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Migration and natural fate of a coal tar creosote plume
2. Mass balance and biodegradation indicators

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Abstract

A source of coal tar creosote was emplaced below the water table at CFB Borden to investigate natural attenuation processes for complex biodegradable mixtures. A mass balance indicated that ongoing transformation occurred for seven study compounds. Phenol migrated as a discrete slug plume and almost completely disappeared after 2 years, after being completely leached from the source early in the study. The *m*-xylene plume migrated outward to a maximum distance at approximately 2 years, and then receded back towards the source as the rate of mass flux out of the source decreased to below the overall rate of plume transformation. Carbazole showed similar behaviour, although the reversal in plume development occurred more slowly. The dibenzofuran plume remained relatively constant in extent and mass over the last 2 years of monitoring, despite constant source input over this period, providing evidence that the dibenzofuran plume was at steady state. Meanwhile, the naphthalene and 1-methylnaphthalene plumes continued to advance and increase in mass over the observation period, although at a decreasing rate. The phenanthrene plume was also subject to transformation, although measurement of the rate was less conclusive due to the higher proportion of sorbed mass for this compound. Three lines of evidence are presented to evaluate whether the observed plume mass loss was due to microbial biodegradation. Measurement of redox-sensitive parameters in the vicinity of the plume showed the types of changes that would be expected to occur due to plume biodegradation: dissolved oxygen and SO_4^{2-} decreased in groundwater within the plume while significant increases were noted for Fe^{2+},

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Mn^{2+} and methane. Further evidence that plume mass loss was microbially-mediated was provided by the accumulation of aromatic acids within the plume. Measurements of phospholipid fatty acids (PLFA) in aquifer material indicated that microbial biomass and turnover rate were greater within the plume than outside: also consistent with biodegradation. Study results highlight the potential for utilizing natural attenuation as a site cleanup approach for dissolved phase plumes from complex organic mixture like coal tar creosote.

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

1. Introduction

The occurrence of compound transformation is often a critical issue in the evaluation of organic contaminant plumes. Even relatively slow rates of transformation may impose significant limitations on the extent of plume migration, compared to the situation where decreases in organic solute concentration are due only to sorption and hydrodynamic processes. Since the environmental risk associated with groundwater contamination is closely related to the distance to which contamination may migrate away from the source, an evaluation of this risk often requires an estimate of the rate and nature of solute transformation. Methods for evaluating plume transformation are generally based on some form of mass balance, using one, two, or three dimensional data, depending on the simplicity of plume, source geometry and nature of the study.

In general, biodegradation of non-chlorinated organic compounds, such as those comprising organic mixtures like petroleum and creosote, is favoured under more oxidizing conditions. A host of studies, as outlined in several review articles (e.g., Grbic-Galic, 1989; Mueller et al., 1989; Grbic-Galic, 1990; Bollag and Kaiser, 1991), have shown that these types of compounds will also biodegrade under various anaerobic conditions (denitrifying, sulphate-reducing, methanogenic and fermentative).

While the ability of naturally occurring microbes to mediate transformation of non-chlorinated organics is well supported by laboratory studies there are limitations on direct transferral of these results to the plume-scale. Evaluation of organic plume biodegradation is made difficult by the complexity of transport and degradation processes in a dynamic groundwater system and, as noted by Madsen (1991), is further complicated by problems inherent in formulating a mass balance in spatially heterogeneous media typically found in the field.

2. Purpose

The purpose of the current paper is to present plume-scale evidence for mass transformation of a complex organic plume in a setting that was designed to simulate a frequent scenario at industrial sites: a fixed source of organic contamination that dissolves slowly into groundwater over time. The field experiment described in this paper was conducted with an emplaced source containing residual coal tar creosote.

Development of a dissolved phase plume occurred under controlled field conditions, making it possible to formulate compound mass balances from three dimensional data collected at an unprecedented density, for this type of plume. Additional lines of evidence are reported to evaluate whether the observed plume mass loss was attributable to biodegradation. Groundwater was monitored for electron acceptors and organic acids to evaluate changes expected with biodegradation. In addition, aquifer solids were examined for indications of microbial adaptation in response to the presence of the plume. An overview of source emplacement and qualitative observations of plume development were provided by King and Barker (this issue).

3. Background

3.1. Mass balance

Probably the most widely applied technique of evaluating plume transformation is a one dimensional approach whereby solute concentrations are monitored along an inferred groundwater flowline. In order to attribute a portion of an observed concentration decrease to compound degradation, the effects of hydrodynamic dilution and sorption must be taken into account. Barker et al. (1986) studied a landfill leachate plume in North Bay, Ontario, and compared concentrations of selected organics along an assumed groundwater flow line to evaluate relative rates of organics degradation. Lyngkilde and Christensen (1992a) were able to use chloride concentrations to correct organics concentrations for hydrodynamic dilution in their study of a landfill leachate plume in Vejen, Denmark. Using a conceptually similar approach, Baedecker et al. (1993) evaluated the behaviour of dissolved volatile organic carbon (DVOC) composed primarily of BTEX compounds, as part of an intensive characterization of an oil spill in Bemidji, MN. DVOC was compared with Ca^{2+}, which was conservative along part of the flowpath, and to a modelled conservative tracer. One dimensional approaches were also used by Ehrlich et al. (1982) in a study of a coal tar distillation and wood-treating plant in St. Louis Park, MN, and by Goerlitz et al. (1985) in an extensive characterization of groundwater contamination at a wood-preserving facility in Pensacola, FL.

Thierrin et al. (1995) used a unique two dimensional approach for determining plume mass loss. A solution of deuterated benzene, toluene, *p*-xylene and naphthalene was injected into a groundwater plume that originated from an underground gasoline storage tank. Injection water also contained bromide as a conservative tracer. The researchers monitored the passage of injected solutes past a row of multi-level piezometers located 17 m from the injection point. By comparing bromide and organics mass, they were able to evaluate for organics transformation and to estimate degradation rates. In a conceptually similar approach Barbaro et al. (1992) injected two slugs of gasoline-contacted water into a landfill leachate plume and calculated the rate of plume transformation by integrating solute breakthrough curves at sequential rows of multi-level samplers.

The three dimensional mass balance approach requires monitoring data from the entire plume, to compare total plume mass at two or more times. Three previous studies have been conducted within the current study area, utilizing dense three dimensional

monitoring to formulate mass balances for injected organic plumes. Mackay et al. (1986) injected water containing five halogenated organic chemicals and two inorganic tracers (chloride and bromide) into the Borden aquifer. Barker et al. (1987) followed the degradation of an injected plume of benzene, toluene and xylene isomers (BTX). Hubbard et al. (1994) conducted simultaneous injection of three organic solute plumes composed of water that had contacted: (1) gasoline only (2) gasoline and methyl–*tertiary* butyl ether (MTBE) and (3) gasoline and methanol. In a study conducted at Columbus Air Force Base in Mississippi, MacIntyre et al. (1993) conducted a three dimensional mass balance of an injected plume containing benzene, *p*-xylene, naphthalene and *o*-dichlorobenzene.

3.2. Electron acceptors

In laboratory studies, microbial utilization of various aromatic, phenolic and heterocyclic compounds has been linked with dissolved oxygen utilization, denitrification (e.g., Kuhn et al., 1988; Major et al., 1988; Hutchins et al., 1991), iron reduction (e.g., Lovley et al., 1989) sulphate reduction (e.g., Haag et al., 1991; Edwards et al., 1992) and methanogenesis (e.g., Godsy et al., 1992; Adrian and Suflita, 1994; Edwards and Grbic-Galic, 1994).

Several field studies have presented geochemical evidence that is consistent with these laboratory results. Dissolved oxygen depletion has been documented for a number of petroleum hydrocarbon plumes (e.g., Barker et al., 1987; Chiang et al., 1989; Wilson et al., 1990) and has been related to biodegradation. In an extensive characterization an oil spill site at Bemidji, MN, Bennett et al. (1993) delineated several characteristic redox zones. They determined that groundwater upgradient of the spill was oxygenated and that dissolved oxygen became slightly depleted as petroleum hydrocarbons began to mix with groundwater. As organic carbon increased, groundwater became anoxic, methane occurred, dissolved iron and manganese increased and redox potentials indicated strongly reducing conditions. Similar redox trends were observed through intensive characterization studies at a creosote-contaminated site in Pensacola, FL (Mattraw and Franks, 1986), and in a landfill leachate plume containing dissolved organics in Vejen, Denmark (Lyngkilde and Christensen, 1992b).

3.3. Microbiological indicators

Several field studies have identified changes in characteristics of microbial populations due to the introduction of organic compounds to groundwater. Godsy et al. (1992) determined that populations of methanogenic bacteria were approximately two orders of magnitude more numerous in pore water and aquifer samples from contaminated areas of the site than in uncontaminated areas. Elevated concentrations of methane within the contaminated areas and the observation of methanogenesis in laboratory microcosms composed with contaminated aquifer material, were evidence that methanogenic microorganisms played a role in the final fate of the contaminants. Madsen et al. (1991)

determined that microorganisms from within a plume associated with buried coal tar waste were capable of mineralizing naphthalene and phenanthrene over a 3-week period while those in pristine samples were not. They also determined that protozoa were more abundant within the plume and attributed this to increase in bacterial numbers due to contaminant utilization, and subsequent protozoan grazing on bacteria.

3.4. Organic metabolites

Several studies have documented the occurrence, in groundwater, of organic acids and other intermediate products associated with biodegradation of plumes from sources such as petroleum fuels, coal tar and creosote. Cozzarelli et al. (1995) detected a wide range of aliphatic and aromatic acids associated with a plume from a gasoline spill in Galloway Township, NJ. Barcelona et al. (1995) detected aliphatic and aromatic acids in groundwater, as transformation products at several petroleum hydrocarbon-contaminated sites, through a reconnaissance level survey. Aliphatic and aromatic acids were also detected in association with the Pensacola creosote plume (Goerlitz et al., 1985). Quinolinone, another metabolite, was detected in both the Pensacola creosote plume and in work previously reported for the current site (Fowler et al., 1994). This compound is a ketone of the *N*-heterocyclic compound quinoline, which is a constituent in creosote. Bennett et al. (1986) determined that quinolinone was produced as a metabolite of quinoline by aerobic microorganisms from the Pensacola site. At the Bemidji site, Cozzarelli et al. (1994) attributed the observed accumulation of organic acids in groundwater to biodegradation of aromatic parent compounds in the anoxic portion of the plume. The authors compared the Bemidji plume to those at Halloway and Pensacola, concluding that depletion of electron acceptors through microbially mediated oxidation of parent aromatics allowed the buildup of organic acids.

4. Methods

4.1. Mass balance

4.1.1. General approach

The quantity of plume compound mass that was transformed between synoptic sampling events was estimated on the basis of dissolved phase concentrations, sorption characteristics and groundwater flux, according to:

$$M_R = M_F - \Delta M_T \quad (1)$$

where M_R = transformed mass, M_T = total mass associated with the plume = $M_D + M_S$, M_D = dissolved mass in the plume, M_S = sorbed mass associated with the dissolved plume and M_F = the quantity of mass input to the plume over a given period (Δt). Fig. 1 is a diagram illustrating the various components of this mass balance approach. As shown, the balance relates to that portion of the plume located at $x > 3.5$ m (2.7 m downgradient of the source) and has been defined in this way to avoid the large errors

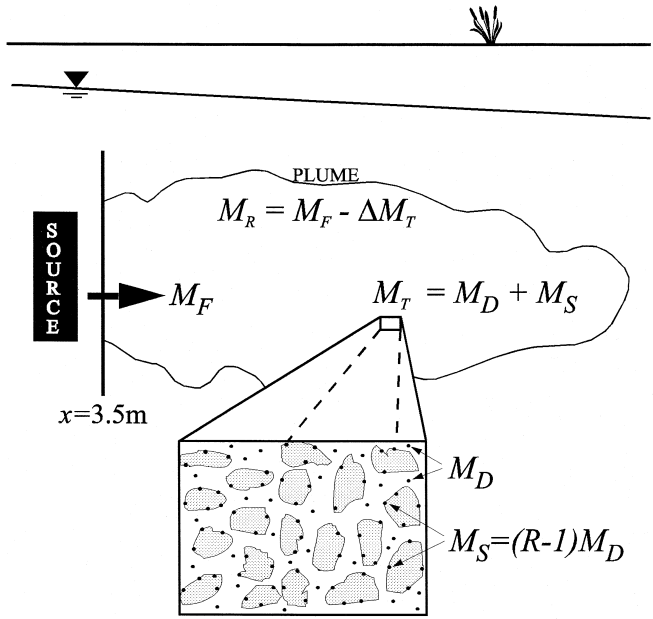

Fig. 1. Conceptualized cross-section showing the main components of the mass balance for the emplaced creosote source.

associated with interpolation of concentration data nearer the source, where lateral concentration gradients are relatively large. By necessity, the compounds selected for mass balance are representative of creosote compounds with relatively minimal to moderate hydrophobicity. The more sorptive compounds did not migrate substantially into the monitoring network over the duration of the experiment (almost 4 years).

4.1.2. Dissolved mass (M_D)

Dissolved mass (M_D) was estimated with data from synoptic plume sampling, which was conducted at six times since source emplacement (t = 55, 278, 439, 626, 1008 and 1357 days). Sufficient plume coverage for calculation of total dissolved mass was obtained for the latter four of these. Dissolved mass has been calculated using a three dimensional interpolation routine in the ENTEC (Surpac, 1995) geostatistical program whereby irregularly spaced three dimensional data are interpolated to a regularly spaced array of three dimensional cells. Additional details on synoptic sampling, analysis and data interpolation were provided by King (1997).

4.1.3. Sorbed mass (M_S)

Due to the hydrophobic nature of the compounds in creosote, a degree of sorption will occur from the aqueous phase to aquifer solids. Furthermore, depending on the hydrophobicity of the compound and the sorbent properties of the aquifer, the quantity of sorbed mass in a given volume of aquifer can be substantially greater than the mass in

solution. Consequently, sorbed mass has potential to be a relatively large component of the mass balance, depending on the compound. Sorption is often approximated as a linear reversible equilibrium process, also known as sorption ideality, whereby dissolved concentration (C) is related to sorbed concentration (S) by a solids partitioning coefficient (K_d), as follows:

$$S = K_d C \tag{2}$$

where K_d is in units of L^3/M and can be used to calculate a retardation factor (R) by:

$$R = 1 + (\rho/\eta) K_d \tag{3}$$

where ρ = bulk density of the porous medium (M/L^3) and η = porosity (dimensionless). Sorbed mass can then be estimated with R, according to:

$$M_S = (R - 1) M_D. \tag{4}$$

Although the assumption of sorption ideality is often applied, laboratory and field experiments have often provided evidence of solute behaviour that deviates from ideality. A review of processes that can lead to these types of deviations is provided by Brusseau and Rao (1989). These authors discuss the significant effects of physical phenomena, such as rate limitations due to diffusion of solute into low hydraulic conductivity particle aggregates or laminae. They also point out the difficulty in estimating the parameters that may control these processes.

In the current study, it was considered that sorption was reasonably approximated by the assumption of ideality, on the basis of previous studies at the site. Curtis et al. (1986) compared laboratory sorption data and field results from an injected plume of bromoform, carbon tetrachloride, tetrachloroethylene, 1,2-dichlorobenzene and hexachloroethane injected at the Borden site. They estimated K_ds by sorption batch testing and by monitoring the migration rate of the plume centre-of-mass. It was concluded that the close agreement of these methods was evidence that the behaviour of the study compounds could be approximated by sorption ideality, although the authors noted that the methods agreed more closely when the plume was near the source. A similar comparison was conducted by Hubbard et al. (1994) for BTEX compounds in a plume of dissolved gasoline injected at the same site. This group of compounds also showed behaviour that was generally consistent with sorption ideality.

Values of K_d for use in mass balance calculations were estimated by two different methods: (1) empirical correlation and (2) laboratory batch test. The first method is widely used and was described by Karickhoff (1984). The basis of this approach is that the organic fraction of the aquifer solids (f_{oc}) is the primary sorbate for hydrophobic compounds in subsurface systems. Further, the partitioning relationship is likened to partitioning of dissolved hydrophobic compounds from an aqueous phase to a liquid organic phase. Accordingly, sets of empirical relationships have been developed to equate partitioning of an organic compound between octanol and water (described by K_{ow}), to partitioning between water and a given porous medium (described by K_d), according to:

$$\log K_d = a \log K_{ow} + \log f_{oc} + b \tag{5}$$

where a and b are empirically derived coefficients. In this case, coefficients for a and b of 0.72 and 0.49 were used and were obtained from empirical correlation experiments conducted by Schwarzenbach and Westall (1981) which included one representative compound (naphthalene) from the seven studied in this experiment. Table 1 shows a compilation of K_ds calculated by this method for the compounds of interest in the Borden study. An f_{oc} value of 0.0002 was used, on the basis of measurements by Mackay et al. (1986), as shown by King and Barker (this issue). The latter paper also provides the values for $\log K_{ow}$ that were used in the calculation.

Sorption coefficients determined by laboratory batch testing are also provided in Table 1. To conduct these tests, Borden sand was placed in 100-ml glass bottles, in contact with serial dilutions of creosote-saturated water. Sorption was inferred from the difference in aqueous concentration between bottles containing sand and bottles with no sand (controls). A relatively low sand to liquid ratio was used (~ 0.2 g/ml) so that the aqueous concentrations of the more hydrophobic compounds would remain well above analytical detection limits. Since this sand:solution ratio did not produce significant changes in aqueous concentrations for the least hydrophobic of the study compounds (m-xylene and phenol), batch test K_ds were not determined for these compounds. Details on batch test methodology and results were provided by King (1997).

Values for K_d estimated by the empirical method have been used for estimating sorbed compound masses for m-xylene and phenol, in subsequent mass balance calculations. In the case of m-xylene, this value was in the range of K_ds derived at the field site through earlier tracer tests by Patrick (1986) and Hubbard et al. (1994), shown in Table 1. For phenol, both the empirical correlation approach and comparison of migration rates for the phenol plume relative to the chloride plume (King and Barker, this issue) indicate that this compound undergoes only minor sorption in Borden sand. It will be shown that in the context of the mass balance, the quantity of sorbed phenol mass was negligible compared to dissolved mass, initial source mass and transformed mass.

Table 1
Estimates of solids partitioning coefficients (K_ds, cm^3/g) for selected compounds and Borden sand

Compound	Batch test	Based on $\log K_{ow}$[a]	Borden tracer tests	
			Patrick (1986)	Hubbard et al. (1994)
phenol	–	0.01 (1.05)	–	–
m-xylene	–	0.11(1.6)	0.13	0.06–0.09
naphthalene	0.22 (2.2)[b]	0.16	–	–
phenanthrene	1.80 (10.87)	1.11	–	–
dibenzofuran	0.67 (4.67)	0.57	–	–
carbazole	0.83 (5.55)	0.29	–	–
1-methylnaphthalene	0.24 (2.31)	0.37	–	–

[a] $\log K_d = 0.72 \log K_{ow} + \log f_{oc} + 0.49$ (Schwarzenbach and Westall, 1981); values used for $\log K_{ow}$ are provided by King and Barker (this issue).
[b] Bracketed values are associated estimates of R, according to $R = 1 + (\rho/\eta)K_d$; these values have been used in subsequent mass balance calculations.

Results from the laboratory batch method were used for the five remaining compounds: naphthalene, phenanthrene, dibenzofuran, 1-methylnaphthalene and carbazole. Earlier field studies at the site have shown that batch results compared reasonably well with observed plume behaviour. Although none of the five compounds were used in these field studies, a wide range of compounds are represented (non-chlorinated aromatics, chlorinated aromatics and aliphatics). Batch testing provided K_ds in the range of the empirical correlation method for the first four compounds listed above, providing a further indication that the sorption coefficients are reasonable. For carbazole, the two methods provided significantly different results. The carbazole K_d value derived from batch testing was used in mass balance calculations, because it was expected to be more site-specific. Retardation values calculated from plume migration rates (King and Barker, this issue) were not used for mass balance purposes, due to the effects of compound transformation on these plumes. In general, transformation causes an apparent increase in retardation because it contributes to a decrease in the rate of plume migration.

4.1.4. Mass flux (F)

Mass entering the plume has been estimated relative to an upgradient plume boundary defined at $x = 3.5$ m (2.7 m from the source), which is the location of a row of multi-level samplers. Mass flux across the plume boundary at a given time (t) is given by:

$$F = qC_{yz} \tag{6}$$

where F = the rate of mass transfer into the plume, across the defined boundary (M/T), q = groundwater flux (L/T) = vn, v = average linear groundwater velocity (L/T) and C_{yz} = plume concentration at $x = 3.5$ m, integrated over a unit area in the y–z plane (M/L). The value used for q in Eq. (6) was 0.03 m/day, based on past site work that evaluated v and n, as discussed by King and Barker (this issue). Data from past studies and the current study indicated that v in the vicinity of the study site is relatively consistent over time. In addition, expected changes to the local flow regime caused by the presence of the more permeable source sand were evaluated with the model FLOWPATH (Waterloo Hydrogeologic Software, 1994) using source and ambient hydraulic parameters described by King and Barker (this issue). Model results (King, 1997) indicated that minimal perturbation of groundwater flowlines was expected in the immediate vicinity of the source and that flowlines (and therefore v) should return to the upgradient configuration within 2 m downgradient of the source.

C_{yz} was determined for each synoptic sampling event, with plume concentrations collected from the row of multi-level samplers located at $x = 3.5$ m, by approximating the following:

$$C_{yz} = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty} C(y,z)\,\mathrm{d}y\,\mathrm{d}z. \tag{7}$$

The approximation was calculated using trapezoidal quadrature, first in the z direction and then in the y direction, with the limits of both integrations set outside the

plume periphery. This method is similar to that used by Freyberg (1986) in an earlier study at the same site, except in the earlier work it was applied only in the z direction.

Total compound mass entering the plume between synoptic sampling events (M_F) is given by:

$$M_F = \int_{t_1}^{t_2} F \mathrm{d}t = \int_{t_1}^{t_2} q C_{yz} \mathrm{d}t \tag{8}$$

This expression was approximated by:

$$M_F = \left(q\left(C_{yz}^1 + C_{yz}^2 \right) \Delta t \right) / 2 \tag{9}$$

where the superscripts ''1'' and ''2'' indicate values of C_{yz} from two consecutive synoptic sampling events. This approach further assumes that interpolation of C_{yz} between synoptic sampling events can be reasonably approximated by a straight line. Profiles of dissolved concentration vs. distance from the source, shown by King and Barker (this issue), indicated that mass influx to the plume changed gradually over time, and that straight line interpolation of mass flux was a reasonable assumption. Application of a dissolution model based on Raoult's law, discussed by King and Barker (this issue), also suggested that a straight line approximation was reasonable.

Additional details of the derivation and estimation for each component in the mass balance were provided by King (1997); a qualitative summary of various sources of uncertainty is provided at the end of the mass balance discussion.

4.2. Electron acceptors

Monitoring of redox-sensitive parameters was conducted at multi-level samplers within, and just outside the creosote plume, at the locations shown on Fig. 2. Samples were collected within 1 week after the last two synoptic sampling events (1008 and 1357 days). Dissolved oxygen was analyzed in the field using CHEMetrics ampoules (CHEMetrics) for the appropriate concentration range: 0–12 ppm, 0–1 ppm and 0–100 ppb. White et al. (1990) described a down-hole technique whereby CHEMetrics ampoules were determined to be reliable for measuring low levels of dissolved oxygen in groundwater. Since the monitoring network for the current study consisted mostly of samplers constructed of small-diameter tubing (3.2 mm O.D.), a method was developed for above ground measurement. Trials showed that it was possible to make repeatable readings of non-detectable dissolved oxygen by this method, using a low range ampoule (0–100 ppb), providing evidence that the method did not result in significant contamination of the sample with atmospheric oxygen.

Laboratory analysis was conducted for Fe^{2+}, Mn^{2+}, NO_3^-, NH_4^+ and SO_4^{2-} and CH_4. Chloride was also analyzed, as a safeguard against mistakenly identifying leachate samples as either background groundwater (no creosote compounds) or creosote plume water (reducing conditions). The leachate plume underlies the creosote plume (see King and Barker, this issue) and is known to be relatively elevated in chloride and sulphate (Nicholson et al., 1983). All samples were stored at 4°C prior to analysis. Iron and

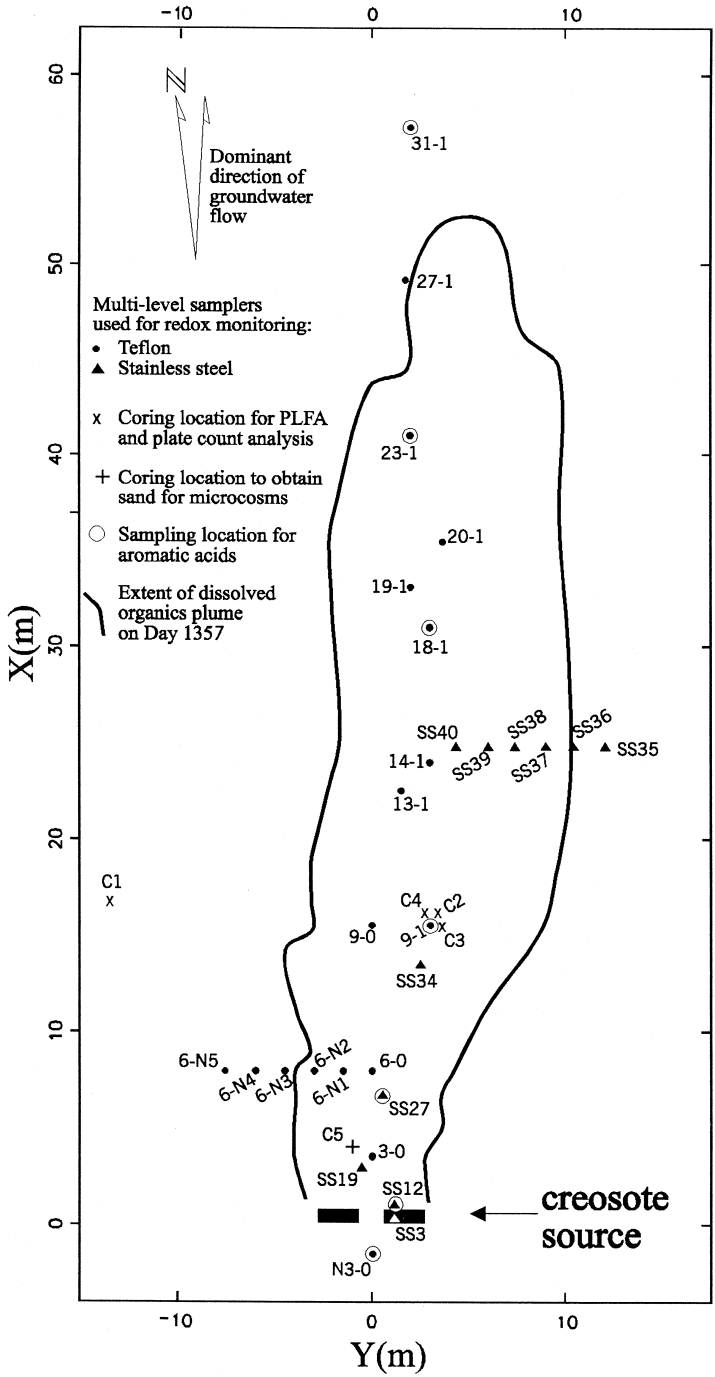

Fig. 2. Plan showing plume monitoring locations for selected redox parameters, aromatic acids and microbiological indicator parameters; locations are shown in relation to plume position as of day 1357.

manganese were analyzed using a Varian Model 1475 Atomic Adsorption Spectrophotometer; samples were field-filtered and acidified to pH 2 with nitric acid. Anion analysis was conducted with a Dionex System 2000 Ion Chromatograph or a Waters Ion Chromatograph. Analysis of NH_4^+ was performed with a colorimetric method using an Alpkem Perstorp Analytical Environmental Flow Solution system. Gas chromatography and flame ionization detection was used for methane analysis. Details on sampling and analytical methodology for redox-related parameters were provided by King (1997).

4.3. Microbial indicators

Microbial characteristics were compared on the basis of phospholipid fatty acids (PLFA), a component of intact cell membranes. A number of researchers have contributed to the development and testing of methods that relate the quantity of PLFA in sediment samples to microbial biomass (e.g., White et al., 1979; Guckert et al., 1985; Balkwill et al., 1988; Ringelberg et al., 1989); detailed analytical methods are provided by Dobbs and Findlay (1993). Extensions of this technique have been reviewed by Tunlid and White (1992) and have been used to relate the relative proportions of groups of PLFA compounds to microbial community structure and metabolic status.

Some of the fatty acid groups that are useful in this type of interpretation include: cyclopropyl fatty acids (e.g., cy17:0 and cy19:0), monoenoics (e.g., $16{:}1\omega 7c$ and $18{:}1\omega 7c$), and *trans* fatty acids (e.g., $16{:}1\omega 7t$ and $18{:}1\omega 7t$). The fatty acid nomenclature indicates: (1) the number of carbon molecules present in the structure (2) the presence or absence of a double carbon bond (3) the location of the double bond relative to the carbon in the ω position and (4) whether the molecule is in *cis* or *trans* formation. The summation of the ratio between certain *trans* and *cis* PLFAs (i.e., $16{:}1\omega 7t/16{:}1\omega 7c$ and $18{:}1\omega 7t/18{:}1\omega 7c$) has been related to changes in cell membranes of gram negative bacteria in response to environmental stresses. In general, larger values are indicative of toxicity or starvation effects. Similarly, gram negative bacteria convert certain monoenoic PLFAs to cyclopropyl fatty acids, as growth rate slows from an exponential to a stationary phase. The summation of the two ratios cy17:0/$16{:}1\omega 7c$ and cy19:0/$18{:}1\omega 7c$ has been used as an indicator of this process, with larger values indicative of a tendency towards stationary growth.

Aquifer cores for analysis of microbial indicator parameters were collected at the four locations shown in Fig. 2. Coring was done with the wireline method described by Zapico et al. (1987) using 5 cm diameter core barrels rinsed with methanol and MilliQ H_2O prior to use. After collection, the cores were split lengthwise and placed in an aseptic hood where subsamples were collected from aquifer material in the central part of the core, not in contact with the core barrel. The core from outside the plume (C1) and one from within the plume (C2) were subsampled from 1.4 to 2.6 m depth, at 20 cm intervals. The sample from the top of the plume core was at or near the top of the plume and the bottom sample was situated near the vertical centre of the plume. The other two plume cores (C3 and C4) which were both collected within 40 cm of C2, were subsampled near the top, middle and bottom of the cored interval (1.4, 2.0 and 2.6 m depth, respectively). All samples were analyzed for PLFA by the method presented by Dobbs and Findlay (1993). In addition, aliquots of selected samples were analyzed for

Table 2
List of aromatic acids and creosote compounds analyzed to evaluate the production of organic metabolites

Creosote compounds ($n = 25$)	Aromatic acids ($n = 11$)
m-xylene, phenol, naphthalene, phenanthrene, dibenzofuran, carbazole, 1-methylnaphthalene, *o*-cresol, $p + m$-cresol, 2,6-dimethylphenol, 2,4 + 2,5-dimethylphenol, 2,3-dimethylphenol, 3,5-dimethylphenol, indole + 2-methylnaphthalene, biphenyl, acenaphthylene, acenaphthene, dibenzofuran, fluorene, anthracene, fluoranthene, pyrene	benzoic acid, 2-methylbenzoic acid, methyl salicylate, 3-methylbenzoic acid, 4-methylbenzoic acid, 2,6-dimethylbenzoic acid, 2,6-dimethylbenzoic acid, 2,3 + 3,5,-dimethylbenzoic acid, 2,4,6-trimethylbenzoic acid, 3,4-dimethylbenzoic acid

total plate counts by standard preparation techniques and incubation under aerobic conditions for 40 days at 10°C. Additional details of PLFA and plate count analyses were provided by King (1997).

4.4. Organic metabolites

Aromatic acids analysis was conducted on a set of samples collected 1486 days after source emplacement. A total of nine samples were analyzed, from the five multi-level sampler locations shown in Fig. 2. Collection, extraction and analysis were conducted according to the procedure provided by Barcelona et al. (1995). The main components of this procedure consist of sample preparation by methyl esterification followed by derivatization with a BF_3/methanol agent, prior to GC/MS analysis. Aliquots of each sample were also analyzed for selected creosote compounds, according to the method outlined by King and Barker (this issue). Creosote compounds and aromatic acids included in the analytical suite are listed in Table 2.

5. Results and discussion

5.1. Mass balance

Mass balance results for the seven selected compounds are summarized in Table 3 and plume-scale transformation rates, expressed in terms of half-lives, are provided in Table 4. Half-lives have been estimated with an iterative model where total plume mass (M_T) at the end of a given time step was calculated on the basis of dissolved mass (M_D), according to:

$$M_T^1 = M_D^1(R - 1) + M_D^1 e^{-\lambda \Delta t} \quad (10)$$

where the superscript ''*1*'' indicates parameter values at the end of the time step, λ is the first order decay constant (T^{-1}) which is related to half-life ($t_{1/2}$) by $t_{1/2} = \ln(2)/\lambda$ and Δt is the length of the time step; a time step of 1 day was used. First order decay has been assumed for the purpose of describing plume mass loss because many field and

Table 3
Summary of mass balance input data and results for the emplaced creosote source plume

Compound Initial source mass[a] (g)	Phenol 1000	*m*-Xylene 2900	Naphthalene 7100	Phenanthrene 8900	Dibenzofuran 3300	Carbazole 240	1-Methylnaphthalene 1400
Plume mass (g)							
Dissolved (M_D)[b]							
439 days	55.7	–	–	–	–	–	–
626	–	135	333	0.033	4.65	1.30	9.52
1008	–	103	435	0.51	4.72	3.09	11.83
1357	–	49.5	565	0.32	4.83	2.88	17.72
Sorbed ($M_S = M_D(R-1)$)							
439 days	2.78	–	–	–	–	–	–
626	–	81.0	400	0.326	17.07	5.92	12.47
1008	–	61.8	522	5.03	17.32	14.06	15.50
1357	–	29.7	678	3.16	17.73	13.10	23.21
Total ($M_T = M_D + M_S$)							
439 days	58.5	–	–	–	–	–	–
626	–	216	733	0.359	21.72	7.22	21.99
1008	–	165	957	5.54	22.04	17.15	27.33
1357	–	76.2	1243	3.16	22.56	15.98	40.93
Mass input to plume							
Flux (F) (g/day)[c]							
626 days	0.0	1.03	2.20	0.003	0.083	0.044	0.135
1008	0.0	0.52	1.09	0.013	0.084	0.037	0.097
1357	0.0	0.29	1.11	0.022	0.081	0.017	0.102
Mass (M_F)(g)[d]							
0–439 days	1000[e]	–	–	–	–	–	–
626–1008	0.0	296	628	3.06	31.9	15.47	44.3
1008–1357	0.0	141	384	6.11	28.8	9.42	34.7
Mass transformed (M_R)(g)($M_R = M_F - \Delta M_T$)							
0–439 days	94.15	–	–	–	–	–	–
626–1008	–	347	404	−2.13	31.2	5.54	39.0
1008–1357	–	227	98.3	8.17	28.3	10.6	21.1

Table 4
Half-lives (in days) for selected plume compounds

Compounds	Monitoring period		
	0–439 days	626–1008 days	1008–1357 days
phenol	99	–	–
m-xylene	–	95	78
naphthalene	–	265	1215
phenanthrene	–	not available	11
dibenzofuran	–	40	41
carbazole	–	110	71
1-methylnaphthalene	–	78	173

laboratory studies of biodegradation have found that it is often reasonably described as a first order process. (e.g., Barker et al., 1987; Wilson et al., 1990; MacIntyre et al., 1993; Thierrin et al., 1995; Nielsen et al., 1996). The first term on the right hand side of Eq. (10) provides an estimate of sorbed mass and the second term represents dissolved mass at the end of the time step, after compound transformation has occurred. Calculation of M_T^1 by this equation assumes that only the dissolved phase undergoes transformation. M_D^1 in this model was evaluated by:

$$M_D^1 = \frac{q\Delta t\left(C_{yz}^0 + \Delta C_{yz}\right)}{R} + M_D^0 \tag{11}$$

where the first term on the right hand side accounts for the new mass added to the plume over the time step, incorporating sorption of a portion of that mass through division by R. For the first time step, C_{yz}^0 is calculated by integration of plume monitoring data from $x = 3.5$ m and ΔC_{yz} is the change in C_{yz} over the time step assuming linear interpolation between synoptic monitoring events. M_D^0 was initially obtained from synoptic monitoring data for the whole plume and, for subsequent time steps was calculated according to:

$$M_D^0 = M_T^1/R. \tag{13}$$

This approach was used to estimate the decay constant (λ) for the period between two synoptic sampling events. The value for λ was adjusted until the model prediction of M_T at the time of the latter event matched the field based estimate of M_T. This rate

Notes to Table 3:
[a] Initial mass was calculated with analytical data for the experimental creosote (King and Barker, this issue) and measurement of the amount of creosote initially emplaced in the source (74 kg).
[b] Calculated from synoptic monitoring data.
[c] $F = qC_{yz}$, where $q = vn$, $v = 0.091$ m/day, $n = 0.33$ and C_{yz} is calculated with synoptic monitoring data from the base of the plume (defined at $x = 3.5$ m).
[d] $M_F = (q(C_{yz}^1 + C_{yz}^2)\Delta t)/2$; assumes linear interpolation of F between synoptic monitoring events.
[e] Estimate based on near-complete removal of initial phenol mass from the source.

of transformation applies at the plume-scale, since it was derived from a plume-scale mass balance; it is expected that transformation rates were variable at discrete locations throughout the plume. In general, it is expected that rates will tend to be more rapid on the plume periphery, where electron acceptors may disperse into the plume from background groundwater, and less rapid in the central core of the plume. Data are not available to evaluate the spatial distribution of transformation rates.

Mass balance calculations indicate that all the selected compounds undergo transformation in the plume, as shown in Table 3. However, estimates of transformed mass and transformation half-lives are generally considered more reliable where little change occurs in mass flux between synoptic sampling events. Large changes in mass flux have more potential to introduce error since the flux may deviate significantly from the assumption of linear interpolation.

Mass and transformation rate estimates for *m*-xylene, naphthalene, phenanthrene and 1-methylnaphthalene were considered most reliable for the period between the last two monitoring events (from 1008–1357 days). Estimates of carbazole transformation were considered most reliable for the period between 626 and 1008 days since mass flux estimates were comparable at the beginning and end of this period. The decrease in carbazole flux at 1357 days is probably due to depletion of carbazole from the source. Mass flux of dibenzofuran was comparable for the last three synoptic sampling events and, consequently, mass and rate estimates are considered most reliable for the two intervening periods.

Mass balance quantification confirmed the qualitative observations of plume behaviour by King and Barker (this issue). Dibenzofuran formed the most stable plume, with nearly constant rates of mass flux between the last three synoptic sampling events (Table 3) and relatively constant dissolved mass. The dibenzofuran plume approached steady state over the study period, where mass flux was approximately balanced by mass transformation. The rate of dibenzofuran transformation was relatively constant over time and the interaction of mass flux and transformation served to keep the plume from advancing further. Presumably, the dibenzofuran plume expanded until the mass flux rate was matched by the plume-scale rate of transformation. This is the first conclusive observation in the literature, of an organic plume approaching a steady state condition, to the knowledge of the authors. The data from this site illustrate that natural transformation processes can halt the advancement of an organic plume, even in the presence of an ongoing source.

Mass balance results indicated that a decreasing trend in carbazole plume mass was developing near the end of the experiment: transformed mass was greater than mass input for the last monitoring period (1008–1357 days). However, in this case plume growth was limited by a decrease in mass flux into the plume, rather than an increase in the overall rate of mass transformation. As shown in Table 3, the original source concentration of carbazole was the lowest of the selected compounds, and the aqueous solubility of carbazole is relatively large: 238.6 mg/l (King and Barker, this issue). Consequently, the decrease in carbazole flux between the last two synoptic sampling events was attributed to significant source depletion with respect to this compound.

A similar process has controlled the development of the *m*-xylene plume. This plume reached a maximum observed mass and extent at 626 days and was subsequently

observed to shrink, as the rate of mass flux decreased to below the rate of mass transformation. The rapid decrease in the rate of mass flux is attributable to the relatively large solubility of *m*-xylene which caused it to become depleted from the source. With more constant flux, the *m*-xylene plume would likely have approached steady state over the monitoring period, similar to dibenzofuran.

For naphthalene, the rate of mass accumulation exceeded the rate of transformation. Given the relatively small magnitude of the latter, it is expected that at least 2 more years of plume growth would have to occur before the two rates approach a balance. Similarly, the 1-methylnaphthalene mass flux also exceeded transformation and it is expected that substantial additional plume growth would occur, prior to stabilization.

Phenol mass balance results showed that almost all of the original mass of phenol in the source (approximately 1 kg) was transformed: by day 439, the phenol plume contained only 6% of the mass originally present in the source. Interpretation of the phenol mass balance is relatively straightforward because, unlike the other selected compounds, phenol was rapidly and completely leached from the source early in the study period. Furthermore, it was subjected to only minor sorption to aquifer solids. The half-life calculated for this transformation ($t_{1/2} = 99$ days) is considered a maximum because it assumes that all the phenol was instantaneously leached from the source into the plume at the beginning of the experiment.

Unlike the other compounds, phenanthrene flux has continued to increase up to the last synoptic sampling event. This is attributed to the higher retardation factor for this compound, which increased the time required for breakthrough to the monitored portion of the plume. The large relative difference in flux rates between days 626 and 1008 caused large error in mass flux calculations for the intervening period, giving rise to a negative estimate for the quantity of mass transformed. The estimate of phenanthrene mass transformation for the subsequent period (1008–1357 days) is considered more reliable but may still contain significant error due to the assumption of linear interpolation between flux measurements. Perhaps the most straightforward evidence of phenanthrene transformation is demonstrated by the decrease in total plume mass between 1008 and 1357 days. Total mass decreased from 5.54 to 3.16 g and, even without considering flux input over this period, this represents a half-life of $t_{1/2} = 49$ days.

In the following, several mass balance components are qualitatively ranked according to the degree to which their inherent uncertainty has potential to affect mass balance results: (1) sorption (i.e., K_d estimates, assumption of uniform f_{oc} distribution, assumption of sorption ideality), (2) linear temporal interpolation of concentrations at the plume input boundary (for input flux estimates), (3) spatial interpolation of concentrations at the plume input boundary (for input flux estimates), (4) spatial interpolation of plume concentrations (for plume mass estimates), (5) analytical uncertainty, (6) groundwater velocity, and (7) aquifer porosity. Each of these components have been discussed separately, either in the current paper or by King and Barker (this issue). The first two components are considered to contribute substantially more uncertainty than the latter five; these two are discussed further below.

The potential for sorption assumptions and sorbed mass estimates to affect mass balance results will generally vary in accordance with the hydrophobicity of the compound. Consequently, for the study compounds it is expected to be largest with

Table 5
Summary of data for selected redox and geochemical indicator parameters; all concentrations are in mg/l. Non-detectable concentrations were handled as ''zeroes'' in calculations

Parameter	Creosote plume			Background			Landfill leachate plume		
	mean	*n*	s.d.	mean	*n*	s.d.	mean	*n*	s.d.
Dissolved O_2	0.13	63	0.16	2.47	18	0.99	0.12	12	0.2
Fe^{2+}	0.2	53	0.97	0	5	0	0.63	14	1.04
Mn^{2+}	0.13	53	0.16	< 0.05	5	0	0	14	0
NO^{3-}	1.51	53	4.69	2.35	5	3.08	5.97	14	12.7
NH^{4+}	0.21	53	0.25	0.62	5	0.42	0.22	14	0.22
SO_4^{2-}	11.6	53	4.19	14.1	5	3.79	46.2	14	30.4
Methane	0	53	0.1	0	2	0	0	13	0.1
Cl^-	1.93	14	0.52	4.04	3	3.13	26.8	6	11

respect to phenanthrene and least for phenol, which is only slightly sorbed. Further, the potential effect of error in sorption coefficient estimates is expected to be greater for periods where there is a large relative change in dissolved mass from the beginning to the end of the period, because sorbed mass is generally expected to be proportional to dissolved mass. The largest relative change in dissolved mass between the sampling events shown on Table 3 was observed for phenanthrene, from 626 to 1008 days. Large relative changes were also observed for *m*-xylene (from 1008 to 1357 days) and carbazole (from 626 to 1008 days). Conversely, dissolved dibenzofuran mass was particularly stable over the two mass balance periods (three synoptic sampling events) shown in Table 3.

The potential for introducing error due to the mass input estimation method (linear temporal interpolation of mass flux measurements) is greatest when the plume of a given compound is limited to within a few metres of the source. As the dispersed front of the plume migrates past the row of multi-level samplers at which input flux is defined ($x = 3.5$ m), there may be a substantial departure from the assumption of linear interpolation. This process is considered to impart relatively large error to phenanthrene

Table 6
Results of mean concentration comparison (*t*-test) for samples collected from within the dissolved creosote plume and background samples collected outside the plume

Parameter	Significant difference at 95% level	Direction of difference
Dissolved O_2	Yes	Background > Plume
Fe^{2+}	Yes	Plume > Background
Mn^{2+}	Yes	Plume > Background
NO^{3-}	No	Not Applicable
NH^{4+}	No	Not Applicable
SO_4^{2-}	Yes	Background > Plume
Methane	Yes	Plume > Background
Cl^-	No	Not Applicable

mass balance results for the period from 626 to 1008 days. Conversely, for the mass balance periods shown on Table 3 the effect was considered to be minimal for the remaining compounds, since they tended to migrate more rapidly than phenanthrene. Flux estimates were particularly stable for dibenzofuran and 1-methylnaphthalene.

5.2. Electron acceptors

Data for selected redox-sensitive parameters and chloride are summarized in Table 5. Dissolved oxygen concentration averaged 0.13 mg/l within the creosote plume and 2.47 mg/l in background samples. A summary of statistical comparisons (*t*-tests) is provided in Table 6 and indicates that this difference was statistically significant. The data support the expectation that dissolved oxygen has been consumed within the plume through

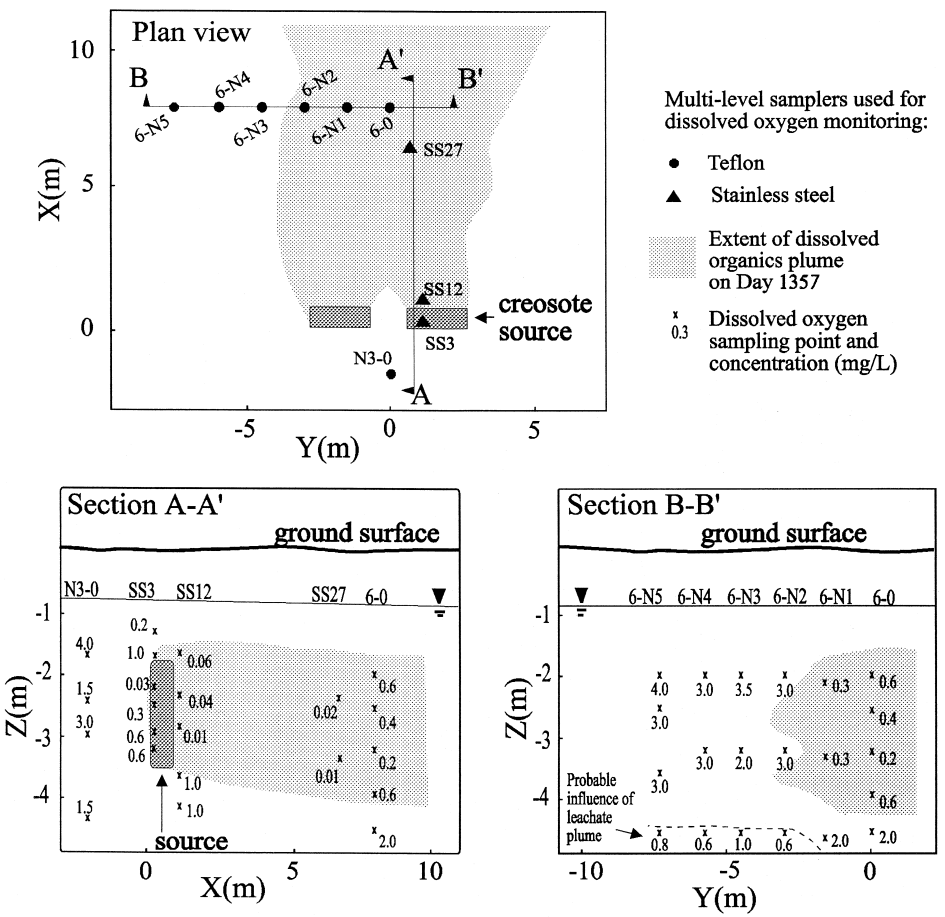

Fig. 3. Plan showing dissolved oxygen monitoring locations along cross-sections oriented parallel to groundwater flow (A–A′) and perpendicular (B–B′); cross-sections show distribution of dissolved oxygen relative to the dissolved creosote plume as of day 1357.

biodegradation of plume organics. Distributions of dissolved oxygen along two cross-sections are shown in Fig. 3. The results shown in this diagram are associated with synoptic monitoring of dissolved creosote compounds conducted at day 1357 and the outline of the organics plume is indicated for comparison. The two cross-sections show that dissolved oxygen concentrations measured within the plume were less than or equal to 0.6 mg/l, while concentrations outside generally ranged from 1.0 to 4.0 mg/l. An area of depleted dissolved oxygen concentration was evident in the lower levels of samplers 6-N2 through 6-N5 and is considered to be attributable to influence from the underlying anaerobic landfill leachate plume.

If biodegradation proceeds in the oxygen depleted portion of the plume, then changes would be expected in the concentration of alternate electron acceptors. A decrease in average nitrate concentration was noted from background groundwater to the plume, which would be consistent with nitrate utilization. However, both NO_3^- and NH_4^+, displayed a high degree of variability and the difference between the plume and background averages was not statistically significant, at the 95% level. Behaviour of other redox-sensitive parameters was more conclusive. Average concentrations of reduced iron and manganese were significantly different between plume and background samples, with the largest occurring within the plume. Average sulphate concentration decreased significantly from 14.1 mg/l in background groundwater to 11.6 mg/l in the plume. A small but significant increase in average methane, from 0.001 mg/l outside the plume to 0.036 mg/l inside, was an indication of a minor degree of methanogenic activity within the plume. Results of samples from the landfill leachate plume are also summarized in Table 5 and, similar to the organics plume, they were indicative of conditions more reducing than background groundwater. All these samples were obtained from depths greater than 4 m, which also supports the suggestion that they are affected by landfill leachate.

5.3. Microbial indicators

PLFA and plate count results are summarized graphically in Fig. 4. Comparison of PLFA concentrations indicate that microbial biomass was greater within the plume than in background aquifer material, presumably due to increased microbial growth on organic carbon in the plume. PLFA data from both within and outside the plume did not show a strong trend with respect to depth. However, plate counts (CFU/g) decreased sharply with depth for the cores collected within the plume. Although plate counts were not determined for background samples, an extensive evaluation of microbial characteristics in uncontaminated zones of the aquifer at a nearby location by Barbaro et al. (1994) generally showed the same trend of decreasing plate counts with depth. These researchers suggested that the trend was related to a similar trend in dissolved oxygen, which increased closer to the water table. Since the plate count analyses by Barbaro et al. (1994) and that conducted for the current study were performed under aerobic conditions, they have provided preferential detection of aerobic microorganisms. Consequently, while the PLFA data from the current study indicated an increase in microbial biomass due to the presence of the plume, plate count data may be more affected by the trend in dissolved oxygen, which generally decreases with depth both inside and outside the plume. The PLFA results indicated that the decrease in aerobic microbes was

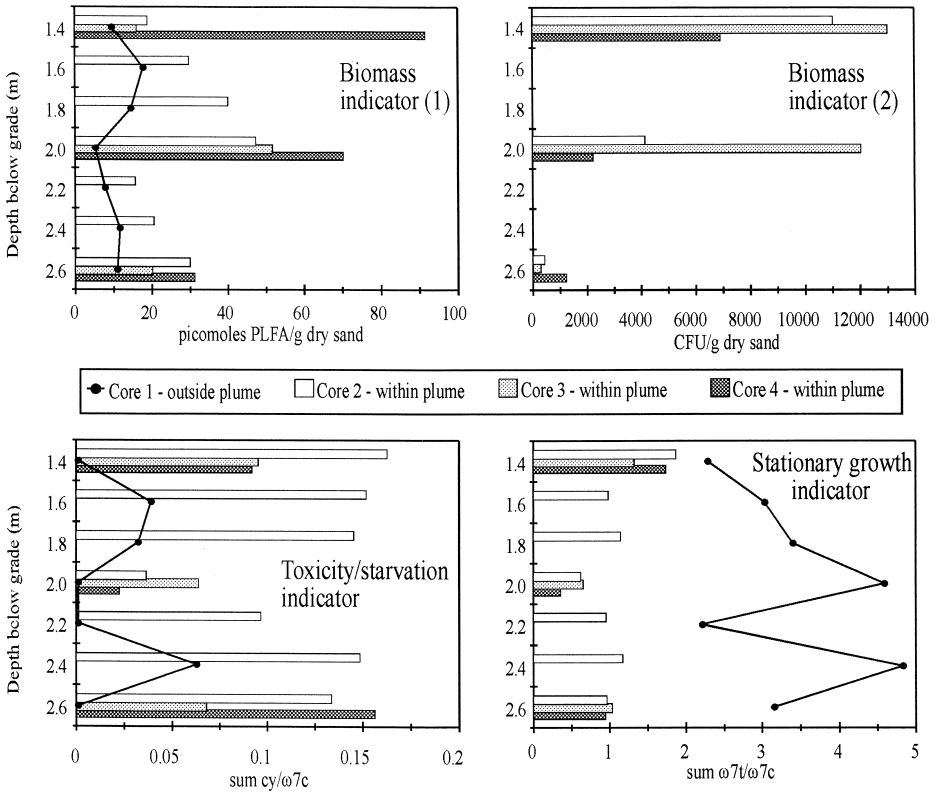

Fig. 4. Indicators of microbial numbers and indicator status in aquifer material collected from within and outside the dissolved creosote plume; the ''Total Biomass'' has been evaluated by the concentration of PLFA (1) and by total plate count (2); the ''Toxicity/starvation'' indicator is determined as the sum of the ratio between certain groups of fatty acids ($16{:}1\omega7t/16{:}1\omega7c + 18{:}1\omega7t/18{:}1\omega7c$); indication of microbial conformity to a ''Stationary growth'' phase is indicated by the sum of another pair of ratio ($\mathrm{cy17{:}0}/16{:}1\omega7c + \mathrm{cy19{:}0}/18{:}1\omega7c$).

generally accompanied by an increase in anaerobic microbes, resulting in no strong trends in biomass with depth.

Fig. 4 also shows results for the PLFA ratio used as indicators of microbial toxicity/starvation and stationary growth. Results for the former provide evidence that microorganisms within the plume were generally under more environmental stress than those in background core. This could be due to a degree of toxicity associated with plume compounds or may be indicative of an imbalance between organic carbon sources and nutrients within the plume. The ratio used to indicate the tendency towards stationary growth were distinctly larger in the background core: evidence that the status of the gram negative community tended towards a stationary growth phase outside the plume and log growth within the plume. This is consistent with a larger turnover rate within the plume due to biodegradation of plume compounds and with the larger biomass, as indicated by total PLFA concentration.

Table 7
Results of groundwater samples used to evaluate for the presence of creosote plume metabolites: aromatic acids, creosote compounds and selected redox indicators

Multi-level sampler	Sample point depth (m)	Total aromatic acids (ppb)	Total creosote compounds (ppb)	Dissolved oxygen (ppm)	Fe^{2+} (ppm)	SO_4^{2-} (ppm)
N3-0	1.8	42	0	> 1	< 0.05	15.4
N3-0	3	278	0	> 1	< 0.05	14.1
SS12	2.93	149	11,834	< 0.01	0.06	9.29
SS27	2.4	753	5535	0.02	0.12	11
SS27	3.3	18,312	1528	0.01	0.42	13.1
9-1	1.8	128	0	0.4	< 0.05	15.7
9-1	2.4	2694	3724	0.5	0.19	12.9
9-1	3.6	356	11,508	0.5	0.24	10.6
18-1	3.2	1509	6050	0.4	0.08	10.8

5.4. Organic metabolites

Table 7 provides a summary of results for selected organic acids and selected redox-related parameters. Samples collected upgradient of the creosote source (N3-0) were intended to provide data representative of background conditions. For the most part, results indicated that this location was not affected by the plume: creosote compounds and Fe^{2+} were not detected, dissolved oxygen was greater than 1 mg/l, and SO_4^{2-} was relatively elevated. However, the presence of relatively low, but detectable, concentrations of aromatic acids at this location was unexpected and may indicate low level presence of aromatic acids in background groundwater.

The aromatic acids concentration immediately downgradient of the source (SS12), was similar to the background range, providing evidence that the source did not contain appreciable amounts of organic acids. Five other samples were drawn from within the plume, as indicated by the presence of detectable creosote compounds; all of these plume samples show distinct evidence of aromatic acids accumulation. Organic acids concentrations within this group ranged from 356 ppb to a maximum of 18,312 ppb. The concentration at the latter location was more than an order of magnitude larger than that of total detected creosote compounds at the same location and almost twice that of detected creosote compounds in the near-source sample (SS12) which is from the most highly concentrated area of the plume. These samples also show concentrations of redox-sensitive parameters that are consistent with plume biodegradation: dissolved oxygen and SO_4^{2-} concentrations were below background and Fe^{2+} was somewhat elevated, as indicated by comparison with the upgradient sample (N3-0).

6. Summary and conclusions

A mass balance exercise showed significant rates of plume transformation for all seven compounds selected for detailed analysis in this study. The interaction of mass

flux into the plume and mass transformation within the plume caused a range of behaviour, depending on the comparative magnitudes of these processes.

For dibenzofuran, these two processes exerted approximately equal influence. The net effect was that the dibenzofuran plume reached an approximate steady state with respect to mass and position, for the last 2 years of monitoring. This is evidence that an organic plume can stabilize, even in the presence of an ongoing source: the first conclusive field observation of this type, of which the authors are aware. Behaviour of the *m*-xylene plume was characterized by initial mass increase followed by a decrease, as the rate of mass flux into the plume decreased to below the rate of plume transformation. Carbazole mass balance results indicated similar behaviour although the process of reversal occurred more slowly and was probably just beginning during the study period. Rates of mass flux into the plume were in excess of transformation for both naphthalene and 1-methylnaphthalene. Additional expansion of these plumes was expected to occur before these two processes approach a balance.

For phenol, the initial rate of mass flux far exceeded plume transformation. The former was so large that the source was rapidly depleted of phenol and a discrete slug-like plume was formed that was subjected to transformation as it migrated down gradient. Almost all of the original phenol mass in the source (approximately 1 kg) was transformed after 439 days. Transformation was also indicated for phenanthrene, although results were less conclusive. This compound is the most hydrophobic of those reported on herein, and the results highlighted the difficulties in evaluating natural attenuation of highly sorptive organic compounds.

Three lines of evidence were used to evaluate whether observed mass loss was due to biodegradation. Selected redox-sensitive parameters generally showed the types of changes that would be expected in association with plume biodegradation. Dissolved oxygen and SO_4^{2-} decreased in groundwater within the plume while significant increases were noted for Fe^{2+}, Mn^{2+}, and methane; NO_3^- behaviour was inconclusive. Further evidence that the observed mass loss was microbially-mediated was provided by accumulation of aromatic acids within the plume. PLFA data also indicated plume biodegradation. Microbial biomass was greater within the plume, presumably due to plume-supported microbial growth. Furthermore, PLFA composition indicated that the rate of microbial turnover was higher in the plume, although it may also show that the plume was somewhat toxic to aquifer microorganisms.

Further work based on the data set reported herein will compare organic compound mass balance results with a mass balance for electron acceptors. A project involving a funnel-and-gate system for dissolved phase plume interception and treatment has been conducted at the site (Lauzon, 1998) subsequent to the natural attenuation study. Ongoing research at the site (Forsey, in progress) involves development of novel methods for in situ oxidation of the emplaced creosote source.

The current study represents a unique and quantitative examination of a dissolved phase creosote plume. Study results highlight the potential for utilizing natural attenuation as a cleanup approach for plumes developing from complex organic mixtures composed of PAHs and aromatic, heteroaromatic and phenolic compounds. However, rates of biotransformation and plume migration are expected to be highly site-specific, varying due to site features such as: physical hydrogeologic regime, groundwater and

aquifer geochemistry, source composition and source configuration. The results further indicate that natural attenuation is most appropriately considered as part of site risk management, since the time required for source zone depletion of the lower solubility compounds (e.g., PAHs and heteroaromatics) is likely to be excessive — possibly requiring from decades to centuries. Consequently, it is reasonable to expect to find that plumes of these types of compounds are either expanding or stable; it is less likely that they will be observed to recede, in the short term. Conversely, for the higher solubility compounds (e.g., phenolics and monoaromatics), there is potential for the combined effects of source depletion and dissolved phase biodegradation to lead to plume shrinkage within a more immediate time frame, ranging from years to decades.

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