

Migration and natural fate of a coal tar creosote plume

1. Overview and plume development

Mark W.G. King ^{a,*}, James F. Barker ^b

^a *Groundwater Insight, 5 Wenlock Grove, Halifax, Nova Scotia, Canada B3P 1P6*

^b *Earth Sciences Department, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1*

Received 19 December 1997; accepted 26 March 1999

Abstract

A volume of sand containing coal tar creosote was emplaced below the water table at CFB Borden to investigate natural attenuation processes for complex biodegradable mixtures. Coal tar creosote is a mixture of more than 200 polycyclic aromatic hydrocarbons, heterocyclic compounds and phenolic compounds. A representative group of seven compounds was selected for detailed study: phenol, *m*-xylene, naphthalene, phenanthrene, 1-methylnaphthalene, dibenzofuran and carbazole. Movement of groundwater through the source led to the development of a dissolved organic plume, which was studied over a 4-year period. Qualitative plume observations and mass balance calculations indicated two key conclusions: (1) compounds from the same source can display distinctly different patterns of plume development and (2) mass transformation was a major influence on plume behaviour for all observed compounds. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Attenuation; Biodegradation; Creosote; Field studies; Groundwater; PAHs

1. Introduction

Many products and wastes derived from coal and oil are mixtures composed of aromatic, heteroaromatic and phenolic compounds. These compounds span a wide range of molecular weights, from the lighter monoaromatics (e.g., BTEX) and phenolic

* Corresponding author. Fax: +1-902-475-1993; E-mail: marking@netcom.ca

compounds to the mid-range, two-to four-ring polycyclic aromatic hydrocarbons (PAHs) and nitrogen, sulphur and oxygen (NSO) heteroaromatics up to the larger PAHs with greater than four rings. These types of complex mixtures are used, or generated, by industries such as coal distillation, petroleum refining, wood treating and metal refining. Accidental spills or past waste disposal practices associated with these industries have resulted in the introduction of these mixtures to groundwater at many industrial sites (e.g., Mattraw and Franks, 1986; Turney and Goerlitz, 1990; Arvin and Flyvbjerg, 1992; Bennett et al., 1993; Kiilerich and Arvin, 1995; Johansen et al., 1997).

Predicting the fate and transport of this type of contamination presents unique problems. However, it has become a common objective, due to heightened interest in natural attenuation as a plume management option, and qualified regulatory acceptance of this approach in many jurisdictions. For example, USEPA, Office of Solid Waste and Emergency Response (1999) state that natural attenuation may provide an alternative means of achieving remedial objectives for a limited set of site circumstances. They define natural attenuation as a “variety of physical, chemical or biological processes that, under favourable conditions, act without human intervention to reduce the mass, toxicity, mobility, volume or concentration of contaminants in soil or groundwater.” They further state that these processes include contaminant dispersion, dilution, sorption and volatilization, as well as chemical and biological stabilization, transformation and destruction.

It is generally acknowledged that many of the study compounds are biodegradable, to some degree (e.g., Mueller et al., 1989), and this property may tend to limit the extent of groundwater contamination. However, due to the complex nature of these plumes, the extent of natural attenuation is not easily predicted. Dissolution is the first step of plume formation and is particularly complicated for mixtures with a wide range of compound solubilities. Further, as dissolution proceeds, a chromatographic separation of compounds occurs along the groundwater flow path, due to variations in the sorptive properties of the constituent compounds. Consequently, the multicomponent ‘plume’ is effectively separated into a series of single-compound plumes, each of which may exhibit distinct sorptive characteristics. Superimposed on this process is the possibility of competition between organic compounds, for dissolved oxygen, or other electron acceptors. A further complication arises because the various compounds may have widely varying tendencies to degrade under aerobic and anaerobic conditions.

2. Study approach and purpose

The focus of the current research is a source of creosote emplaced below the water table at CFB Borden in August, 1991. Since the time of emplacement, a complex plume of dissolved organics formed under natural gradient conditions, and detailed monitoring was conducted to determine the extent of mass loss. The overall purpose of this research was to contribute to the understanding of natural attenuation as it relates to complex hydrocarbon plumes. The controlled field experiment described herein represents a unique setting and approach for this type of research. It is based on an emplaced source

and should therefore provide a reasonable analog to contaminated industrial sites. However, data have been collected at a level of detail that would typically not be feasible on an industrial site. The relatively high density of data points allows a more conclusive evaluation of organic mass distribution and transformation, using a mass balance approach. Creosote, the organic liquid used in this study, was selected because it is a complex mixture of biodegradable hydrocarbons, typical of many other organic mixtures.

This paper provides an overview of the research and also provides a qualitative description of plume development, based on dissolved phase monitoring. In a companion paper (King et al., this issue), a more quantitative, mass balance approach is used to determine the occurrence and amount of organic compound transformation and multiple lines of evidence are used to evaluate whether the observed plume transformation is due to biodegradation.

3. Background

Evidence of widespread microbial presence in the subsurface environment is now well-documented (e.g., Wilson et al., 1983; Ghiorse and Balkwill, 1983; Barbaro et al., 1994) and widely accepted. The ability of indigenous microbes, especially bacteria, to degrade a wide range of organic substances has also been conclusively demonstrated. Atlas (1981) provided some early general observations about the ability of microbes to metabolize compound groups typically associated with petroleum. He indicated that heteroaromatic NSO compounds with a small number of rings may be biodegradable, as may monoaromatic compounds and PAHs with two to four rings. Mueller et al. (1989) provided an overview of biodegradation for a similar range of compounds, with reference to environmental contamination by creosote. They cited several laboratory studies where biodegradation of PAHs, heteroaromatics and phenolic compounds has been demonstrated and where specific strains of microbes able to utilize these compounds have been isolated from environmental samples. However, they pointed out that of these three groups, much less is known about biodegradation processes for the heteroaromatics. Dyreborg et al. (1997) demonstrated biodegradation of nitrogen-, sulphur- and oxygen-heteroaromatics under a variety of redox conditions. Flyvberg et al. (1993) demonstrated biodegradation for the range of compounds (phenols and aromatic hydrocarbons) that were present in creosote-contaminated groundwater under nitrate-reducing conditions.

Biodegradability of organic compounds is more easily demonstrated in the laboratory than in the field, and the method most often used involves microcosms. A review of general microcosm techniques is provided by Pritchard and Bourquin (1983). In general, a quantity of the compound in question is placed in a sealed vessel with some combination of soil and water. Trials are conducted with both active and sterilized microcosms so that biotic mass loss can be differentiated from abiotic losses. However, there are limitations with regard to extending these types of results to natural systems. These are primarily related to disruption of the dynamic process that may occur in the

field and to difficulty in duplicating field environmental conditions in the laboratory. Alexander (1985) also cautions that degradation rates may be highly dependent on organic compound concentrations, making it difficult to apply results from one microcosm experiment to the continuum of concentrations usually encountered in the groundwater plumes. Consequently, large-scale field experiments have potential to provide results that are more representative.

In recent years, natural biodegradation has received considerable attention as a potential remediation strategy for hydrocarbon contamination of groundwater (National Research Council, 1993). This is probably a response to a combination of factors: the high cost of remediation by more active means and the poor results that have characterized these efforts, to date (e.g., review of pump-and-treat limitations by Mackay and Cherry (1989)). Given that biodegradability has been demonstrated in the laboratory for so many organics, it would appear that a strong case for using natural attenuation as a remediation strategy is already made. However, two issues remain: (1) as mentioned earlier, laboratory results may not be representative of the field and (2) even if biodegradation is occurring in the field, it may not be sufficient to isolate the contaminated site from the surrounding environment. Consequently, to use natural microbial attenuation as a remedial strategy, field biodegradation must first be proven and then quantified. Madsen (1991) has laid out guidelines for evaluating the occurrence, but not the rate, of *in situ* biodegradation. The approach is based on: (1) contaminant distributions that indicate diminishing concentrations in excess of hydrodynamic dilution; (2) associated changes in reactants concentrations (e.g., electron acceptors, nutrients, metabolites); and (3) laboratory evidence demonstrating that subsurface microbes are able to utilize the organic(s) in question and field evidence of microbial distribution that correlates with contaminant distribution.

Such a unified approach was used by Klecka et al. (1990) to demonstrate natural bioremediation of PAHs and phenolic compounds in groundwater at a previous charcoal manufacturing plant in Michigan. The authors used a combination of organics and inorganics monitoring, laboratory microcosms and assessment of biological activity. Madsen et al. (1991) demonstrated natural bioremediation of PAHs at a coal tar disposal site in a shallow aquifer using a combination of groundwater monitoring for organics and inorganics and inferences from subsurface microbial ecology. The authors found a relationship between distribution of protozoa and plume organics and suggested that the population of the former increased because they were grazing on bacteria that were growing on plume organics.

The USGS has conducted two major studies that probably represent the most intensive characterizations of natural bioremediation processes, to date. At the site of a crude oil spill in Bemidji, Minnesota, researchers showed the development of redox zones in groundwater due to the spill as well as evolution of metabolites from biodegradation of crude oil compounds (Cozzarelli et al., 1994). The other USGS study was conducted at a former wood preserving site in Pensacola, Florida (Matraw and Franks, 1986). Natural bioremediation of plume organics (primarily PAHs and phenols) was inferred by changes in plume inorganic geochemistry indicative of redox reactions. The occurrence of fatty acids as organic metabolites was another indication of biodegradation (Goerlitz et al., 1985). A greater than expected decrease in metabolite concentra-

tions along the groundwater flow path was interpreted as evidence of subsequent metabolite biodegradation (Godsy et al., 1992).

In general, field studies of natural biodegradation at actual sites have used a one-dimensional approach: changes in organic and inorganic chemistry along the groundwater flow path are related to background conditions in order to evaluate plume biodegradation. One of the strengths of these types of studies is that they represent the complexity of hydrogeologic and contaminant conditions that are typical of industrial contamination. However, this complexity also imposes a limitation. Since three-dimensional characterization of the source and plume is not usually possible, there is limited ability to formulate interpretations based on mass balance and distribution and an associated limitation on determining plume-scale rates of biodegradation.

Other natural biodegradation studies have used controlled field experiments to avoid problems associated with poorly defined sources and plumes. This approach has typically involved injection of a measured slug of water containing known concentrations of organics. Barker et al. (1987) injected a slug containing benzene, toluene and xylenes (BTX) into the Borden aquifer. They monitored the resulting plume and were able to calculate mass balances to determine the persistence of the organics over time. In a similar study at Columbus Air Force Base, MacIntyre et al. (1993) injected a slug containing four organics: two aromatics, a PAH and a chlorinated compound. Again, the authors were able to use a mass balance approach to determine plume-scale decay rates.

Controlled field studies based on slug-type plumes have an advantage over those using actual groundwater contamination occurrences, because the researchers know the precise mass and composition of the organic substrate and the time period over which it was introduced. Also, since the approximate migration path of the plume is known in advance, plume monitoring can be more focused, and conducted in greater detail. However, a shortcoming of this approach is that it does not provide a realistic analog to actual contaminated sites because: (1) plume concentrations near source zones may often be much higher than the relatively low concentrations used in slug injection tests and (2) since the slug injection is short-lived, the resulting plume is transient, moving through the aquifer as a slug until it disappears completely. Consequently, the slug injection plume will not display aspects of long-term behaviour, such as an approach to steady state, which may be of particular interest for plumes originating from fixed sources.

4. Site description

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 350 m north of a landfill that operated from 1970 to 1976. Several hydrogeological studies have been conducted at this location over the past 15 years and, consequently, many of the parameters affecting the fate and transport of solutes in groundwater have been evaluated in exceptional detail. A summary of groundwater and aquifer parameters is provided in Table 1.

The site is underlain by an unconsolidated sand aquifer consisting of medium- to fine-grained sand. These deposits are glacio-lacustrine in origin and grade into silts and

Table 1
Characteristics of the Borden aquifer

Parameter	Method/Result	Source
Mineralogy	analysis of bulk sample by X-ray diffraction: 58% quartz, 19% feldspars, 14% carbonates, 7% amphiboles, 2% chlorite	Mackay et al. (1986)
Porosity	volume-weighted arithmetic mean of 36 samples: 0.33	Mackay et al. (1986)
Bulk density	volume-weighted arithmetic mean of 36 samples: 1.81 g/cm ³	Mackay et al. (1986)
Solids density	volume-weighted arithmetic mean of 36 samples: 2.71 g/cm ³	Mackay et al. (1986)
Organic carbon content	average of 0.02%; ranging from 0.01% to 0.09%	Mackay et al. (1986)
Hydraulic conductivity	(a) slug tests at 26 points; mean of 7×10^{-5} m/s; (b) falling head permeameter tests with 1279 samples; overall geometric mean of 9.75×10^{-5} m/s	Mackay et al. (1986); Sudicky (1986)
Depth to water table	Varies with time from ground surface to 1.5 m below grade	Linderfelt and Wilson (1994)
Hydraulic gradient	ranged from 0.002 to 0.0053 over first 2 years of current study period; time-weighted average of 0.0039	Linderfelt (1994)
Ground water flow direction	ranged from N11°W to N50°E over first 2 years of current study period; predominant flow direction was N21°E	Linderfelt (1994)
Ground water velocity	(a) 1038 day tracer test: 0.091 m/day; (b) 476 day tracer test: 0.0933 to 0.0947 m/day; (c) 108 day tracer test: 0.081 m/day; (d) emplaced source monitoring: 0.066–0.085 m/day	Mackay et al. (1986); Hubbard et al. (1994); Patrick (1986); this study
Apparent dispersivity	(a) tracer test with 11 m plume displacement: $\alpha_L = 0.08$ m, $\alpha_{TH} = 0.03$ m, $D_{TV} = 10^{-10}$ m ² /s; (b) tracer test with approx. 60 m plume displacement: $\alpha_L = 0.36$ m, $\alpha_{TH} = 0.039$ m	Sudicky et al. (1983); Freyberg (1986)

clays at a depth of approximately 9 m. 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. The current experiment has been conducted within this unaffected zone.

Chemistry of background groundwater (unaffected by the leachate plume) at the site was examined by Nicholson et al. (1983) and Mackay et al. (1986) and also through the current study. A summary of results is provided in Table 2. The groundwater is relatively hard with low dissolved organic carbon. Dissolved oxygen was determined to

Table 2
Background groundwater characteristics

Parameter	Range	Source
Calcium	50–100 mg/l	1,2
Magnesium	2.4–6.1 mg/l	1,2
Sodium	0.9–2.0 mg/l	1,2
Potassium	0.1–1.2 mg/l	1,2
Alkalinity (as CaCO ₃)	100–250 mg/l	1
Chloride	1–3 mg/l	1,2,3
Sulphate	10–30 mg/l	1,3
Nitrate	< 0.6–6 mg/l	1,2,3
TDS	380–500 mg/l	1
DOC	< 0.7 mg/l	2
DO	0–8.5 mg/l	2,3
Temperature	6–15°C	1,2,3
pH	7.1–7.9	1,2,3

1—Nicholson et al. (1983).

2—Mackay et al. (1986).

3—This study.

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 was 2 to 3 mg/l. The landfill leachate plume located is characterized by nondetectable dissolved oxygen (Barbaro et al., 1992) as well as major ion concentrations that are generally at least an order of magnitude greater than those that occur in background groundwater (Nicholson et al., 1983).

5. Creosote composition and properties

Creosote is used as an industrial wood preservative and is a thin oily liquid. 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). Creosote may consist of up to 200 chemicals (Mueller et al., 1989): approximately 85% PAHs by mass, 10% phenolic compounds and 5% oxygen-, sulphur-, and nitrogen-heteroaromatic compounds. The range of the component solubilities varies by several orders of magnitude. For example, literature values for the solid solubility of phenol range up to several tens of thousands of milligrams per liter (MacKay et al., 1992), while values for chrysene, a four-ring PAH, are generally in the order of a few micrograms per liter.

The raw creosote used in this study was obtained from Carbochem in Mississauga, Ontario, Canada. It was amended with certain phenolic, heterocyclic and aromatic compounds to enhance the capability to observe the behaviour of these compound groups. To 69.5 kg of raw creosote, the following was added: 0.45 kg carbazole (a heteroaromatic compound), 0.50 kg *p*-cresol, 1 kg phenol (both phenolic compounds) and 3 kg *m*-xylene (a monoaromatic). The density of the modified creosote was 1.03

Table 3
Physicochemical data for selected creosote compound

Compound	Molecular weight	Pure compound solubility ^a (mg/l)	Melting point ^a (°C)	Log K_{ow}^b
<i>m</i> -xylene	106.2	196	−47.4	3.12
phenol	94.1	82,000	43	1.50
2,6-dimethylphenol	122.2	6150	49	2.26
naphthalene	128.2	31.7	81	3.35
phenanthrene	178.2	1.3	101	4.52
anthracene	178.2	0.075	216	4.50
dibenzofuran	168.2	10.03	86.5	4.12
carbazole	167.2	1.03	247	3.72
pyrene	202.3	0.14	156	5.00
1-methylnaphthalene	142.2	28.5	−22	3.87

^aFrom MacKay et al., 1992.

^bFrom Sangster, 1989.

g/ml. Physicochemical properties of 10 compounds representative of the main groups of compounds found in creosote are provided in Table 3.

6. Methods

6.1. Source emplacement

The creosote source was emplaced on August 28, 1991, and is shown schematically in Fig. 1. To install the source, sealable sheet piling (Starr et al., 1991) was vibrated into the ground in a rectangular array (5 × 1.5 m). The sand inside the sheet piling was excavated after it was dewatered with a shallow dewatering well. The creosote was added to the source sand in a cement mixer at an overall mixture of 74 kg of creosote to approximately 5800 kg of sand. This mixture resulted in a creosote content of approximately 7% of the source pore volume, which was well below residual saturation of approximately 18%, estimated through previous laboratory testing. Consequently, the creosote was expected to be immobile within the source sand. Several kilograms of NaCl was also mixed into the source sand, to provide a conservative tracer during source dissolution and plume development.

Borden sand was not used for the source material since the addition of creosote to the sand would result in some decrease in porosity that could inhibit the movement of groundwater through the source. Instead, a coarser sand was used, with a hydraulic conductivity of approximately 3.6×10^{-4} m/s, based on sieve analyses (Devlin, 1994) —approximately five times greater than Borden sand. Column tests by Forsey (in progress) showed that creosote addition reduced the hydraulic conductivity of source sand was reduced by less than 10%. Consequently, groundwater flow through the source was not expected to be inhibited by the presence of creosote. Additional information and

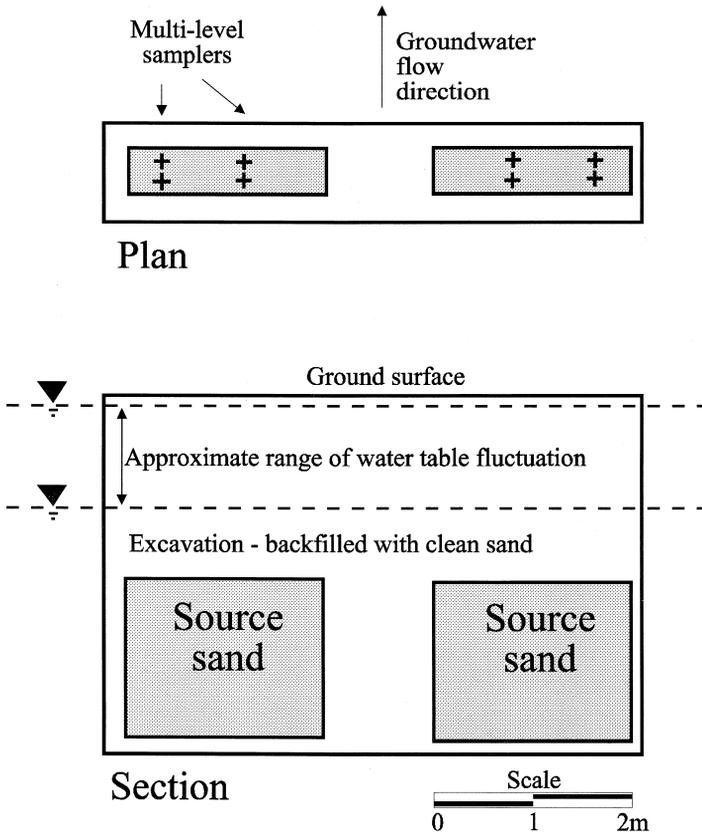


Fig. 1. Configuration of creosote source: (top) plan view showing location of multilevel samplers installed through source and (bottom) view of section perpendicular to the direction of groundwater flow.

interpretation of groundwater and creosote compound flux out of the source is provided by King et al. (this issue). Additional details of source installation are provided by Malcolmson (1992).

6.2. Plume monitoring network

The creosote source was emplaced hydraulically upgradient of an existing network of multilevel samplers, shown in Fig. 2. The network was originally constructed for a plume study conducted in the early 1980s (Mackay et al., 1986). Since then, it has been augmented and modified by three subsequent studies (Patrick, 1986; Berry-Spark et al., 1988; Hubbard et al., 1994). In addition, 12 bundle piezometers were added along the west side of the system for the current study, and specifications of these are provided by King (1997). The horizontal spacing of the samplers is closer near the source (down to approximately 1 m) and increases to approximately 4 m at the downgradient extent of the system.

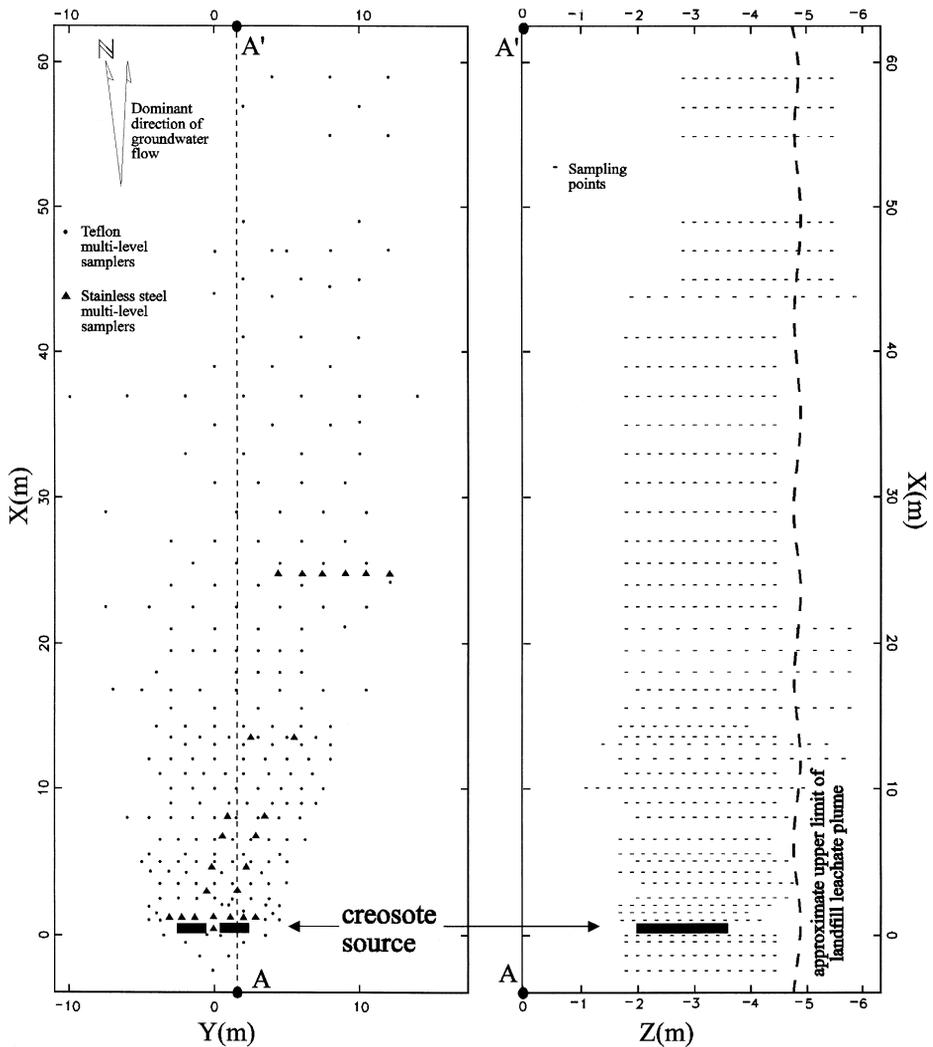


Fig. 2. Location of the creosote source and plume monitoring network: (left) plan view of multilevel samplers used for synoptic sampling and (right) approximate vertical distribution of sampling points along, or adjacent to, section AA' .

Fig. 2 also shows a profile of the monitoring points along a cross-section ($A-A'$) that approximates the plume centre line. The samplers are typically constructed with 14 sampling levels with a vertical spacing of 20 cm or, less frequently, 30 cm. This spacing was intended to approximate the vertical correlation scale estimated for hydraulic conductivity of the Borden aquifer (Sudicky, 1986). The samplers typically span a depth range of approximately 1.8–4.4 m below grade, with maximum depth increasing to 5.5 m at the downgradient end of the system.

Sampler construction was based on a design developed in earlier studies at the Borden site (Cherry et al., 1983), and similar methods were used for installation. In the ‘near-source’ zone of the plume ($x \leq 35$ m), samplers are constructed of 3.2 mm o.d. flexible teflon tubing, to minimize sorption of hydrophobic organics to sampling materials. Within the monitoring period of this study, only chloride, phenol and naphthalene showed appreciable solute migration beyond this zone. Outside this zone, most samplers are constructed with 3.2 mm o.d. polyethylene tubing.

6.3. Plume sampling

Synoptic plume sampling was conducted six times after source emplacement. The purpose of this type of sampling was to provide detailed, three-dimensional data for determining changes in plume distribution and mass with time. A summary of the synoptic monitoring program is provided in Table 4. In total, more than 7800 samples were analyzed for the six synoptic monitoring events. These data are provided in entirety by King (1997).

In addition, approximately 20 sampling points, located throughout the plume, were monitored approximately monthly over the 4-year duration of this study and data are provided by King (1997). In part, the standard teflon multilevel samplers were used for this ‘time series’ monitoring. However, the monitoring system was also augmented with a series of 40 additional multilevel samplers for this purpose. These samplers were constructed with 3.2 mm o.d. stainless steel tubing, for the purpose of minimizing sorption of hydrophobic organics. This was considered especially important since some of these samplers were actually installed within and just outside the creosote source. Each of these piezometers consisted of from seven to 13 monitoring points, again separated by a vertical distance of 20–30 cm. Locations are indicated on Figs. 1 and 2; specifications are provided by Neilsen and Hansen (1992).

Synoptic samples were collected in 18 ml glass hypovials and capped with crimped aluminum caps lined with teflon-coated silica septa. A vacuum manifold system constructed to collect 14 samples simultaneously, and identical to that used in earlier studies at the site (Mackay et al., 1986; Hubbard et al., 1994), was used for sample collection. In collecting samples, all the sampling tubes associated with a given multilevel sampler were connected to the manifold and a vacuum was applied to the system to draw groundwater into the sample bottles. At least 50 ml of groundwater was pumped through the system and the sample bottles, for purging before sample collection.

Table 4
Summary of synoptic monitoring program

Date	Days after source emplacement	Number of samples analyzed
Oct. 22–23, 1992	55	450
June 1–3, 1992	278	755
Nov. 9–10, 1992	439	564
May 11–21, 1993	626	2809
May 30–June 3, 1994	1008	1634
May 15–19, 1995	1357	1632

After collection, samples were capped as rapidly as possible to minimize volatilization. They were then placed in coolers and transported to the University of Waterloo for analysis. A similar procedure was used for collection of time series samples except that 45 ml glass hypovials and a single-tube vacuum system were used. Samples were not augmented with bacterial inhibitors; an evaluation of the effect of sample holding times indicated that the maximum duration required for the large synoptic sampling events (1 week) did not introduce systematic bias to the analytical results.

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 at creosote sites, and included two phenolic compounds (phenol and 2,6-dimethylphenol), five PAHs (naphthalene, 1-methylnaphthalene, anthracene, pyrene and phenanthrene), two heteroaromatic compounds (carbazole and dibenzofuran) and an aromatic compound (*m*-xylene). 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 (based on 45 ml) were prepared by adding 9 g NaCl to promote solvent partitioning of all analytes and 1 ml 1 N HCl to enhance partitioning of phenolic compounds. Samples were then capped and allowed to stand for 24 h before addition of 3 ml solvent (dichloromethane). Samples were then placed on a shaker for 20 min 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 μ 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 μ l. Additional details of the analytical methodology were provided by King (1997).

6.4. Source composition

Quantitative analytical results for 10 organic compounds in the creosote used for this study are shown in Table 5 and original data are provided by Malcolmson (1992). As indicated, these 10 compounds comprise 39% of the mixture. Identification of many of the remaining compounds was conducted on a qualitative basis using Gas Chromatography/Mass Spectrometry (GC/MS) analysis. Creosote samples were extracted by three different methods in order to identify a wide range of compounds, with major components presented in Table 6. A 'hydrocarbon' fraction, extracted with toluene was dominated by PAHs with occurrence of an oxygen heteroaromatic (dibenzofuran). Extraction with methanol yielded a 'resin' fraction that was dominated by phenols, substituted phenols and nitrogen heteroaromatics (e.g., isoquinoline and benzocarbazole). A third extraction was performed by treating a creosote sample with a dilute solution of NaOH, followed by extraction to dichloromethane. The residual aqueous layer was then acidified and extracted again with dichloromethane to yield an 'acid' fraction that was

Table 5
Quantitative analysis of creosote and compound properties

Compound	Concentration ^a (mg/kg creosote) (<i>n</i> = 8)	Liquid solubility ^b (mg/l)	Estimate of initial effective solubility (mg/l)	
			Raoult's law ^c	Batch test
<i>m</i> -xylene	39,000	196 ^d	11	14
phenol	14,000	160,000	3500	1400
2,6-dimethylphenol	190	13,700	3.2	not detected
naphthalene	96,000	151	17	12
phenanthrene	120,000	9.9	0.99	0.44
anthracene	12,000	8.6	0.086	not detected
dibenzofuran	44,000	53.4	2.1	1.6
carbazole	3300	239	0.72	0.23
pyrene	39,000	3.9	0.11	0.03
1-methylnaphthalene	19,000	28.5 ^d	0.57	1.7
Fraction of total mass quantified	0.39			

^aAnalyses performed after amendment with additional compounds (*m*-xylene, carbazole, *p*-cresol, and phenol).

^bCalculated with Eq. (2) using pure compound solid solubilities (S_L^i), melting temperature (T_M^i) from MacKay et al. (1992) and system temperature (T) of 15°C.

^cCalculated with Eq. (1) (see text for assumptions).

^dLiquid solubility (S_L^i) is identical to pure compound solubility, since compounds are liquid at system temperature.

dominated by phenol, substituted phenols and oxygen heteroaromatics. Additional details on this analysis were provided by King (1997).

6.5. Source dissolution and leachate composition

An extension of Raoult's law to partitioning between an aqueous phase and an organic mixture can be used to generate a qualitative prediction of how the composition of source leachate might be expected to change over time. According to this approach, 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 pure compound solubility. MacKay et al. (1991) pointed out two assumptions inherent in this approach: (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 activity coefficient for the solute in water is equal to the mole fraction solubility of the component. Shiu et al. (1988) incorporated these assumptions when they stated the concentration form of Raoult's law as:

$$C^i = x^i S_L^i, \quad (1)$$

where C^i is the aqueous concentration of compound i , x^i is the mole fraction of i in the organic mixture and S_L^i is the pure compound liquid solubility. For compounds that are

Table 6
Qualitative analysis of creosote composition

Compound	Relative conc.	Compound	Relative conc.
<i>Hydrocarbon fraction^a</i>			
indene	+	cyclopenta phenanthrene	++
naphthalene	++++	fluoranthene	+++
2-methyl naphthalene	+++	pyrene	+++
1-methyl naphthalene	++	benzo(a)fluoranthene	+
acenaphthalene	+	benzophenanthrene	++
biphenyl	+	chrysene	++
dimethylnaphthalenes	+	benzofluoranthene(b)	+
dibenzofuran	++	benzofluoranthene(E)	+
fluorene	+++	benzo(E)pyrene	+
phenanthrene	++++	benzo(A)pyrene	+
anthracene	++	perylene	+
methyl phenanthrenes	++	benzperylene	+
<i>Resin fraction^a</i>			
phenol	++	methyl indole	+
methyl phenols	+++	carbazole	+
dimethyl phenols	+++	benzoquinolines	+++
ethyl, methyl phenols	+	nitrosocarbazole(?)	++++
isoquinoline	++++	anthracene carbonitrile	++
benzene acetonitrile	+++	fluorene carbonitrile	++
methylquinolines	++	flurantheneamine	+
dimethylquinolines	++	benzocarbazoles	++
<i>Acid fraction^a</i>			
phenol	+	methyl naphthalenols	+++
2-methyl phenol	++	biphenyl-ols	++
4-methyl phenol	+++	dibenzofuranols	+++
dimethyl phenols	++++	phenanthrenols	+++
ethyl, methyl phenol	+	benzonaphthofurans	+++
naphthalenols or phenyl furans	+++		

^aSee text for description of analytical methodology.

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):

$$S_L^i = S_S^i \exp[6.8(T_M^i/T - 1)], \quad (2)$$

where S_S^i is solid solubility, T_M^i is melting point (°K) and T is 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.

Several studies have examined the degree to which various organic mixtures, that are complex in composition, 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 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 seven PAHs conformed to ideal behaviour within a factor of two.

In order to evaluate the applicability of the ideal behaviour assumption to the creosote used in this study, initial source leachate concentrations calculated with Raoult's law were compared with concentrations predicted from laboratory batch dissolution tests, and results are shown in Table 5. Calculation of the former was done with Eq. (1) using pure compound liquid solubilities directly from the literature or calculated on the basis of literature values for S_S^i and T_M^i . In order to estimate mole fractions (x^i) for the 10 quantified compounds, an average molecular weight of 150 was assumed for the unquantified portion of the creosote (61%) on the basis of qualitative comparison between GC retention times for identified and unidentified compounds. The batch test evaluation of effective solubility was conducted by adding approximately 5 g of creosote to each of three 70 ml glass crimp top hypovials. The bottles were then filled background Borden groundwater, then sealed with teflon-lined caps and stored in the dark at 10°C for 1 month. One water sample and two creosote samples were then removed from each bottle, for analysis of equilibrium concentrations. Complete methodology and results for the batch test were provided by Malcolmson (1992).

Comparison of the two sets of results indicates that Raoult's law may provide a useful approximation of initial creosote dissolution, with concentrations of most compounds corresponding within a factor of four. Near-source plume data, presented by King et al. (1994), indicated that initial concentrations in leachate from the emplaced source also showed reasonable agreement with the Raoult's law prediction.

A model based on a further application of Raoult's law was used to evaluate expected changes in source leachate composition over time. To do this, it was necessary to account for the removal of compound mass from the immobile NAPL phase by a mobile aqueous phase (groundwater) and to calculate the resulting changes in NAPL phase mole fractions. The leachate concentration (C_1^i) at the end of a given time step can be approximated by:

$$C_1^i = x_1^i S_L^i = \left((M_0^i - qA\Delta t C_0^i) / M_0^T \right) S_L^i, \quad (3)$$

where the subscripts 0 and 1 denote $t = 0$ and $t = 1$, respectively, C^i in this case is in units of moles per L^3 , M^i is moles of I in the NAPL phase, q is Darcy flux through the source (L/T); A is the cross-sectional area of the source perpendicular to the direction of groundwater flow (L^2) and M^T = total moles of all compounds in the NAPL phase. The result of applying this model to the emplaced creosote source is shown in Fig. 3. An initial value for C_0^i was obtained from the Raoult's law estimate of initial leachate concentration. Further, it was again assumed that dissolution of the identified compounds reached equilibrium in all groundwater flowing through the source, that the average molecular weight of the unidentified compounds (61% by weight) was 150 and that these compounds were insoluble. A sensitivity analysis of these latter two assumptions indicated that model results were qualitatively similar, over the period shown in

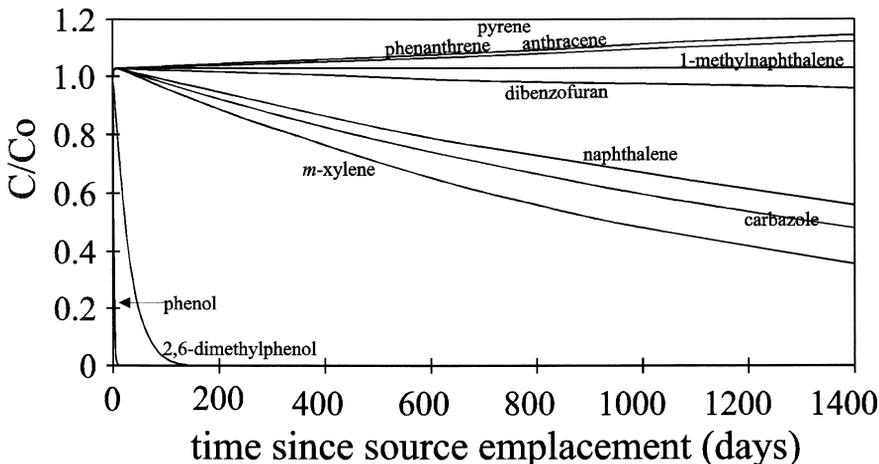


Fig. 3. Aqueous concentration of selected creosote compounds in groundwater leaving the emplaced source; predicted according to model based on Raoult's law (see text for model assumptions).

Fig. 3 (1400 days), when these two parameters were varied within reasonable ranges: molecular weight from 120–200 and liquid solubility up to 30 mg/l. A groundwater flux (q) of 0.03 m/day has been used, based on the determination of ambient groundwater velocity (0.091 m/day) and porosity (0.33) by Mackay et al. (1986). A relatively short time step of 0.25 days was used up to 100 days, to allow for the relatively rapid depletion of phenolic compounds. Subsequently, the time step was increased to 1 day.

A similar approach was used by King et al. (1994) and was determined to produce reasonable agreement with leachate from the emplaced creosote source. Consequently, the modelling results shown in Fig. 3 were used as a framework for qualitative prediction of trends in source leachate composition. As shown, concentrations of phenol and 2,6-dimethylphenol in source leachate were expected to decrease relatively rapidly, causing a small initial increase in concentrations of the other eight compounds, to slightly greater than $C/C_0 = 1$. *m*-Xylene, carbazole and naphthalene concentrations are expected to decrease significantly over the study period, but to remain detectable. Meanwhile, concentrations of 1-methylnaphthalene, phenanthrene, anthracene, dibenzofuran and pyrene were expected to remain relatively consistent.

6.6. Potential sources of error

A series of field and laboratory QA/QC samples and experiments were conducted to evaluate: (1) possible systematic error in field and laboratory methodology, (2) methods precision and (3) variability of the sampled media (groundwater with organic solute). Results are summarized below and details were provided by King (1997).

In general, the analytical procedure imparted a positive bias to measurements in the upper end of the concentration range and a negative bias in the lower end of the range.

The total range of these biases was $\pm 10\%$. However, phenol results showed a larger and consistently negative bias in the range of 50%, indicative of poor recovery for this compound. Correction of groundwater results for phenol recovery was not performed because the initial source mass of phenol was well-known (a measured quantity was added to the creosote) and phenol disappeared to trace mass relatively rapidly, as discussed qualitatively later in this chapter and quantitatively by King et al. (this issue). Analytical results for other compounds were not corrected for percentage recovery since they were generally within acceptable ranges. Measurement precision, evaluated as percentage standard error, did not display an apparent trend with respect to solute concentration.

Samples were extracted and analyzed as rapidly as possibly. However, due to the large number of samples associated with the synoptic monitoring, holding times for some unextracted samples and extracted samples were as long as 1 week and 4 months, respectively. The largest delays in extraction and analysis were experienced for the 626 day synoptic monitoring event, since it incorporated the largest number of samples. An experiment to evaluate the effect of holding times over this range, for both water samples and sample extracts, indicated that systematic bias was not introduced. Through another experiment, it was determined that sample concentrations were not significantly decreased by sorption to the teflon tubing in the multilevel samplers or the sampling manifold. Apparently, changes were minimized by the sampling procedure that included 50 ml purge prior to sample collection.

Evaluation of field blanks, composed of deionized water flushed through the manifold sampler after sample collection, indicated some potential for cross-contamination due to the manifold sampler. In a small portion (< 10%) of field blanks, there was evidence that naphthalene was introduced from the previous sample, although it was not noted for any other compounds. Where carry-over of naphthalene occurred, concentrations in the blank were typically 1% of that in the previous sample. Results indicated that some minor, apparent 'smearing' of the naphthalene plume may occur due to cross-contamination. The effect on naphthalene plume mass calculation should be much less than 1%, since the carried over concentrations should be low, and should only be an issue at the periphery of the plume. Results from samples collected in series at the same monitoring points indicated that solute concentrations were not sensitive to the volume of groundwater recovered for sampling.

7. Results and discussion

7.1. General

The following is a qualitative description of plume development for chloride and seven organic compounds: phenol, *m*-xylene, naphthalene, dibenzofuran, phenanthrene, carbazole and 1-methylnaphthalene. Plume data are presented in three different formats to assist in visualization of plume behaviour. First, a series of horizontal plan-view diagrams are shown that depict contours based on the maximum concentration detected

at each multilevel sampler (Figs. 4–8) for chloride and the first four organic compounds listed above. Contours start at $x = 2.7$ m from the source, since steep concentration gradients at closer proximity to the source make it difficult to determine contour locations.

Figs. 9 and 10 are concentration plots of selected plume compounds; these concentrations have been normalized to the cross-sectional area of the source, transverse to the direction of groundwater flow. The downgradient face of the source is defined as being in the y - z plane, where the z axis is vertical and the y axis is horizontal and perpendicular to groundwater flow. The cross-sectional area of the source in this plane is defined as $\Delta y_s \Delta z_s$ and is equal to 6.8 m^2 . The x -axis, orthogonal to the y - z plane, is approximately parallel to groundwater flow.

The normalized concentrations shown in Figs. 9 and 10 were calculated through the following procedure: (1) three-dimensional plume concentration data were interpolated to a regularly spaced, three-dimensional array of grid cell centre points, using the ENTEC (Surpac, 1995) geostatistical package; grid cell dimensions are given by $\Delta x_{GC} \Delta y_{GC} \Delta z_{GC}$, and the concentration at the centre point (C_{xyz}) is indicative of the average concentration in the cell; additional details on the gridding procedure were provided by King (1997). (2) All the concentrations from the first set of grid cells downgradient of the source ($C_{x_1 y_{1...n} z_{1...n}}$) were then added to yield a concentration

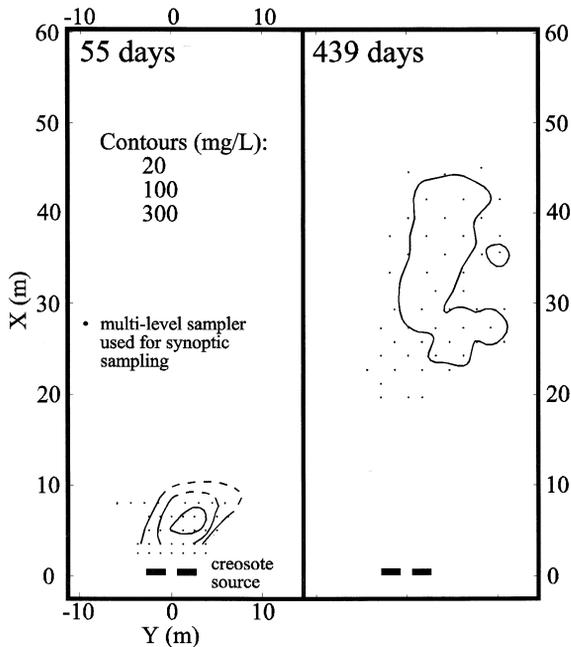


Fig. 4. Contour plans of chloride concentrations at two different times after source emplacement; each plan indicates the multilevel samplers that were monitored; contours are based on the maximum concentration at each sampler.

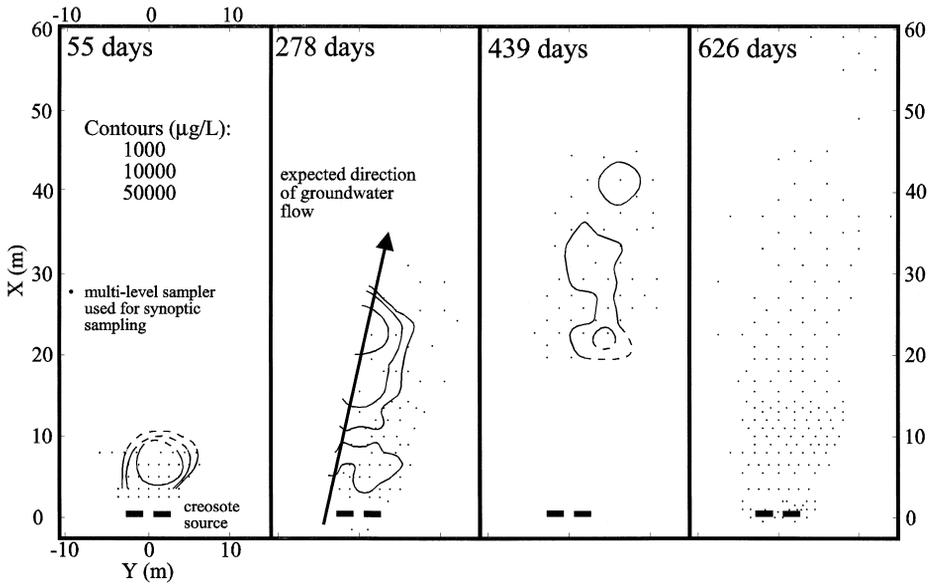


Fig. 5. Contour plans of phenol concentrations at four different times after source emplacement; each plan indicates the multilevel samplers that were monitored; contours are based on the maximum concentration at each sampler.

for the first x step in the grid ($C^{GC} x_1$), normalized to the volume of one grid cell, according to:

$$C^{GC} x_1 = \sum C x_1 y_1 \dots z_1 \dots \quad (4)$$

(3) This grid cell-normalized concentration was then transformed to a source-normalized concentration ($C^S x_1$) by considering the cross-sectional area of the source ($\Delta y_S \Delta z_S$), as per:

$$C^S x_1 = C^{GC} x_1 ((\Delta y_{GC} \Delta z_{GC}) / (\Delta y_S \Delta z_S)). \quad (5)$$

(4) The procedure was then repeated for all subsequent x steps in the grid, to the downgradient extent of the plume.

This approach to describing the dissolved phase plumes from the creosote source incorporates all of the dissolved concentration results for the given set of synoptic data (Figs. 9 and 10). It has an advantage over widely used methods of plume depiction, such as plan view contours and centre line concentration profiles, in that it provides a more accurate indication of longitudinal plume mass distribution and it allows distributions to be readily compared over time. Also, the area under the curves is indicative of the quantity of dissolved mass in the plume.

Time series data for two monitoring points within the plume ($x = 6.7$ m, $y = 0.55$ m and $z = 3.30$ m; $x = 24.85$ m, $y = 4.45$ m and $z = 3.60$ m) are shown in Fig. 11.

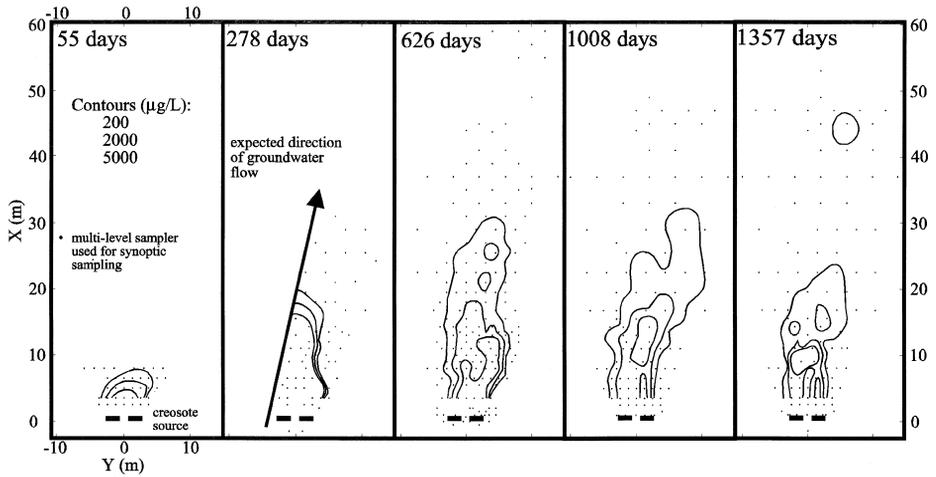


Fig. 6. Contour plans of *m*-xylene concentrations at five different times after source emplacement; each plan indicates the multilevel samplers that were monitored; contours are based on the maximum concentration at each sampler.

7.2. Chloride

Sodium chloride was added to the source during emplacement to produce a conservative chloride plume for use in evaluating average linear groundwater velocity. The presence of this plume has some potential to inhibit biodegradation. However, it is

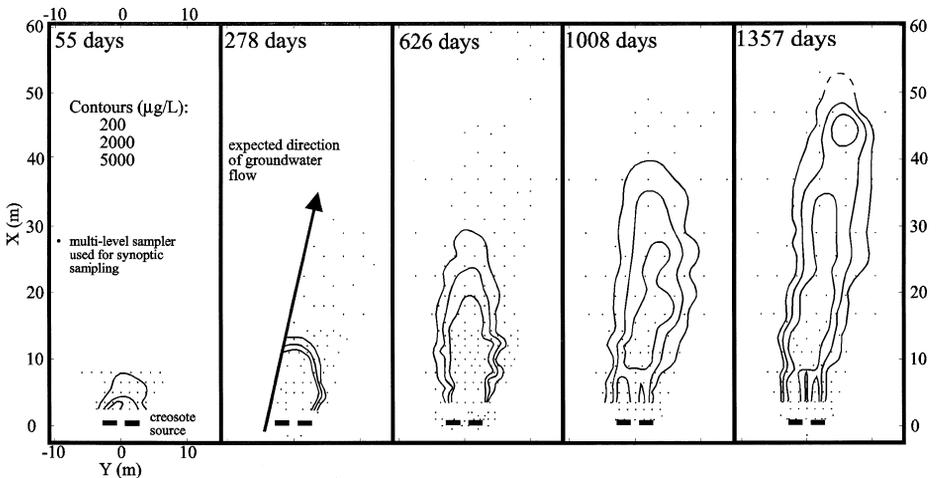


Fig. 7. Contour plans of naphthalene concentrations at five different times after source emplacement; each plan indicates the multilevel samplers that were monitored; contours are based on the maximum concentration at each sampler.

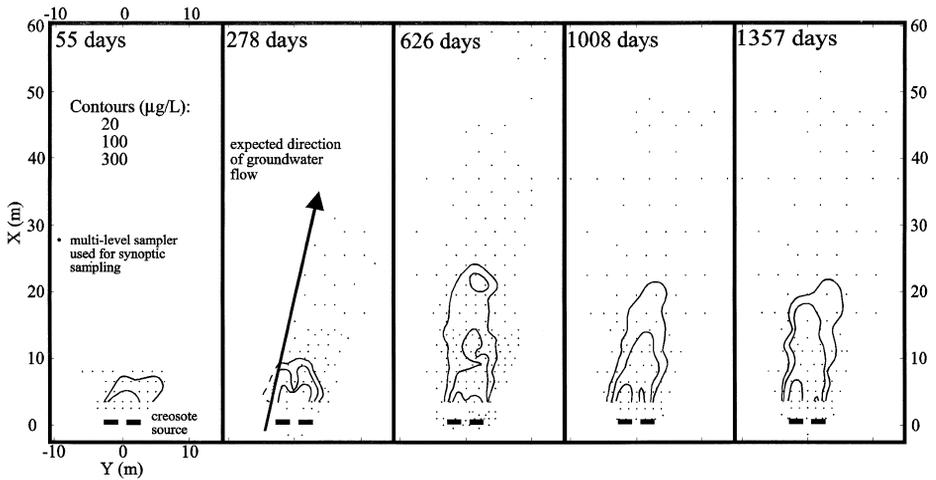


Fig. 8. Contour plans of dibenzofuran concentrations at five different times after source emplacement; each plan indicates the multilevel samplers that were monitored; contours are based on the maximum concentration at each sampler.

considered that the inhibitory effect was minimal: a detailed mass balance presented by King et al. (this issue) indicated detectable mass loss for all of the monitored compounds, and an evaluation of biodegradation indicators suggested that this mass loss was due to biodegradation.

Velocity estimates determined through the current study were used primarily for comparison with earlier estimates to evaluate whether the latter were reasonable for current use. At 55 days, the chloride plume was showing signs of detaching from the source, indicating that the source NaCl was becoming depleted (Fig. 4). By 439 days, the chloride plume was completely detached and was migrating as a discrete slug. The longitudinal distribution of chloride concentration is shown in Fig. 9 and, assuming that the maximum chloride concentration in source leachate occurred at early time, average linear groundwater velocity (v) can be estimated according to:

$$v = x/t, \quad (6)$$

where x = distance at which $C/C_0 = 0.5$ (estimated by data interpolation) and t = time of synoptic monitoring (days after source emplacement). In this case, C_0 is estimated as the maximum concentration observed on the curve (C_{\max}). The estimate of groundwater velocity based on the longitudinal chloride distribution profile at 439 days was 0.085 m/day and the parameter values used to calculate this velocity are shown in Table 7. Groundwater velocity was also estimated with chloride time series data from two selected points, shown in Fig. 11. Again, Eq. (6) is used to calculate velocity; however, in this case x was constant (at each point), while t varied. Results, shown in Table 7, indicate a velocity of 0.066 m/day based on data from $x = 6.7$ m and 0.083 m/day using data from $x = 7.3$ m.

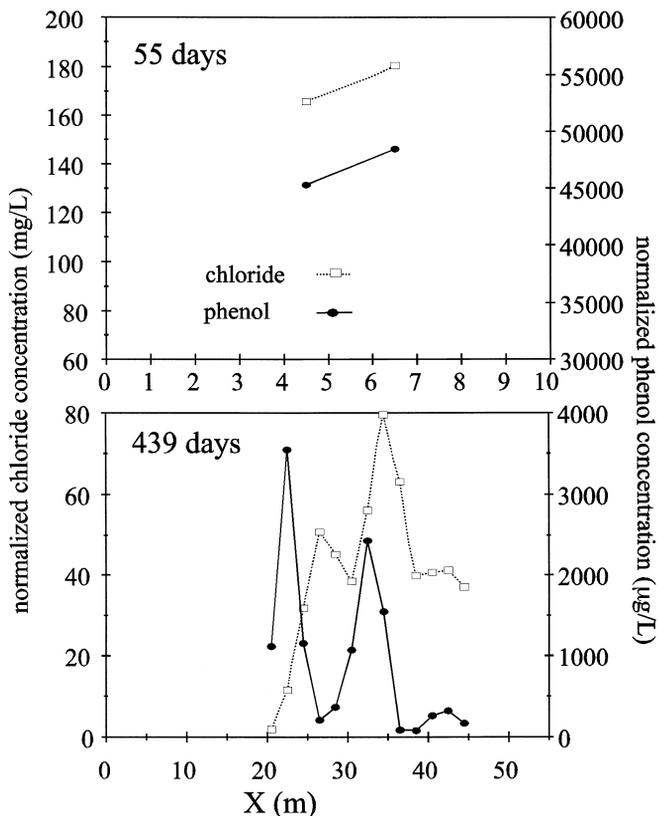
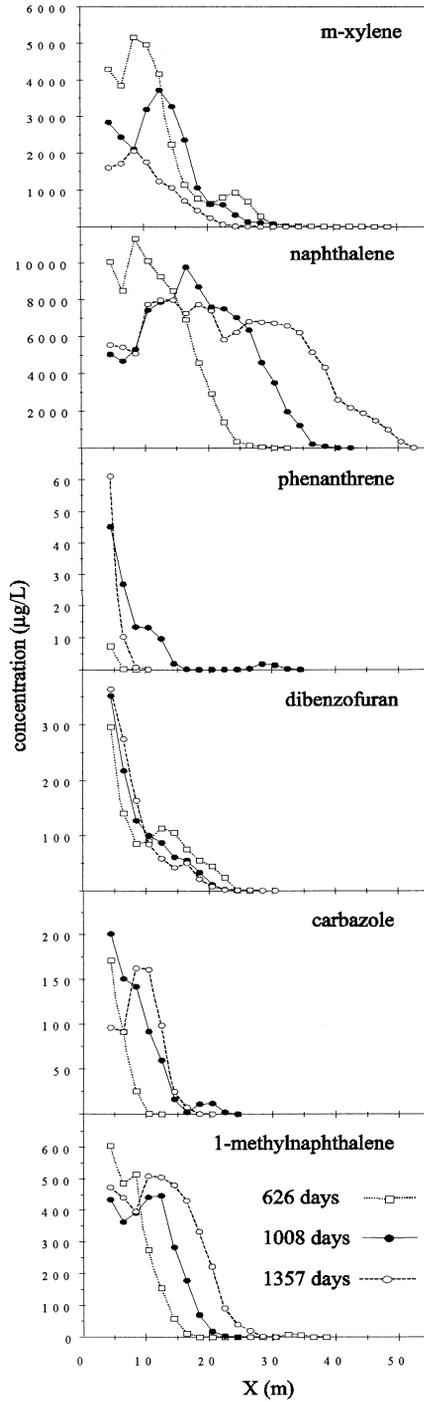


Fig. 9. Profiles of dissolved chloride and phenol concentrations at 55 and 439 days after source emplacement; concentrations are normalized to the cross-sectional area of the creosote source (in the $y-z$ plane); profiles are in the approximate direction of groundwater flow.

The velocity estimates obtained by the two methods (from longitudinal chloride distribution and from time series data at two points) are in reasonable agreement with estimates from Mackay et al. (1986), Hubbard et al. (1994), and Patrick (1986), shown in Table 1. All three of these studies were based on injected plumes and were therefore able to utilize a preferred velocity estimation approach based on centre of plume mass, described by Freyberg (1986). Average linear groundwater velocity determinations from previous studies at this site were applied in the current study on the basis that: (1) current velocity estimates were in reasonable agreement with previous determinations and (2) previous determinations were obtained by a preferred approach. This velocity was subsequently used to estimate mass flux from the source to the plume (King et al., this issue).

Fig. 10. Profiles of dissolved concentrations of selected plume organics at 626, 1008 and 1357 days after source emplacement; concentrations are normalized to the cross-sectional area of the source (in the $y-z$ plane) and are oriented in the approximate direction of groundwater flow.



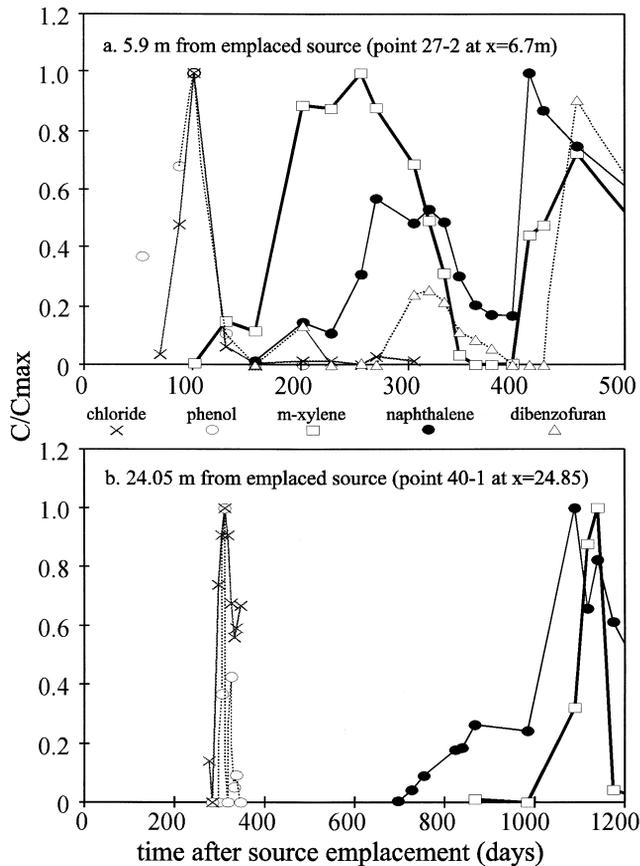


Fig. 11. Time series plots for chloride and selected organics concentrations at two monitoring points downgradient of the emplaced creosote source.

7.3. Phenol

As shown in Fig. 3, phenol concentration in source leachate was expected to decrease relatively rapidly, due to the high solubility of this compound which causes it to be

Table 7
Summary of data for estimation of average linear groundwater velocity

Data type	Approximate point at which $C/C_{max} = 0.5$ occurs	Corresponding velocity estimate (m/day)
Synoptic monitoring at $t = 439$ days after source emplacement (Fig. 9)	$x = 38 \text{ m}^1$	0.085
Time series at $x = 6.7 \text{ m}^a$ (Fig. 11)	$t = 89$ days	0.066
Time series at $x = 24.85 \text{ m}^a$ (Fig. 11)	$t = 290$ days	0.083

^aThe downgradient boundary of the emplaced source occurs at $x = 0.8 \text{ m}$.

quickly depleted from the source. This is confirmed by Fig. 5 which shows that by 55 days the phenol plume started to detach from the source. By 278 days, the plume migrated as a discrete slug and by 439 days, further spreading and a decrease in peak concentrations had occurred. Extrapolation of the plume trajectory to 626 days would suggest that a significant portion of the plume should have been encountered in synoptic samples collected at this time; however, only isolated traces of phenol were detected. This suggests that the decrease in plume concentrations observed from 278 to 439 days continued, to the point that the compound was almost completely transformed at 626 days.

Comparison of the longitudinal distribution of phenol mass with that of chloride (Fig. 9) supports the suggestion that significant transformation of phenol is occurring along the groundwater flow path. At 55 days, peak normalized concentrations of phenol and chloride are 48000 $\mu\text{g}/\text{l}$ and 180 mg/l , respectively. Later, at 439 days, it was apparent that the mass distribution of these two plumes was still similar in shape. However, peak chloride concentration had decreased to 79.6 mg/l , approximately 44% of the 55-day concentration. Meanwhile, peak phenol concentration had decreased more sharply, to approximately 7% (3600 $\mu\text{g}/\text{l}$). A quantitative mass balance is presented by King et al. (this issue).

Data from the two time series sampling points (Fig. 11) indicate that the advancement of the phenol plume compared closely with chloride and therefore that the former was not significantly sorbed to Borden sand. However, synoptic data from 439 days (Fig. 9) provide a more detailed basis for evaluating a retardation factor (R) for phenol. The similar, but slightly offset, curves of phenol and chloride mass distribution at 439 days indicate a slight degree of phenol retardation, which can be estimated according to:

$$R = d_{\text{cl}}/d_{\text{ph}}, \quad (7)$$

where d_{cl} is the distance from the source to a given point on the chloride curve and d_{ph} is the distance from the source to the corresponding point on the phenol curve. This expression is a modification of a typical form for retardation: $R = v_{\text{gw}}/v_{\text{sol}}$, where $v_{\text{gw}} = d_{\text{gw}}/t$ is the average linear velocity of groundwater and $v_{\text{sol}} = d_{\text{sol}}/t$ is the transport velocity of the solute for which R is being calculated. In the case of Eq. (7), v_{gw} is assumed to be approximated by the velocity of chloride (a conservative solute) and R is being calculated for phenol. Furthermore, the time constant has been removed from the equation, to allow calculation of R on the basis of migration distance only.

This method (Eq. (7)) provides an R estimate for phenol of approximately 1.05. However, given the evidence of phenol mass loss, this can be considered an upper limit for R : mass loss from the front of the plume would cause an apparent decrease in the rate of plume migration. The reader is referred to King et al. (this issue) for results of alternative methods used to estimate R , and for a comparison of method results.

7.4. *m*-Xylene

As discussed above, chloride and phenol dissolved relatively quickly from the source and subsequently migrated as detached solute slugs. As illustrated on Fig. 11, this slug-like behaviour was also approached, during early time, by the other solutes shown

in the plot (*m*-xylene, naphthalene and dibenzofuran). However, in the case of these other solutes, complete detachment from the source did not occur. This early slug-type behaviour may be due to initial rapid flushing of organic solute from the source during rebound of the water table, immediately after source emplacement.

Comparison of time series curves for *m*-xylene and chloride (Fig. 11) show that the migration of the former was apparently retarded with respect to the conservative tracer (chloride). At monitoring point 27-2 ($x = 6.7$ m; 5.9 m from source), an R of approximately 2.5 was indicated by the lag between the curves which, in this case, is estimated by:

$$R = t_{\text{org}}/t_{\text{Cl}}, \quad (8)$$

where t_{Cl} = time required to reach maximum chloride concentration and t_{org} = time required to reach maximum organic compound concentration. The derivation of this expression for R is similar to Eq. (7), except that in this case, d (the distance to the time series monitoring point) is constant, while t (the time required for the solutes to migrate to this point) varies. Maximum concentration has been used as the reference point in this equation, on the basis of the apparent ‘slug-type’ behaviour in the early time series data, for most of the solutes shown. On this basis, it is assumed that the maximum concentration approximates the centre of mass of the associated slug.

Meanwhile, a similar calculation for 40-1 ($x = 24.85$ m) yielded an R of 3.7. This increase in R was probably due to transformation of *m*-xylene along the flow path, to the degree that the plume migration is curtailed. Inspection of the *m*-xylene plume contour plans (Fig. 6) shows that plume reached a maximum observed extent at 626 days and then the plume front was observed to withdraw back toward the source at 1008 days and further again at 1357 days.

The observation of *m*-xylene plume drawback, is also shown by the plot of longitudinal mass distribution in Fig. 10. This figure also shows a decrease in plume mass over time, providing evidence of transformation. Evidence of decreasing *m*-xylene flux into the plume is shown by lower concentrations at the influent end of the plume (which has been delineated at $x = 2.7$ m). This trend is in general agreement with the expected trend of *m*-xylene dissolution, shown in Fig. 3. These observations suggest that the plume has drawn back due to a combination of *m*-xylene transformation within the plume and decrease in *m*-xylene influx from the source. That is, the rate of flux decreased to below the rate of plume transformation, leading to a decrease in the size and mass of the plume.

7.5. Naphthalene

The plan views of naphthalene plume development (Fig. 7) show a relatively consistent rate of plume growth and, as of 1357 days, the plume was still expanding. Comparison of longitudinal mass distribution profiles (Fig. 10) shows that plume mass also increased during this period. The near-source concentrations on the profiles are evidence that the strength of source leachate, with respect to naphthalene, had decreased between each of the last three snapshots, which is in general agreement with the trend predicted by Raoult’s law (Fig. 3). However, it is evident that there was still sufficient flux of naphthalene into the plume to support plume expansion.

Time series sampling results (Fig. 11) show that naphthalene was retarded with respect to chloride migration. At the point closest to the source ($x = 6.7$ m), the arrival of the naphthalene peak lagged behind that of the chloride peak, indicating an R of approximately 2.6. Further downgradient ($x = 24.05$ m), this factor increased to 3.5, indicating that the forward progression of the naphthalene plume has decreased somewhat with time, although this is not apparent in the plume contour plans.

7.6. Dibenzofuran

Time series monitoring at $x = 6.7$ m shows that the migration rate of dibenzofuran is slower than that of chloride by an R of 3.12. The compound was not detected at the other selected time series monitoring point. Plan views of the dibenzofuran plume (Fig. 8) show that it did not migrate appreciably in the 2-year duration between the last three synoptic monitoring events and this observation is also supported by the longitudinal concentration profiles in Fig. 10. The profiles also show that dibenzofuran flux into the plume was similar at the time of the last two synoptic sampling events, which is consistent with the nearly constant rate of source dissolution predicted by Raoult's law and shown in Fig. 3.

The lower input flux indicated for 626 days (Fig. 10) is likely due to the higher R for this compound. The higher R has increased the time required for the front of the dibenzofuran plume to migrate fully into the monitoring network. Consequently, at 626 days, dibenzofuran concentrations are continuing to increase slightly, at the upgradient edge of the monitoring network. For the latter two monitoring events (1008 and 1357 days), there is strong evidence that the dibenzofuran plume is at steady state, where mass flux into the plume is balanced by mass transformation within the plume.

7.7. Phenanthrene

This compound was more highly retarded than naphthalene and *m*-xylene and was not detected at the two selected time series sampling points. Near-source concentrations of phenanthrene in the longitudinal concentration profiles (Fig. 10) indicate that flux of this compound into the plume increased over the last three snapshots. This probably has less to do with an increase in source strength than with the highly retarded plume front gradually moving into the monitored zone. After relatively rapid expansion of the phenanthrene plume from 626 to 1008 days, it was observed to recede and decrease in mass, as of 1357 days.

7.8. Carbazole

Longitudinal profiles of carbazole concentration in Fig. 10 show that the plume advanced over the period from 626 to 1008 days, but remained relatively stable from 1008 to 1357 days. Unlike dibenzofuran, carbazole loadings into the plume have not been consistent over the monitoring period. Near-source concentration reached an observed maximum of approximately 200 $\mu\text{g}/\text{l}$ at 1008 days and then decreased to

approximately 100 $\mu\text{g}/\text{l}$ at 1357 days, which is generally consistent with the decline in source leachate concentration predicted by Raoult's law (Fig. 3). The low near-source concentration at 626 days may be due to a lag time required for the plume to migrate into the monitored zone.

7.9. 1-methylnaphthalene

Development of the plume for this compound followed a trend similar to that of naphthalene. Inspection of plume longitudinal profiles in Fig. 10 indicate that plume position advanced and plume mass increased at a relatively consistent rate over the monitoring period. Also similar to naphthalene, the rate of flux into the plume decreased over time although to a lesser degree than naphthalene. This dissolution trend is generally consistent with the Raoult's law prediction. However, in comparison to naphthalene, the rate of plume migration was slower.

8. Summary and conclusions

In general, trends in compound flux from the source were qualitatively consistent with predictions based on Raoult's law. Selected organic compounds displayed an entire spectrum of plume behaviour. Phenol was completely dissolved from the source relatively early in the study and migrated downgradient as a discrete slug. Minimal detection of phenol in synoptic monitoring at 626 days indicated that this compound was substantially transformed. The *m*-xylene plume was observed to migrate to a maximum observed distance at 626 days and then to recede back toward the source as the rate of flux into the plume decreased to below the rate of plume transformation.

The phenanthrene plume was also observed to recede, although the flux of phenanthrene into the plume continued to increase up to the last synoptic monitoring event. Advancement of the carbazole plume was similar in that the rate of advancement had decreased, or possibly halted, in the most recent snapshot. However, in the case of carbazole, mass flux from the source also decreased, probably in response to source depletion with respect to this compound.

The plume of dibenzofuran remained relatively constant in extent during the last 2 years of monitoring. A relatively constant rate of dibenzofuran dissolution from the source, and a matching rate of plume transformation are considered the causes of this apparent steady state behaviour. Two of the selected compounds, naphthalene and 1-methylnaphthalene, continued to migrate outward despite apparent decreases in their respective input fluxes over time.

Acknowledgements

The authors wish to thank Drs. John Cherry, Neil Thompson and Michael Barcelona for thoughtful review of this work. We also thank Dr. Michael Rivett and a second reviewer (anonymous) for helpful and constructive comments on the original manuscript.

Special thanks are extended to Kim Hamilton for extensive field and laboratory assistance; Heather Malcolmson for supervising the source installation; Jeanet Nielsen and Susanne Hansen for collecting some of the early data. Financial assistance was provided by the Natural Sciences and Engineering Research Council of Canada.

References

- Alexander, M., 1985. Biodegradation of organic chemicals. *Environmental Science and Technology* 18, 106–111.
- Arvin, E., Flyvbjerg, J., 1992. Groundwater pollution arising from the disposal of creosote waste. *Journal of the Institution of Water and Environmental Management* 6, 646–652.
- Atlas, R.M., 1981. Microbial degradation of petroleum hydrocarbons: an environmental perspective. *Microbiology Reviews* 45, 180–209.
- Barbaro, J.R., Barker, J.F., Lemon, L.A., Mayfield, C.I., 1992. Biotransformation of BTEX under anaerobic, denitrifying conditions: field and laboratory observations. *Journal of Contaminant Hydrology* 11, 245–272.
- Barbaro, S.E., Albrechtsen, H.J., Jensen, B.K., Mayfield, C.I., Barker, J.F., 1994. Relationship between aquifer properties and microbial populations in the Borden aquifer. *Geomicrobiology Journal* 12, 203–219.
- Barker, J.F., Patrick, G.C., Major, D., 1987. Natural attenuation of aromatic hydrocarbons in a shallow sand aquifer. *Ground Water Monitoring Review*, Winter, pp. 64–71.
- Bennett, P.C., Siegel, M.J., Baedecker, M.J., Hult, M.F., 1993. Crude oil in a shallow sand and gravel aquifer: I. Hydrogeology and inorganic chemistry. *Applied Geochemistry* 8, 529–549.
- Berry-Spark, K.L., Barker, J.F., MacQuarrie, K.T., Major, D., Mayfield, C.I., Sudicky, E.A., 1988. The behaviour of soluble petroleum product-derived hydrocarbons in groundwater. Petroleum Association for the Conservation of the Canadian Environment. PACE Phase III Report No. 85-3.
- Cherry, J.A., Gillham, R.W., Anderson, E.G., Johnson, P.E., 1983. Migration of contaminants in groundwater at a landfill: a case study: 2. Groundwater monitoring devices. *Journal of Hydrology* 63, 31–49.
- Cline, P.V., Delfino, J.J., Rao, P.S.C., 1991. Partitioning of aromatic constituents into water from gasoline and other complex solvent mixtures. *Environmental Science and Technology* 25, 914–920.
- Cozzarelli, I.M., Baedecker, M.J., Eganhouse, R.P., Goerlitz, D.F., 1994. The geochemical evolution of low-molecular-weight organic acids derived from the degradation of petroleum contaminants in groundwater. *Geochimica et Cosmochimica Acta* 58, 863–877.
- Devlin, J.F., 1994. Enhanced in situ biodegradation of carbon tetrachloride and trichloroethene using a permeable wall injection system. PhD Thesis, University of Waterloo, Waterloo, Ontario.
- Dyregborg, S., Arvin, E., Broholm, K., 1997. Biodegradation of NSO-compounds under different redox-conditions. *Journal of Contaminant Hydrology* 25, 177–197.
- Flyvbjerg, J., Arvin, E., Jensen, B.K., Olsen, S.K., 1993. Microbial degradation of phenols and aromatic hydrocarbons on creosote-contaminated groundwater under nitrate-reducing conditions. *Journal of Contaminant Hydrology* 12, 133–150.
- Forsey, S., in progress. In situ chemical oxidation of creosote residuals. PhD Thesis, University of Waterloo, Waterloo, Ontario.
- Freyberg, D.L., 1986. A natural gradient experiment in solute transport in a sand aquifer: 2. Spatial moments and the advection and dispersion of nonreactive tracers. *Water Resources Research* 22, 2031–2046.
- Ghiorse, W.C., Balkwill, D.L., 1983. Enumeration and morphological characterization of bacteria indigenous to subsurface environments. *Developments in Industrial Microbiology* 24, 213–239.
- Godsy, E.M., Goerlitz, D.F., Grbic-Galic, D., 1992. Methanogenic biodegradation of creosote contaminants in natural and simulated groundwater ecosystems. *Ground Water* 30, 232–242.
- Goerlitz, D.F., Troutman, D.E., Godsy, E.M., Franks, B.J., 1985. Migration of wood-preserving chemicals in contaminated groundwater in a sand aquifer at Pensacola, Florida. *Environmental Science and Technology* 19, 955–961.
- Hubbard, C.E., Barker, J.F., O'Hannesin, S.F., VanderGriendt, M., Gillham, R.W., 1994. Transport and fate of dissolved methanol and methyl-tertiary-butyl-ether, and monoaromatic hydrocarbons in a shallow sand aquifer. American Petroleum Institute Publication No. 4601.

- Johansen, S.S., Hansen, A.B., Mosbæk, H., Arvin, E., 1997. Identification of heteroaromatic and other organic compounds in groundwater at creosote-contaminated sites in Denmark. *Ground Water Monitoring and Remediation* 17 (2), 106–115.
- Kiilerich, O., Arvin, E., 1995. Factors affecting the distribution of aromatic compounds around manufactured gas plants. *Land Contamination and Reclamation*, 3 (special issue 4), 33–10–13–11.
- King, M.W.G., Malcolmson, H., Barker, J.F., 1994. Groundwater plume development from a complex organic mixture. *Proceedings Petroleum Hydrocarbons and Organic Chemicals in Ground Water: Prevention, Detection and Restoration*, Houston, Texas, November 2–4.
- King, M.W.G., 1997. Migration and natural fate of a coal tar creosote plume. PhD Thesis, University of Waterloo, Waterloo, Ontario.
- King, M.W.G., Barker, J., Devlin, J.F., Butler, B.J., this issue. Migration and natural fate of a coal tar creosote plume: 2. Mass balance and biodegradation indicators.
- Klecka, G.M., Davis, J.W., Gray, D.R., Madsen, S.S., 1990. Natural bioremediation of organic contaminants in ground water: Cliffs-dow Superfund site. *Ground Water* 28, 534–543.
- Lee, L.S., Hagwall, M., Delfino, J.J., Rao, P.S.C., 1992a. Partitioning of polycyclic aromatic hydrocarbons from diesel fuel into water. *Environmental Science and Technology* 26, 2104–2110.
- Lee, L.S., Rao, P.S.C., Okuda, I., 1992b. Equilibrium partitioning of polycyclic aromatic hydrocarbons from coal tar into water. *Environmental Science and Technology* 26, 2110–2115.
- Linderfelt, W.R., 1994. Field study of capture zones in a shallow sand aquifer. Ph.D. Thesis, New Mexico Institute of Mining and Technology, Socorro, New Mexico.
- Linderfelt, W.R., Wilson, J.L., 1994. Field study of capture zones in a shallow sand aquifer. In: Dracos, Stauffer (Eds.), *Transport and Reactive Processes in Aquifers*. Balkema, Rotterdam, pp. 289–294.
- MacFarlane, D.S., Cherry, J.A., Gillham, R.W., Sudicky, E.A., 1983. Migration of contaminants in groundwater at a landfill: a case study: 1. Groundwater flow and plume delineation. *Journal of Hydrology* 63, 1–29.
- MacIntyre, W.G., Boggs, M., Antworth, C.P., Stauffer, T.B., 1993. Degradation kinetics of aromatic organic solutes introduced into a heterogenous aquifer. *Water Resources Research* 29, 4045–4051.
- Mackay, D.M., Cherry, J.A., 1989. Groundwater contamination: pump-and-treat remediation. *Environmental Science and Technology* 23, 630–636.
- Mackay, D.M., Freyberg, D.L., Roberts, P.V., 1986. A natural gradient experiment on solute transport in a sand aquifer: 1. Approach and overview of plume movement. *Water Resources Research* 22, 2017–2029.
- MacKay, D., Shiu, W.Y., Maijanen, A., Feenstra, S., 1991. Dissolution of non-aqueous phase liquids in groundwater. *Journal of Contaminant Hydrology* 8, 23–42.
- MacKay, D., Shiu, W.Y., Ma, K.C., 1992. *Illustrated Handbook of Physical–Chemical Properties and Environmental Fate for Organic Chemicals*, Vols. 1–4. Lewis Publishers.
- Madsen, E.L., 1991. Determining in situ biodegradation. *Environmental Science and Technology* 25, 1663–1673.
- Madsen, E.L., Sinclair, J.L., Ghiorse, W.C., 1991. In situ biodegradation: microbiological patterns in a contaminated aquifer. *Science* 252, 830–833.
- Malcolmson, H., 1992. Dissolution of an Emplaced Creosote Source, CFB Borden, Ontario. Project Master's Report, University of Waterloo, Waterloo, Ontario.
- Matraw, Jr., H.C., Franks, B.J. (Eds.), 1986. *Movement and Fate of Creosote Waste in Ground Water*, Pensacola, Florida: US Geological Survey Toxic Waste-Ground-Water Contamination Program. Water Supply Paper 2285.
- Mueller, J.G., Chapman, P.J., Pritchard, P.H., 1989. Creosote-contaminated sites—their potential for bioremediation. *Environmental Science and Technology* 23, 1197–1201.
- National Research Council, 1993. *In situ bioremediation: when does it work?* National Academy Press, Washington, D.C.
- Neilsen, J.S., Hansen, S.S., 1992. Fate and transport of creosote compounds under natural conditions in a sand aquifer at CFB Borden, Ontario, Canada. 33-Point Project, Department of Environmental Engineering, Technical University of Denmark.
- Nicholson, R.V., Cherry, J.A., Reardon, E.J., 1983. Migration of contaminants in groundwater at a landfill: a case study. *Journal of Hydrology* 63, 131–176.
- Patrick, G.C., 1986. A natural gradient tracer experiment of dissolved benzene, toluene and xylenes in a shallow sand aquifer. MSc Thesis, University of Waterloo.

- Priddle, M.W., MacQuarrie, K.T.B., 1994. Dissolution of creosote in groundwater: an experimental and modelling investigation. *Journal of Contaminant Hydrology* 15, 27–56.
- Pritchard, P.H., Bourquin, A.W., 1983. The use of microcosms for evaluation of interactions between pollutants and microorganisms. In: Marshall, K.C. (Ed.), *Advances in Microbial Ecology*. Plenum, New York, pp. 133–214.
- Sangster, J., 1989. Octanol–water partition coefficients of simple organic compounds. *Journal of Physical Chemistry Reference Data* 18, 1111–1229.
- Shiu, W.Y., Ng, A.L.Y., Mackay, D.M., 1988. Preparation of aqueous solutions of sparingly soluble organic substances: ii. Multicomponent systems—hydrocarbon mixtures and petroleum products. *Environmental Toxicology and Chemistry* 7, 125–137.
- Starr, R.C., Cherry, J.A., Vales, E.S., 1991. Sealable joint sheet pile cutoff walls for preventing and remediating groundwater contamination. Proceedings: Ontario Ministry of the Environment Technology Transfer Conference, Toronto, Ontario, November 25–26.
- Sudicky, E.A., 1986. A natural gradient experiment on solute transport in a sand aquifer: spatial variability of hydraulic conductivity and its role in the dispersion process. *Water Resources Research* 22, 2069–2082.
- Sudicky, E.A., Cherry, J.A., Frind, E.O., 1983. Migration of contaminants in groundwater at a landfill: a case study: 4. A natural gradient dispersion test. *Journal of Hydrology* 63, 81–108.
- Turney, G.L., Goerlitz, D.F., 1990. Organic contamination of ground water at Gas Works Park, Seattle, Washington. *Ground Water Monitoring Review*, Summer, pp. 187–198.
- USEPA, Office of Solid Waste and Emergency Response, 1999. Use of Monitored Natural Attenuation at Superfund, RCRA Corrective Action, and Underground Storage Tank Site (Directive 9200.4-17p).
- Wilson, J.T., McNabb, J.F., Balkwill, D.L., Ghiorse, W.C., 1983. Enumeration and characterization of bacteria indigenous to a shallow water-table aquifer. *Ground Water* 21, 134–142.