 wood treatment facilities, half of which are inactive, exist in the United States (USEPA, 1992). More than 60 of these sites are on the USEPA National Priorities (Superfund) List.

## Dissolution

When a compound partitions between two phases to the degree that equilibrium is reached the chemical activities for the compound are, by definition, equal in both phases such that (Lane and Loehr, 1992):

$$a_i = x_i^a \gamma_{b_i}^a = x_i^o \gamma_{b_i}^o \quad (1)$$

where  $a_i$  is the activity of solute  $i$ , the superscripts  $a$  and  $o$  signify the aqueous and organic phases, respectively,  $x_i$  is the mole fraction of  $i$  in each phase and  $\gamma_{b_i}$  is the activity coefficient of  $i$  in each phase. A simplification of this equilibrium relationship is often applied on the basis of Raoult's law. This law was originally used to define the linear relationship between partial pressure of a component in the headspace over a multi-component liquid and the mole fraction of that component in the liquid (Laidler and Meiser, 1982). In terms of partial pressure, a liquid is termed "ideal" if it conforms to this linear relationship. For the extension of Raoult's law to partitioning between an aqueous phase and an organic mixture, components in the mixture are said to display ideal behaviour if they partition linearly to the aqueous phase in proportion to the product of their mole fraction in the organic phase and their mole fraction solubility.

Two assumptions are inherent in this approach (Mackay et.al., 1991): 1) the activity coefficient in the organic phase is equal to unity - a reasonable approximation for organic mixtures composed of compounds with similar chemical properties and 2) the inverse of the solute activity coefficient is equal to the mole fraction solubility of the component. Incorporating these two assumption into equation 1 gives the mole fraction form of Raoult's law :

$$x_i^a = x_i^o X_i^a \quad (2)$$

where  $X_i^a$  is the mole fraction solubility of for the pure component in contact with water. Rewriting equation 2 in terms of the concentration gives (Shiu et.al., 1988):

$$C_i^a = x_i^o S_i \quad (3)$$

where  $C_i^a$  is aqueous concentration and  $S_i$  is the pure component liquid solubility. For compounds that are solid in pure form and at the temperature of the given system, liquid phase solubility can be calculated with the following (Shiu et.al., 1988):

$$S_l = S_s \exp[6.8(T_m/T-1)] \quad (4)$$

where  $S_s$  is solid solubility,  $T_m$  is melting point ( $^{\circ}$ K) and  $T$  is the system temperature. For compounds that are solid at the system temperature, the calculated liquid solubility will be greater than the solid solubility but, as pointed out by Mackay et.al. (1991), the dissolved concentration can never exceed the latter. Values of these parameters for the compounds selected for this study are provided in Table 1.

Several studies have examined the degree to which various compositionally complex organic mixtures conform the Raoult's law model of ideal behaviour. Cline et.al. (1991) determined, through batch-type testing, that a variety of 30 gasolines conformed closely to Raoult's law. Aqueous partitioning of eight PAHs from four different diesel fuels was investigated with batch tests by Lee et.al. (1992a) and determined to be well described (within a factor of two) by

**Table 1. Creosote compound properties and initial concentrations**

	Molecular weight*	Melting point* (deg C)	Solid solubility* (mg/L)	Liquid solubility* (mg/L)	Creosote composition (mg/L) (n=8)
m-Xylene	106.2	-48	200	200	39659
Phenol	94.1	43	82000	123650	14486
2,6-dimethylphenol	122.2	27	7800	8164	200
Naphthalene	128.2	81	31.7	112.00	98943
Phenanthrene	178.2	101	1.3	7.40	127414
Anthracene	178.2	216	0.07	5.5	12708
Dibenzofuran	168.2	86	10	40.2	45055
Carbazole	167.2	247	1	159	3374
Pyrene	202.3	156	0.14	2.80	40315
1 m-Naphthalene	142.2	-22	28.5	28.50	19701

Fraction of total mass identified

0.39

\* Information sources: WCGR, 1992 and Verschuere, 1983.

\*\* all analysis performed after amendment with additional compounds (m-xylene, carbazole, p-cresol and phenol)

assuming ideal behaviour. A similar degree of agreement was reported by Lee et.al. (1992b) for partitioning of PAHs from eight different coal tar samples, also with batch tests. Priddle and MacQuarrie (1994) examined the solubility of creosote with a dynamic column experiment. In a mass transfer rate test, five of the seven PAHs for which they analyzed conformed to ideal behaviour within a factor of two.

#### Field Site

The field research site is located at Canadian Forces Base (CFB) Borden, approximately 80 km northwest of Toronto, Ontario, Canada. It is in an unused sand pit situated approximately 350m north of a municipal landfill that operated from 1970 to 1976. Several hydrogeological studies have been conducted at this location over the past 15 years. Geology and local-scale hydrogeology of the area was discussed in detail by MacFarlane et.al. (1983). Mackay et.al. (1986) discussed the hydrogeology and groundwater quality in the sand pit area. Only details relevant to dissolution of the creosote source are discussed here.

The site is underlain by an unconsolidated sand aquifer consisting of medium- to fine-grained sand. These deposits are glaciolacustrine in origin and grade into silts and clays at a depth of approximately nine metres. MacFarlane et. al. (1983) and Nicholson et. al. (1983) discussed the inorganic chemistry and migration of a groundwater leachate plume originating from the landfill and underlying the sand pit study site at depths ranging from 6 to 7 m. From the water table to the top of the leachate plume, groundwater is largely unaffected by the landfill. A study of the groundwater flow system in the sand pit was conducted by Linderfelt et.al. (1994) at the same time as the study reported herein. They reported that the water table in the sand pit ranges from the surface to a depth of approximately 1.5 m. Estimates of hydraulic conductivity by Mackay et. al. (1986) indicated a mean value of approximately

$7 \times 10^{-5}$  m/s. Mean porosity was estimated at 0.33 and the average linear velocity of groundwater was estimated at 0.091m/day

Chemistry of background groundwater (unaffected by the leachate plume) at the site was examined by Nicholson et. al. (1983) and Mackay et. al. (1986). The groundwater is relatively hard with low dissolved organic carbon. Dissolved oxygen was determined to be variable but in general the aquifer was aerobic with oxygen ranging up to 8.5 mg/L. Data collected through this study indicate that the dissolved oxygen concentration in groundwater directly upgradient of the creosote source is 2 to 3 mg/L.

## **METHODS**

### **Sample Analysis**

The analytical methodology used for the study was developed for quantification of creosote compounds in groundwater, sand and pure creosote. Compounds selected for analysis were intended to be representative of the main groups of compounds found in creosote and included two phenolic compounds (phenol and 2,6-dimethylphenol), five PAHs (naphthalene, 1-methylnaphthalene, anthracene, pyrene and phenanthrene) and two heterocyclic compounds (carbazole and dibenzofuran). M-xylene was included in the analytical suite as a representative petroleum hydrocarbon. Analysis was also conducted for several other compounds but due to the variable availability of analytical standards, only the 10 compounds above were analyzed throughout the whole experimental period.

Groundwater samples (typically 45 mL) were prepared by adding 9 g NaCl to promote partitioning of all analytes and 1 mL 1N HCl to enhance partitioning of phenolic compounds. Samples were then capped and allowed to stand for 24 hours before addition of 3 mL dichloromethane. Samples were then placed on a shaker for 20 minutes at 350-400 rpm and 1 mL of the solvent was removed to an autosampler vial. Pure creosote was prepared for analysis by dissolving a 10  $\mu$ L sample in 10 mL dichloromethane and then transferring 1 mL to an autosampler vial.

Extracts were injected into a Hewlett Packard 5890 Gas Chromatograph (GC) equipped with an HP7673A autosampler and Flame Ionization Detector (FID). The temperature program for analysis was as follows: 40 °C for 0.5 min, 15 °C/min to 300 °C, hold 10 min. The carrier gas was helium with a flow rate of approximately 24 mL/min. The injector temperature from the GC was 275 °C, FID temperature was 325 °C and injection volume was 3 $\mu$ L.

### **Creosote Characterization**

Raw creosote was amended with certain compounds so it would be more widely representative of typical composition (Meuller, 1989). To 69.5 kg of creosote the following compounds were added: 0.45 kg carbazole, 0.50 kg p-cresol, 1 kg phenol. M-xylene was also added (3 Kg), to provide a compound representative of petroleum hydrocarbon sites. The density of the modified creosote was 1.03 g/mL.

### **Batch Dissolution**

A batch dissolution test was conducted to evaluate the effective solubility ( $S_e$ ) for selected compounds. Additional details of the experiment are provided by Malcolmson (1992). Into

each of three glass crimp-top hypovials a quantity of creosote was added (between 4.21 and 6.51 g) and the remainder of the bottle was filled with background Borden groundwater (between 62.28 and 72.66 mL). The bottles were then sealed with teflon-lined caps and stored in the dark at approximately 10 °C for one month. One water sample was removed from each bottle for analysis of equilibrium aqueous concentration and duplicate samples of creosote were removed from each bottle for analysis of equilibrium creosote concentrations.

### Field Source Emplacement and Monitoring

The creosote source was emplaced hydraulically upgradient of an existing multi-level bundle piezometer network. The system was first used for the joint Stanford-Waterloo natural gradient tracer test conducted from 1982 to 1985 (Mackay et al., 1986). The network has been modified and added to in subsequent studies, including this one, and the current layout of the near-source piezometers in relation to the creosote source is shown in Figure 1. Since this paper is concerned only with data collected within the source, subsequent description will focus on methodology directly related to the source.

The creosote source, shown in Figure 2, was emplaced on August 28, 1991. Details of the source installation are provided by Malcolmson (1992). Sealable sheet piling (Starr et al., 1991) was vibrated into the ground in a rectangular array (5 X 1.5 m). The sand inside the sheet piling was excavated after it was dewatered with two shallow dewatering wells. The source sand was mixed with creosote in a cement mixer at less than 5% creosote by volume; laboratory testing had indicated that it should be effectively immobile at this concentration. A total of approximately 74 kg of creosote was added to approximately 5800 kg of sand.

Borden sand was not used for the source material since the addition of creosote to the sand would result in some decrease in porosity which would inhibit the movement of groundwater through the source. Instead a coarser sand was used, with a hydraulic conductivity of approximately  $3.59 \times 10^{-4}$ , based on sieve analyses (Devlin, 1994) - approximately 5 times greater than Borden sand. Porosity of the source sand was estimated at 0.31 (Malcolmson, unpublished data) and it was calculated that with the creosote addition the porosity would effectively decrease to approximately 0.29. Work in progress will provide a detailed evaluation of groundwater flux through the source. However, preliminary hydraulic modelling indicates that the flux rate through the source should be similar to the ambient groundwater flux rate in the vicinity of the monitoring system. On that basis, a total flow rate through the source of  $0.204 \text{ m}^3/\text{day}$  ( $0.030 \text{ m}^3/\text{day}/\text{m}^2$  cross-sectional area) was used as an estimate of the amount of groundwater contacting the source.

Bundle piezometers were installed within the source at locations shown in Figure 2. Each piezometer consisted of either 11 or 13 monitoring points, separated by a vertical distance of 20 to 30 cm and constructed of 3 mm ID stainless steel tubing. To install the piezometers, a 5 cm ID aluminum tube fitted with an aluminum tip was vibrated into the ground with a vibrating hammer. The tip was then knocked out of the end of the aluminum tube and the bundle was inserted. The aluminum tube was then pulled out of the ground allowing the sand to collapse around the bundle.

Samples have been collected from a few selected piezometers within the source on an approximately monthly basis, up to the present. In addition, more intensive "snapshot" sampling of approximately 30 points within the source, was conducted several times since the source was emplaced. In this paper we will discuss a time series of samples collected from

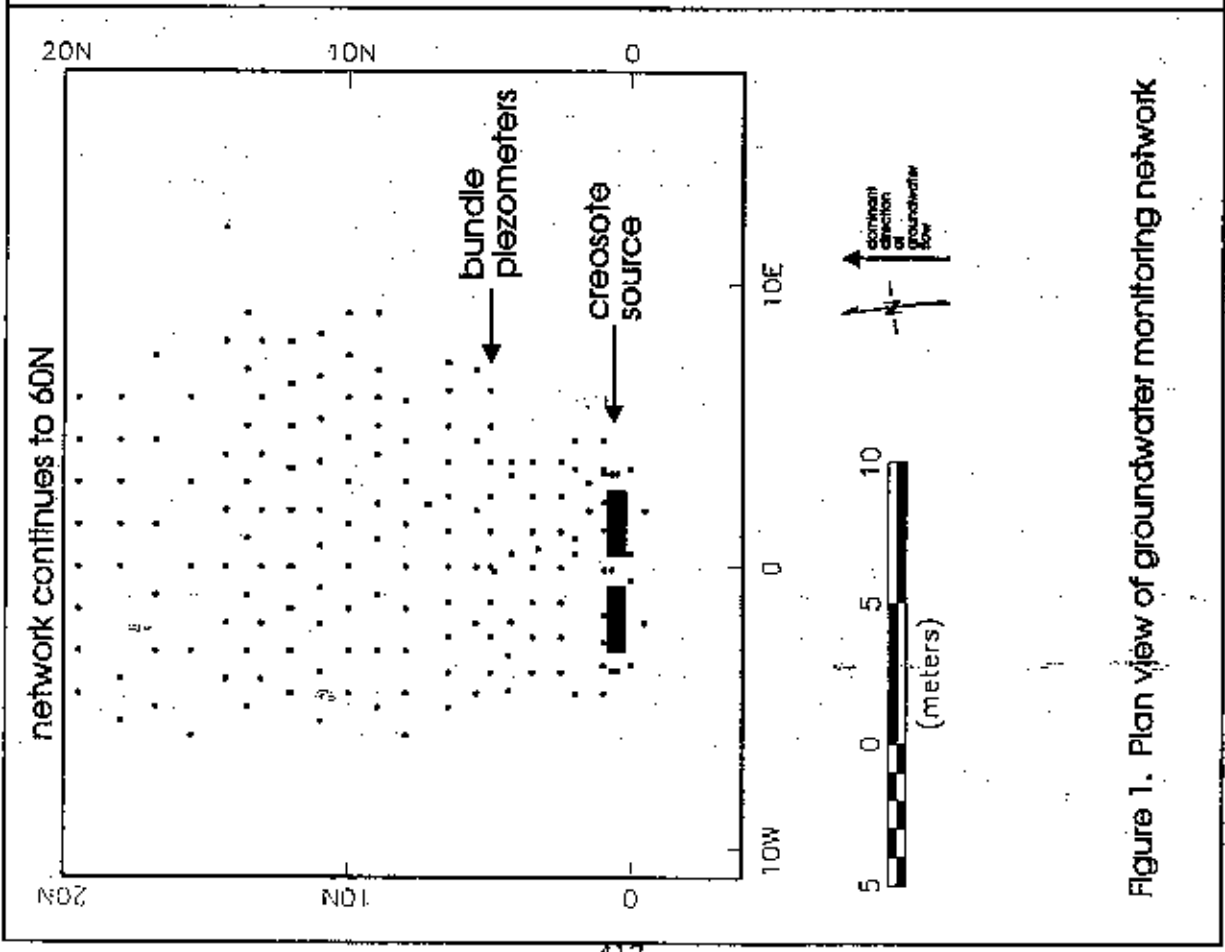


Figure 1. Plan view of groundwater monitoring network

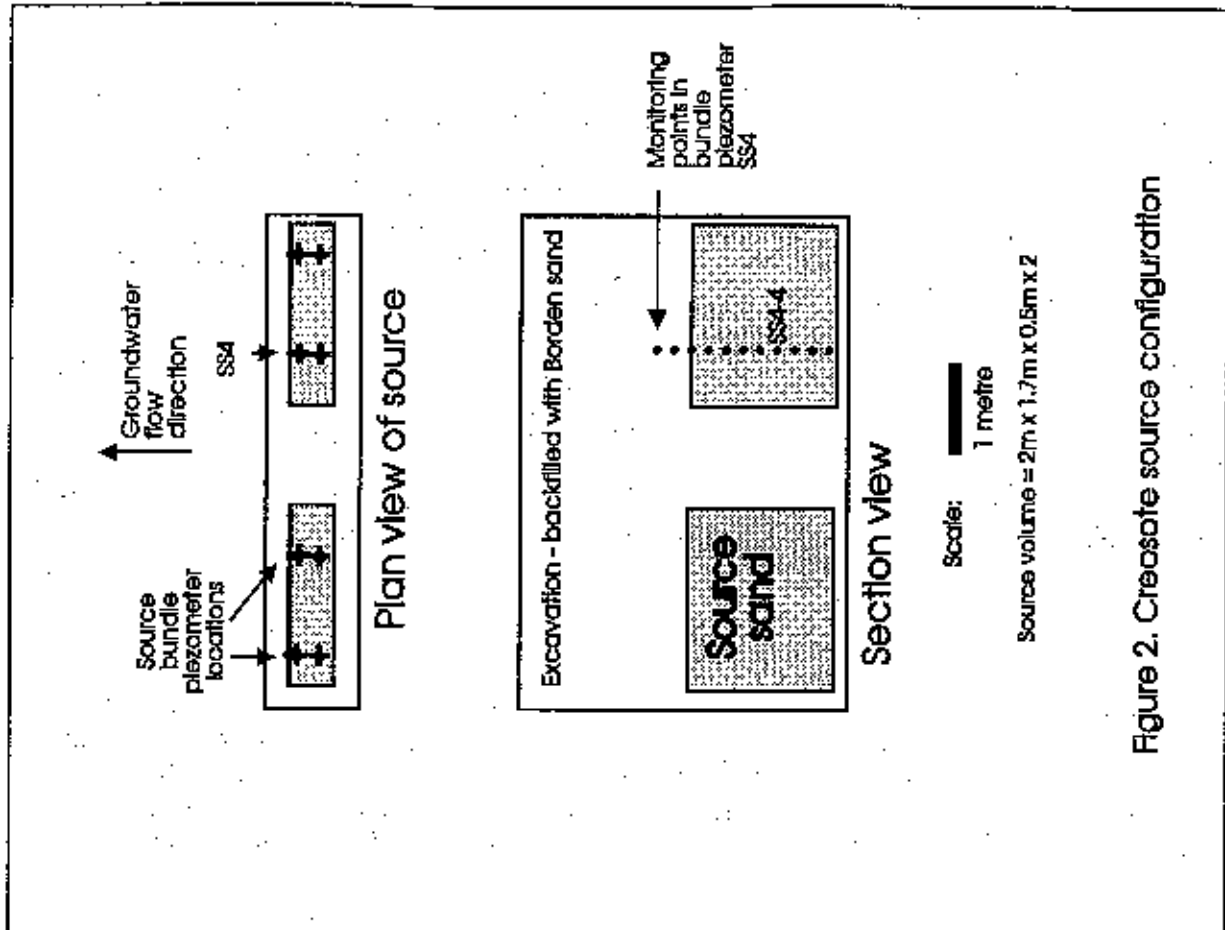


Figure 2. Creosote source configuration



one point (SS4-4 shown on Figure 2) and two sets of snapshot samples collected at 55 and 1008 days. All groundwater samples were collected in 60 mL hypovials using a suction sampling head. This device is fitted to the top of the sample bottle and contains two ports: an outlet port attached to a suction pump and inlet port attached to a piezometer tube. When a vacuum is drawn on the outlet, groundwater is drawn in through the inlet. At least one tubing volume was purged before sample collection. Additional details on sample collection are provided by Malcolmson (1992) and Nielsen and Hansen (1992).

## RESULTS AND DISCUSSION

### Creosote Characterization

Averages of analytical results for eight samples of the altered creosote (analyzed prior to field source emplacement and after amendment with four additional compounds) are shown in Table 1.

### Batch Test

Results of batch testing were used to calculate  $S_i$  by rearranging equation 3. The creosote mole fractions used in this case were those calculated for creosote from the batch test bottles at the end of the equilibration period. A molecular weight of 200 was assumed for the unidentified portion of the creosote. Values for  $C_i^a$  were taken directly from analysis of the water. Calculated  $S_i$  values are shown in Table 2 and are compared with literature values (or those calculated with equation 4, as required).

Comparison of these two values gives some measure of the ideality of the creosote in terms of dissolution behaviour. Lee et.al. (1992a) use a "factor of two" as a guide for evaluating the agreement between Raoult's law predictions and measured solubility, and hence the ideality of the organic liquid. The ratios between  $S_i$ 's calculated from the batch test results and those from the literature are shown in Table 2. Raoult's law provides a satisfactory prediction (within a factor of two) of batch results for m-xylene, naphthalene and dibenzofuran but phenol, phenanthrene, carbazole and pyrene are overestimated. Since 2,6-dimethylphenol and anthracene were not detected in the aqueous samples, they were also overestimated. Only 1-methylnaphthalene was significantly underestimated by Raoult's law.

### Field Results

Results from batch testing were used as an updated estimate of  $S_i$  for application to the field data. The product of the batch-derived  $S_i$  and the initial creosote mole fraction (Table 2) was used as the Raoult's law prediction of expected initial effective solubility ( $S_e$ ) from the field creosote source. Conceptually, the  $S_e$  determined in this manner can be considered the expected concentration if a small volume of water contacted a much larger volume of creosote such that the mass loss from the organic phase does not cause a significant change in mole fractions, even for the most soluble compounds. Mole fractions of the initial creosote were again calculated using an assumed average molecular weight of 200 for the unidentified portion of the creosote. Estimates of initial  $S_e$  (aqueous concentrations in equilibrium with initial creosote) are shown in Table 2.

**Table 2. Comparison of equilibrium aqueous concentrations from literature and application of Raoult's law to batch dissolution results**

	Creosote mole fractions*	Pure compound solubility (mg/L)		Ratio (1) : (2)	Aqueous concentration in equilibrium with creosote (mg/L)**
		(1) literature values	(2) Batch dissolution tests (n=3)		
m-Xylene	0.37	200	225	0.9	14.4
Phenol	0.15	123650	52787	2.3	1388
2,6-dimethylphenol	0.00	8164	not detected	-	0
Naphthalene	0.77	112	94	1.2	12.4
Phenanthrene	0.72	7.4	3.6	2.1	0.44
Anthracene	0.07	5.5	not detected	-	0
Dibenzofuran	0.27	40.2	33.9	1.2	1.6
Carbazole	0.02	159	67	2.4	0.23
Pyrene	0.20	2.80	0.98	2.9	0.03
1 m-Naphthalene	0.14	28.5	71.0	0.4	1.7

\* assumes average molecular weight of 200 for unidentified creosote compounds

\*\* calculated with batch-test pure compound solubility and mole fractions of initial creosote

Figure 3 depicts the evolution of Se, based on Raoult's law, for selected creosote compounds (m-xylene, naphthalene, dibenzofuran and phenanthrene) dissolving from the emplaced creosote source. These curves were calculated with a simple spreadsheet model using the assumptions stated above and also assuming that the unidentified portion was insoluble. The value used for groundwater flux through the source was 0.204 m<sup>3</sup>/day, for reasons discussed earlier. For the purposes of the calculations it was assumed that all the groundwater passing through the source during a given time step reaches equilibrium with the creosote, according to equation 3. At the beginning of the next time step, the mass dissolved into the aqueous phase during the previous step was subtracted from the creosote and mole fractions were recalculated. Calculations for the first 100 days were performed with a relatively short time step (0.25 days) to minimize the error of this approximation during the time that phenol mole fraction is changing rapidly. The time step was subsequently increased to 5 days since the remaining analyzed compounds are less sensitive to this type of error due to their relatively low solubilities.

Also shown on Figure 3 are groundwater concentrations at level 4 of multi-level piezometer SS4, installed within the creosote source. The location of this monitoring point is shown on Figure 2, denoted as SS4-4. This level was selected for demonstration because it has been monitored consistently and has maintained relatively consistent concentrations. In some other monitoring points small blobs of pure phase creosote have occasionally been recovered during sampling and have caused an apparent, but erroneous, increase in dissolved concentrations. The model based on Raoult's law approximates most of the field data within a factor of two, although considerable scatter is apparent in the measurements. The significant decreases in concentration predicted over the monitoring period for m-xylene and naphthalene are evident in the measured data. Dibenzofuran deviates most from the predicted behaviour. Nonideality of the creosote is not considered to be the cause of the

difference since the pure compound liquid solubility used to calculate the initial  $C_e$  was determined through batch testing. Rate-limited dissolution (i.e., limited by contact time between groundwater and source creosote) is also not suspected as the cause since it does not appear to have limited concentrations of the other three compounds, although it cannot be ruled out. Potential causes under review include analytical uncertainty in characterization of the initial creosote (eg., co-elution of an unidentified compound with dibenzofuran) and the batch test samples.

Figure 4 shows concentration profiles in SS4 for m-xylene, naphthalene, dibenzofuran and phenanthrene at 55 days and 1008 days after emplacement of the creosote source. M-xylene and naphthalene show more variable depletion between sample sets. This increase in variability of aqueous concentrations with time, which is best illustrated by the naphthalene profiles, may result from heterogeneous distribution of creosote mass in the source. Care was taken during installation to keep the creosote-sand mixture consistent. However, cores

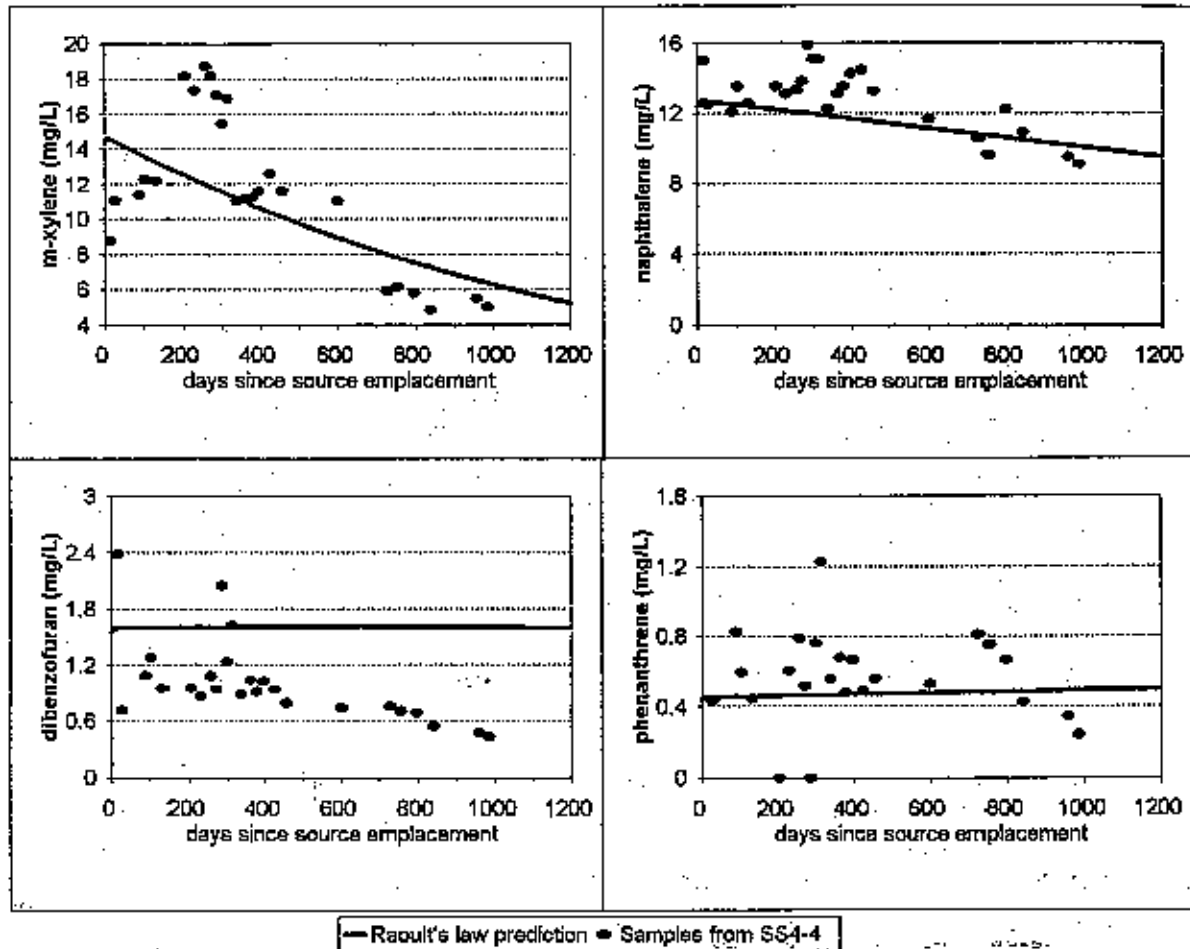


Figure 3. Comparison of dissolved concentrations of creosote compounds (m-xylene, naphthalene, dibenzofuran and phenanthrene) in groundwater within the creosote source with concentrations predicted by applying Raoult's law; values for pure compound liquid solubility have been determined with batch dissolution tests.

collected from the source shortly after emplacement indicated considerable variability in creosote concentration (data not shown). In portions of the source that contained less creosote mass, higher solubility compounds such as naphthalene and m-xylene may have been depleted as indicated by aqueous concentrations that are much lower than expected in some locations. Less spreading was observed for dibenzofuran and phenanthrene concentrations, probably as a result of lower solubility. However, an overall decrease in dibenzofuran was observed and is difficult to explain since the predicted Se stays constant over this period. The obvious decrease in the measured values may indicate that the mole fraction in the initial creosote was less than that indicated by analysis.

A further illustration of increasing variability in aqueous concentrations of the more soluble compounds is shown in Figure 5. The measured data are from samples collected at points throughout the creosote source at 55 days and 1008 days. As shown in the plot of naphthalene vs. dibenzofuran, concentrations of both compounds showed relatively little

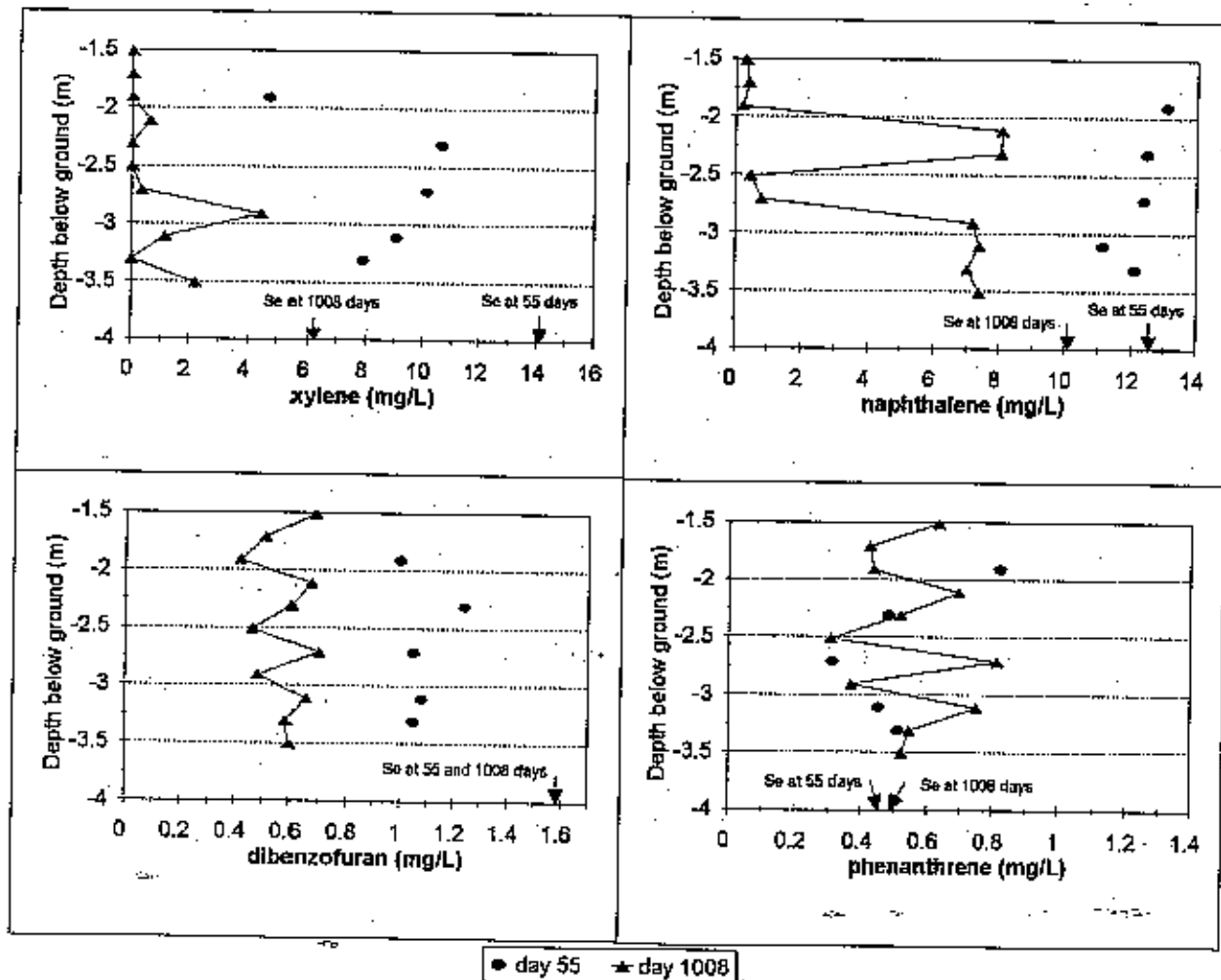


Figure 4. Concentrations of selected creosote compounds in multi-level piezometer SS4 at 55 days and 1008 days after source emplacement; effective solubilities (Se) shown are as predicted by Raoult's law (location of SS4 shown on Figure 2).

variation throughout the source at 55 days. However, a considerable spread in the naphthalene data became apparent by 1008 days. Dibenzofuran concentration decreased but in a relatively consistent manner. A similar trend is noted for naphthalene vs. phenanthrene, with the exception that no decrease is apparent for phenanthrene after 1008 days.

Figure 5 also shows expected trends of compound ratios according to the Raoult's law model. These have been extended to 10,000 days to cover the range of measured concentrations. As expected, the data for dibenzofuran does not fit the prediction: again it appears that a lower initial mole fraction is indicated for dibenzofuran. However, data for naphthalene vs. phenanthrene and naphthalene vs. m-xylene show a reasonable agreement with the curves, with considerable scatter noted. At 55 days, most of the data points are located in a cluster at the early time part of the curves. However, by 1008 days the data are distributed along most of the length of the curves. Consequently, within the confines of the parameters used in the model, up to 10,000 days would be required for naphthalene and m-xylene concentrations to

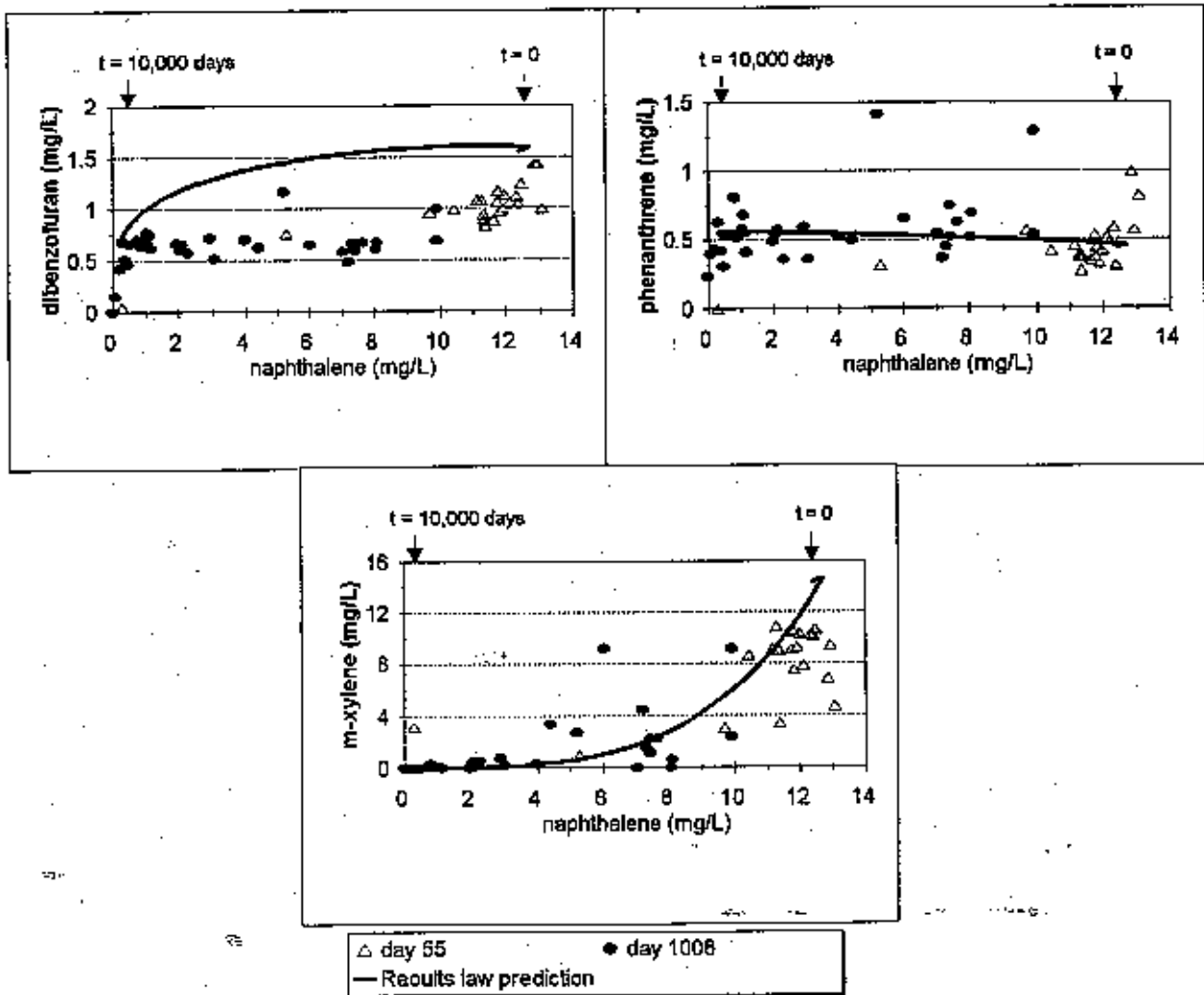


Figure 5. Dissolved naphthalene concentration vs. dibenzofuran, phenanthrene and m-xylene in groundwater throughout the creosote source; 55 days and 1008 days after source emplacement; duration of the Raoult's law model simulation is from 0 to 10,000 days (note: the small bend at right end of each curve is due to rapid depletion of the phenol mole fraction).

decrease as low as those measured in many of the 1008 day samples. This result is consistent with the suggestion of variable initial concentrations of creosote throughout the source, since the effect of lowering the initial concentration is similar to that of extending the period of dissolution. The observation that the more soluble compounds have been depleted by as much as ten times sooner than predicted may therefore indicate that at some locations, initial creosote concentration was an order of magnitude less than expected.

It is notable that with the processes indicated above, it is possible for groundwater migrating out of a contaminant source area to have a consistent composition initially even though the NAPL distribution is heterogeneous. With time, zones of low NAPL concentration could become depleted of the more soluble compounds. Composition of groundwater leaving the source would then become variable with respect to the more soluble compounds while concentrations of the less soluble compounds remain relatively consistent. This compositional variability may be important in terms of estimating dissolved mass flux from organic mixtures with a wide range of compound solubilities. On an actual contaminated industrial site, where contact time will typically be much longer, groundwater plumes evolving from these types of mixtures are likely to be even more variable in cross-section: more time is available to magnify the effects of heterogeneous NAPL phase distribution. In such a circumstance, considerable care is required to make a reasonable estimate of contaminant mass flux from a source area into a groundwater plume.

## CONCLUSIONS

Results of dissolution batch tests showed that Raoult's law provided a reasonable estimate (within of factor of 2) of the effective solubility of four of ten analyzed creosote compounds. The effective solubility of m-xylene, naphthalene and phenanthrene in groundwater at one point in the emplaced creosote source was satisfactorily predicted by Raoult's law over a period of 1000 days, but dibenzofuran behaviour was not well predicted. The deviation for dibenzofuran is considered to be related to experimental methodology rather than nonideality of the creosote with respect to this compound.

The degree of variability in groundwater composition throughout the creosote source increased dramatically in a relatively short time for m-xylene and naphthalene. It is evident that at many individual points the Raoult's law model would not have provided a satisfactory prediction. Comparison of the Raoult's law model to groundwater concentrations throughout the source provided an indication that the increasing variability was due to heterogeneous initial distribution of pure phase creosote. This observation has implications for interpreting organic plume data at sites contaminated with complex organic mixtures with a wide range of compound solubilities.

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