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Fate of organic contaminants in the redox zones of a landfill leachate pollution plume (Vejen, Denmark)

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ABSTRACT

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Samples from 75 sample locations in a landfill leachate pollution plume reveal a significant disappearance of specific organic compounds (SOC's) within the first 100 m of the plume. Only the herbicide Mecoprop® (MCPP) migrates further. Since sorption and dilution cannot account for the decreasing concentrations, degradation is considered to be the governing process. Non-volatile organic carbon shows a corresponding fate probably acting as a substrate for the microbial processes. The first 20 m of the plume are methanogenic/sulfidogenic, judged on the chemistry of the groundwater, followed by a significant ferrogenic zone exhibiting a substantial capacity to degrade the SOC's. The presence of intermediary products (here an oxidized camphor compound) supports the concept of degradation within the ferrogenic zone. This investigation draws the attention to the significant natural attenuation of organic contaminants and to the so far neglected ferrogenic zone in controlling the fate of organic contaminants in leachate plumes.

INTRODUCTION

Leachates from municipal as well as hazardous landfills contain a broad spectrum of xenobiotic organic compounds (Beckerath, 1985; Harkov et al., 1985; Först et al., 1989) that may migrate into the surrounding aquifer, if the leachate collection system is insufficient or, in the case of older landfills, completely missing. For hazardous landfills, several reports in the literature document transport of xenobiotic organic contaminants over long distances

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(e.g., Williams et al., 1984; Jackson and Patterson, 1989; Lesage et al., 1990), whereas the reports for municipal landfills are fewer and more ambiguous with respect to the extent of organic contaminant migration (e.g., Reinhard et al., 1984; Barker et al., 1986). Leaking of organic xenobiotic substances from landfills into the surrounding groundwater has become of substantial concern with the recognition that a substantial number of such organic compounds posses a potential danger to human health (e.g., Brown and Donnelly, 1988)

In the case of the municipal landfill, the leachate typically contains — as well as the xenobiotic organic compounds — high concentrations of organic matter originating from the degradation of the landfilled organic waste. This organic matter, for example, may include fatty acids and humic- and fulvic-like compounds that may act as a large pool of substrate for microbial activities in the aquifer, potentially also affecting the fate of the xenobiotic organic compounds. This migration of reduced leachate into the aquifer may, through the microbial utilization of the organic carbon in the leachate, leads to the development of a redox zone sequence that ranges from methanogenic conditions close to the landfill, over sulfidogenic (sulfate-reducing), ferrogenic (iron-reducing), manganogenic (manganese-reducing), and nitrate-reducing conditions, to aerobic conditions at the outskirts of the leachate pollution plume. The presence of various redox zones downgradient from a landfill is seen as a key to understand the fate of xenobiotic organic compounds in leachate pollution plumes. Degradation of xenobiotic organic compounds at low concentrations is supposedly linked to the microbial degradation of dissolved organic carbon and the terminal electron acceptor available in the various redox zones of the plume. Lyngkilde and Christensen (1992) identified a thermodynamically sound redox sequence ranging over a distance of 370 m from methanogenic to aerobic conditions in the pollution plume at the Vejen Landfill (Denmark). The purpose of the present paper is to correlate the distribution of dissolved organic carbon and specific xenobiotic organic compounds to the redox environments of the pollution plume in order to identify which environments are controlling the fate of the organic contaminants.

THE VEJEN LANDFILL LEACHATE POLLUTION PLUME

Waste disposal at Vejen Landfill (Vejen, Denmark) started in 1962 and terminated in 1981 and involved municipal as well as industrial waste. The landfill has no engineered leachate collection system, and a substantial fraction of the leachate is leaking into a shallow, unconfined, aerobic, sandy, glacioalluvial aquifer. The aquifer is confined at the bottom by a clay deposit found at ~20-m depth close to the landfill, but rising to only 10-m depth at 400–500 m downgradient from the landfill. Occasionally small clay lenses are found in the aquifer; one substantial lens is stretching out in the aquifer from below the landfill. The pore flow velocity is estimated to 150–200 m yr^{-1}.

The leachate pollution plume at Vejen Landfill has been mapped by Lyngkilde and Christensen (1992) with respect to inorganic pollutants and dominating redox environments. The redox zone map is based on groundwater samples characterized with respect to redox sensitive compounds such as oxygen, nitrate, nitrite, ammonium, manganese, iron, sulfate, sulfide and methane. A methanogenic zone was found just downgradient from the landfill, followed by sulfidogenic, ferro-/manganogenic, nitrate-reducing and aerobic conditions equivalent to the unpolluted groundwater of the aquifer. The methanogenic zone was <50 m in length and aerobic conditions were found ~ 300 m downgradient from the landfill.

MATERIALS AND METHODS

Borings

Based on data on concentrations of dissolved organic carbon (NVOC: non-volatile organic carbon) and preliminary gas chromatography–mass spectrometry (GC–MS) screening of groundwater samples from the permanent borings used by Lyngkilde and Christensen (1992), a dense sampling network was established within the first 65 m downgradient of the landfill. A total of 82 sampling points within 130 m from the landfill were used in this study (cf. Fig. 1).

The borings were established by ramming into the aquifer iron pipes supplied with 10-cm screens at the tip as previously described by Lyngkilde and Christensen (1992). At each location two permanent sampling screens

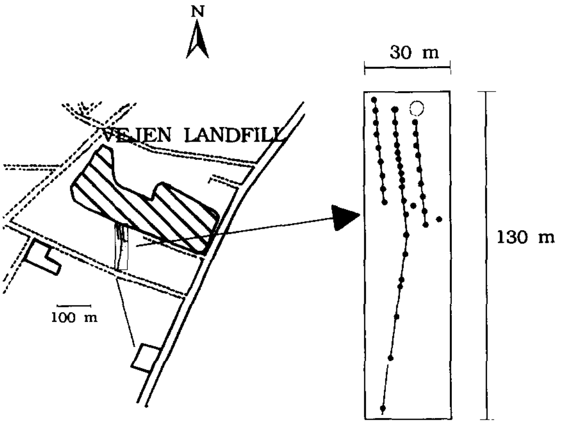

Fig. 1. Locations of groundwater sample points for mapping the distribution of organic compounds of the leachate plume at Vejen Landfill, Denmark.

were established at different depths. To insure that the screens were established in the main pollution plume, specific conductivity profiles were established at selected locations prior to deciding the depth of the sampling screens.

In seven cases, no water could be sampled from the established screens because the screens were clogged or located in a silt layer.

Groundwater was sampled through a Teflon® tube lowered into the iron pipe pressurized by nitrogen as described by Lyngkilde and Christensen (1992).

Groundwater characterization procedures

Redox sensitive species as well as inorganic compounds and physical parameters, used for characterizing pollution levels and general groundwater quality, were quantified in all collected groundwater samples. The redox sensitive species were: oxygen, nitrate, nitrite, ammonium, Mn(II), Fe(II), sulfate, sulfide and methane. The other group of parameters included: chloride, calcium, total alkalinity, chemical conductivity, temperature, pH and redox potential. The sampling techniques used, as well as equipment and analytical methods are described by Lyngkilde and Christensen (1992). Based upon concentrations of redox-sensitive parameters, every groundwater sample collected was assigned a redox status in accordance to the guidelines given by Lyngkilde and Christensen (1992), defining each sample as aerobic, nitrate-reducing, ferro-/manganogenic, sulfidogenic or methanogenic.

Analysis for NVOC with a detection limit of 0.05 mg L^{-1} C was conducted on preserved groundwater samples on a Dohrmann DC-*80*® TOC (total organic carbon) analyzer. Preservation was done by pressure filtering 50 mL of groundwater through a 0.15-μm membrane-filter (Schleicher and Schnell OE*65*®, Ref. No. *404 216*) into a polyethylene vial containing 0.5 mL conc. sulphuric acid.

Groundwater samples for analysis of specific organic compounds (SOC's) were collected in 50-mL measuring flasks made of glass that were gently filled by lowering the Teflon® sampling tube to the bottom of the flasks. After 2–3 volumes of overflow the flasks were stoppered by glass stoppers and the samples were immediately transported to the field laboratory. A volume of groundwater was withdrawn from each sample vial by use of a pipette leaving exactly 50 mL of sample. Exactly 500 μL of 10 *M* NaOH were added to the sample together with 500 μL pentane containing trichlorobromomethane (4.0 mg L^{-1}), heptane (3.4 mg L^{-1}), isopropylbenzene (4.3 mg L^{-1}) and hexadecane (3.9 mg L^{-1}) as internal standards. After vigorously shaking for 2 min, the sample vials were stored in the cold, with the bottoms up to prevent the pentane phase evaporating, until further manipulation in the laboratory could take place. For the analysis of chlorinated aliphatics and neutral/basic pentane-extractable non-polar components, the pentane phase was used directly for injection on a gas chromatograph (GC) using trichlorobromomethane as an internal standard for the quantification of halogenated aliphatics with detection limit for tetrachloromethane at 0.1 μg L^{-1}. Chlorinated aliphatics were quantified using an electron capture detector (ECD). Heptane, isopropylbenzene and hexadecane were used as internal standards for quantifying compounds detected on a flame ionization detector (FID), using their relative ratio as a check that none of them were present in the groundwater samples. Detection limits for benzene was 0.5 μg L^{-1}. The GC conditions for these quantifications are outlined below. After analysis of pentane-extractable species, phenolic compounds were derivatized with acetic acid anhydride and extracted for analysis on GC. Also neutral to basic, medium-polar compounds are detected in this procedure. The pentane was discharged and 45 mL of the water sample were transferred to a glass tube equipped with a screw cap supplied with a Teflon®-lined rubber support. The sample was neutralized to $pH = 7.0 \pm 0.2$ with concentrated phosphoric acid, and 1 g of borax was added and dissolved. 2 mL of pentane with *2*-bromophenol (1 mg L^{-1}) and *2,4*-dibromophenol (2 mg L^{-1}) as internal standards and 200 μL acetic acid anhydride were added and the tube was shaken on a mechanical shaker (240 rpm) for 3 min. After the first shaking, 2 mL ethylether were added and the tube was shaken under similar conditions for another 2 min.

Instrumentation

Qualitative determinations of SOC's were performed on a Carlo Erba QMD *1000*® quadropole mass spectrometer in scanning mode: 10–650 amu in 0.9-s scanning time, 0.1-s interscanning time, using electron impact of 70-eV ionizing energy. Injector, transfer line and source temperatures were 250°, 250° and 200°C, respectively. The oven temperature was kept isothermally at 40°C for 10 min, increased by 20°C min^{-1} to 115°C and kept for 2 min, then increased by 10°C min^{-1} to a maximum of 250°C and kept for 15 min. The column was a JandW DB-5®, 60 m × 0.32-mm OD, 1-μm film thickness. Helium was used as a carrier gas at flow rate of 1.5 mL min^{-1} at oven temperature of 40°C. 2-μL sample was injected.

Quantitative determination of SOC's was performed on a Carlo Erba Mega *500*® gas chromatograph equipped with a J&W column DB-52®, 30 m × 0.53-mm OD, 1.5-μm film thickness. Nitrogen was used as a carrier gas at 10 mL min^{-1} at 40°C. The injector temperature was kept at 250°C for all analyses.

For the analysis of chlorinated aliphatics the column effluent was split between an ECD and a FID in a ratio of 1:20. The temperature of the ECD was kept at 275°C and the initial oven temperature at 40°C, rising with 15°C min^{-1} to 110°C and kept for 1 min. The injected amount was 0.5 μL.

For the analysis of other pentane-extractable components like benzene and substituted benzenes, the FID was kept at 275°C. The initial oven temperature was 40°C, rising with 15°C min^{-1} to 115°C and kept for 1 min, and rising with 20°C min^{-1} to 250°C and kept for 5 min. The injected amount was 3 μL.

For the analysis of phenols and neutral to basic, medium-polar compounds, the FID was kept at 275°C. The initial oven temperature was 80°C, rising by 15°C min^{-1} to 250°C and kept for 10 min. The injected amount was 3 μL.

RESULTS AND DISCUSSION

Distribution of NVOC *in the leachate plume*

The concentration of bulk organic matter downgradient of the landfill is expressed in terms of NVOC. The NVOC varies between 300 and 500 mg L^{-1} C close to the landfill and between 10 and 20 mg L^{-1} C about 130 m downgradient of the landfill. The concentration of NVOC decreases with distance from the landfill. This is to be expected from dilution of the plume, from degradation and, if the plume is not at steady state, also from sorption effects.

Fig. 2 shows the NVOC concentration over a period of 285 days in borings

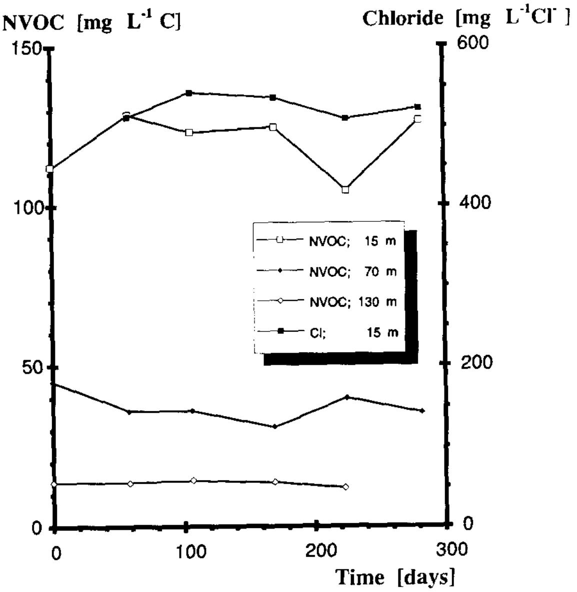

Fig. 2. NVOC concentrations over a 285-day period in the pollution plume at three different distances downgradient from Vejen Landfill. Also shown are the chloride concentrations 15 m downgradient of the landfill. No chloride data are available at day 0.

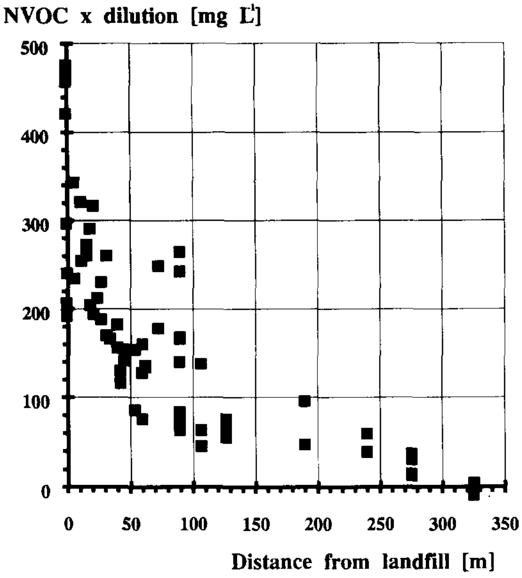

Fig. 3. Concentration of organic matter (NVOC) in the groundwater downgradient from the Vejen Landfill as a function of distance. All concentrations have been corrected for dilution according to chloride concentrations.

located in the pollution plume at three different distances downgradient of the landfill: 15, 70 and 130 m, respectively. Also depicted in Fig. 2 are the chloride concentrations 15 m downgradient of the landfill. The chloride concentrations indicate a nearly constant input over time. The groundwater pore flow in the transect is estimated to 150–200 m yr^{-1}. These results indicate that the plume is in fact stationary. Thus, the diminishing of NVOC concentrations with distance from the landfill should not be ascribed to sorption, but to degradation and/or dilution.

To quantify the dilution of the pollution plume at a specific location downgradient of the landfill, chloride is regarded as a conservative tracer only affected by dilution and practically insensible to any mechanisms of degradation or sorption. The dilution factor, F, accounts for the dilution based on chloride concentrations and is calculated as:

$$F = (C_0 - C_B)/(C - C_B)$$

where C is the chloride concentration of the groundwater sample; C_0 is the chloride concentration in the start of the plume; and C_B is the average chloride concentration (20 mg L^{-1}) of the unpolluted groundwater outside the plume. Fig. 3 shows the dilution-corrected concentrations of NVOC as a function of distance from the landfill along the main transect shown in Fig. 1. Data from distances more than 130 m downgradient from the landfill were obtained from the investigation of redox zones described in Lyngkilde and Christensen (1992). Accounting for dilution, Fig. 3 shows that degradation most likely is responsible for the fate of NVOC in the leachate plume. It seems that substantial removal of NVOC takes place within a distance of 100 m downgradient from the landfill whereafter concentrations stabilize on an elevated level compared to unpolluted groundwater samples. According to the redox zones identified by Lyngkilde and Christensen (1992), degradation takes place under methanogenic/sulfidogenic and ferrogenic conditions. Ideally, Fig. 3 should show concentration of NVOC as a function of retention time since, only under ideal conditions, is the retention time proportional to the distance from the landfill. The geology of the aquifer immediately downgradient of the landfill is not described in detail but some severe inhomogeneities have been observed during the establishment of the borings. This may to some extent explain the scatter observed in Fig. 3.

Specific organic compounds (SOC's) identified

Table 1 summarizes the results from GC–MS analysis of SOC's in groundwater samples from three locations at varying distance downgradient from the landfill: 5, 19 and 39 m, respectively. Table 1 only includes compounds found in significant concentrations. Most of these compounds are commonly found at landfill sites (e.g., Barker et al., 1988; Gordon et al., 1988). Benzene and the substituted benzenes probably originate from gasoline products deposited in the landfill. Industrial waste is considered to be responsible for the presence of substituted phenolic species. The broad spectrum of bicyclo-compounds is difficult to account for. Camphor is originally extracted from plant material (*Laurus camphora*) and possibly all the bicyclo compounds originate from plant material in the landfill. Although camphor is an old pharmacopoeia, it does not seem likely that these compounds should have been deposited in the landfill by pharmaceutical industry.

The samples presented in Table 1 represent sampling points located within the most concentrated part of the pollution plume as identified by chemical conductivity measurements. The concentrations of benzene-like compounds, naphthalenes and camphor are quantitatively correct. However, for the remaining compounds the extraction efficiency of the applied analytical method — as well as the detector response — is not known, and the stated concentrations should be considered as semi-quantitative within the range of some factors. However, the relative concentrations of these compounds between the different groundwater sampling points can be compared without restrictions. Table 1 shows that the concentrations of SOC's decrease rapidly with distance from the landfill, and in a distance of 40 m only few compounds exceed concentrations of 10 μg L^{-1}.

TABLE 1

Concentrations of NVOC, chloride, and specific organic compounds (SOC's) in the groundwater at three locations downstream from Vejen Landfill, Denmark

	Distance from landfill (m)		
	5	19	39
NVOC (mg L^{-1} C)	346	257	82
Chloride (mg L^{-1})	1,125	984	589
Benzene	3	3	2
Toluene	39	5	1
Benzene, ethyl-	96	75	9
Xylenes, *p-/m-*	224	33	2
Xylene, *o-*	16	7	1
Benzene, C$_3$- isomer	27	12	< 0.2
Benzene, C$_3$- isomer	21	13	< 0.2
Benzene, C$_3$- isomer	48	32	< 0.2
Benzene, C$_3$- isomer	36	24	1
Benzene, *1,3,5*-trimethyl- (mesitylene)	11	9	< 0.2
Benzene, *1*-propenyl-	8	6	1
Benzene, C$_4$- isomer	3	3	4
Benzene, C$_4$- isomer	10	4	< 0.2
Benzene, C$_4$- isomer	9	5	1
Benzene, C$_4$- isomer	6	4	< 0.2
Benzene, C$_4$- isomer	4	5	1
Benzene, C$_4$- isomer	5	3	< 0.2
Benzene, *1,2,3,5*-tetramethyl- (isodurene)	3	2	< 0.2
Benzene, *1*-methyl-*2*-propyl	5	3	< 0.2
Naphthalene	24	10	2
Naphthalene, *2*-methyl-	5	< 0.2	< 0.2
Naphthalene, *1*-methyl-	6	1	< 0.2
7-Oxabicyclo[*2.2.1*]-heptane, *1*-methyl-*4*-(*1*-methylethyl)-	6	< 0.5	< 0.5
2-Oxabicyclo[*2.2.2*]-octane, *1,3,3*-trimethyl-	8	5	1
Bicyclo[*2.2.1*]-heptane-*2*-one, *1,3,3*-trimethyl- (*d*-fenchone)	126	177	21
Bicyclo[*2.2.1*]-heptane-*2*-one, *1,7,7*-trimethyl-, (±)- (camphor)	426	474	46
Bicyclo[*2.2.1*]-heptane, *2,2*-dimethyl-*3*-methylene-	72	56	2
Bicyclo[*3.1.1*]-heptane-*2*-one, *3,6,6*-trimethyl-	41	6	4
Bicyclo[*2.2.1*]-heptane-*2,5*-dione, *1,7,7*-trimethyl-	12	10	9
Phenol, chloro-methyl isomer	33	30	11
Phenol, *6*-chloro-*2*-methyl-	11	10	11

The concentrations are average values from 2 to 3 samplings. All concentrations are μg L^{-1}, unless stated otherwise. SOC's are determined by GC–MS analysis.

TABLE 2

Specific organic compounds found in trace amounts in the groundwater downstream of Vejen Landfill, Denmark (see also Table 1)

Cyclohexanemethanol, α,α,4-trimethyl-2-Ethyl-4-methylthiazole
Phenol, C_1- isomer
Phenol, C_2- isomer
Phenol, C_4- isomer
Hydrazine, 1,1-diphenyl-2-(2,4,6-trinitrophenyl)-Benzenesulfonamide, N-butyl-

Table 2 summarizes compounds detected only in trace amounts and typically found in the groundwater only within 0–10 m from the landfill. The analyses performed are not exhaustive, and some classes (especially polar compounds) are excluded.

In order to supplement the GC–MS-determined compounds listed in Tables 1 and 2, a special effort was made by the Water Quality Institute (Denmark) to determine phenoxy acid-based herbicides in the leachate plume (derivatization with 2,2,2-trifluoroethanol prior to GC analysis). The herbicide 2,4-D® (2-(2,4-dichlorophenoxy)-propanoic acid) was found in trace concentrations (1 μg L^{-1}), while Mecoprop®, MCPP (2-(4-chloro-2-methylphenoxy)-propanoic acid) was identified in high concentrations (250 μg L^{-1}) close to the landfill and substantial concentrations at the end of the 130-m transect studied in this investigation (95 μg L^{-1}). MCPP was the most significant single trace compound found in the leachate pollution plume.

Distribution of SOC's *in the leachate plume*

The decreasing concentrations of SOC's downgradient from the landfill may be due to, as in the case of NVOC, sorption, dilution and degradation.

Since the concentrations of SOC's found in the leachate plume have been determined within a short period (2 months) the importance of sorption cannot be judged from the stationarity of the plume. However, evaluation of travel distances based on relative velocities, pore flow velocities and expected time period since leaching started indicates that sorption is not significant for the compounds present in Table 1. Larsen et al. (1989) determined in laboratory systems the sorption of several leachate pollutants onto aquifer materials, including aquifer material from Vejen. Naphthalene was one of the most retarded compounds, among the compounds listed in Table 1, showing relative velocities of 0.15–0.75 (relative to water). Assuming a minimum leaching period of 10 yr, and a minimum pore flow velocity of 100 m yr^{-1}, naphthalene will have migrated — if not subject to degradation — 150–750 m downgradient of the landfill. A distance that exceeds the 130 m considered in this investigation.

In order to account for dilution, the observed concentrations of SOC's have been multiplied with the dilution factor based on chloride concentrations and, as for NVOC, plotted as a function of distance from the landfill (Fig. 4). The different groups of organic compounds are all nearly vanished 100 m downgradient of the landfill with the exception of benzene and possibly one of the chlorinated phenol isomers. However, the actual benzene concentrations are so low (0.5–3 $\mu g\ L^{-1}$) in the plume that degradation and dilution is indistinguishable.

The dilution-corrected concentrations plotted in Fig. 4 show that a substantial degradation of all these grouped organic compounds take place in this aquifer being polluted by leachate for 10–15 yr. The major degradation takes place within 50 m from the landfill and nearly all SOC's have disappeared within 100 m. This is also the area where the bulk part of the NVOC is being degraded (Fig. 3).

The large scatter of dilution-corrected concentrations observed within the first 10–20 m from the landfill (Fig. 4) is partly due to the fact that samples actually representing groundwater from outside the plume and hence low in SOC's and low in chloride, also have been included in the data presentation. Even after the dilution correction has been accomplished, these samples show very low values of SOC's. These samples resemble, with respect to SOC's and chloride, the samples obtained farther downgradient the plume and in order to avoid any subjective evaluation of which samples belong to the plume and which are from outside the plume, all collected samples analyzed for SOC's have been included in Fig. 4.

The herbicide Mecoprop® (MCPP), the most significant SOC in the plume, does not show any signs of degradation within the studied 130 m of the plume. However, supplementary sampling showed that MCPP disappears farther downgradient in the plume. Based on the mapping of the plume, it cannot be determined whether MCPP disappears in the nitrate-reducing or in the aerobic zone. Laboratory experiments (Heron and Christensen, 1992) have shown that MCPP is degradable under aerobic conditions but nitrate-reducing experiments have so far failed to show any MCPP degradation.

Governing redox conditions

The first 100 m of the aquifer downgradient from the landfill, where substantial degradation of NVOC and SOC's takes place according to Figs. 3 and 4, are strictly anaerobic according to Lyngkilde and Christensen (1992), which is verified by redox characterization of each sample obtained for organic analysis in this study. Since this suggests a wide spectrum of SOC's to be degradable in this long established (10–15 yr) anaerobic aquifer, a closer look at the governing redox environments is warranted.

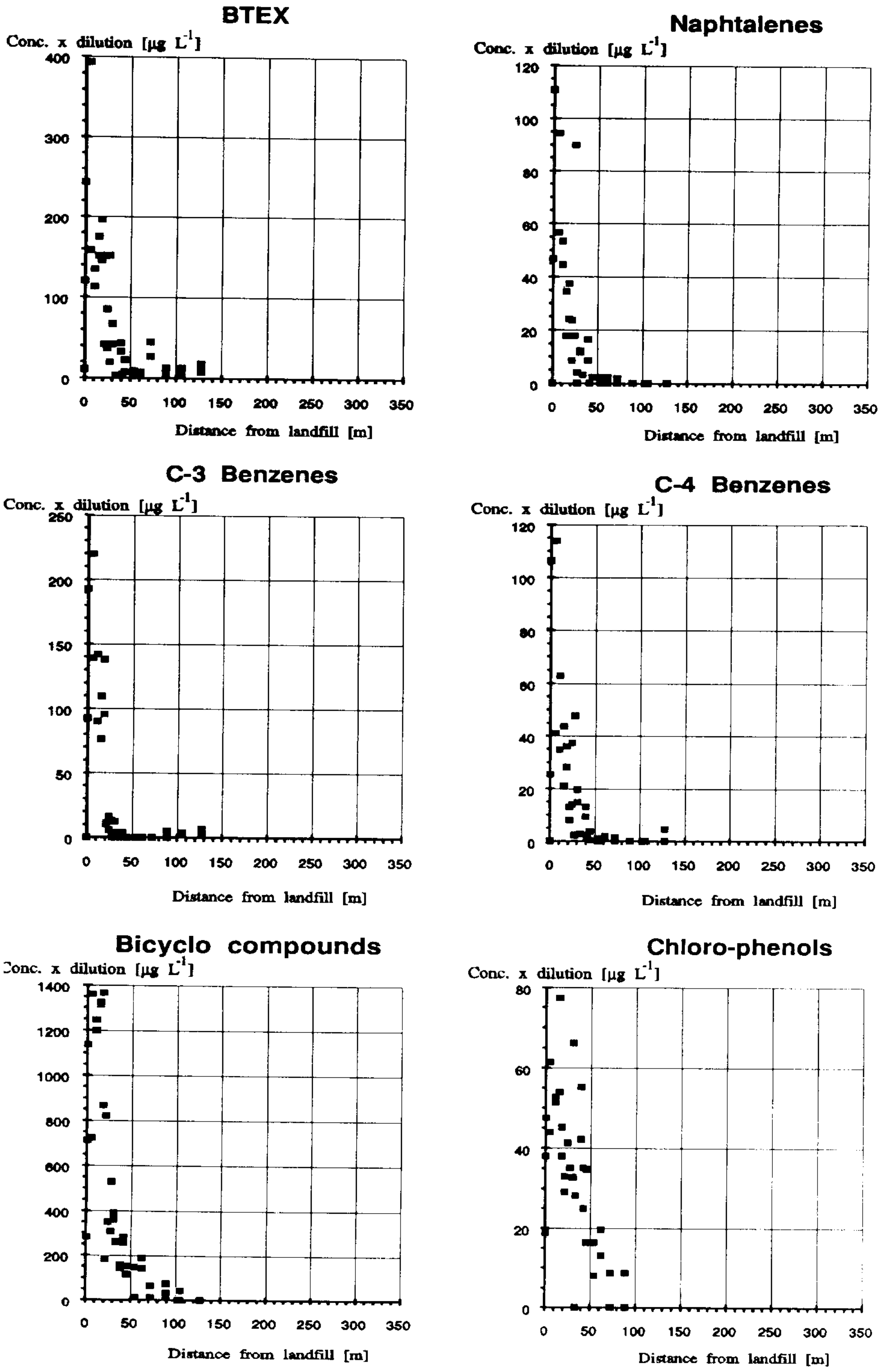
BTEX
Conc. x dilution [$\mu g\ L^{-1}$]
400
300
200
100
0
0 50 100 150 200 250 300 350
Distance from landfill [m]
Naphtalenes
Conc. x dilution [$\mu g\ L^{-1}$]
120
100
80
60
40
20
0
0 50 100 150 200 250 300 350
Distance from landfill [m]
C-3 Benzenes
Conc. x dilution [$\mu g\ L^{-1}$]
250
200
150
100
50
0
0 50 100 150 200 250 300 350
Distance from landfill [m]
C-4 Benzenes
Conc. x dilution [$\mu g\ L^{-1}$]
120
100
80
60
40
20
0
0 50 100 150 200 250 300 350
Distance from landfill [m]
Bicyclo compounds
Conc. x dilution [$\mu g\ L^{-1}$]
1400
1200
1000
800
600
400
200
0
0 50 100 150 200 250 300 350
Distance from landfill [m]
Chloro-phenols
Conc. x dilution [$\mu g\ L^{-1}$]
80
60
40
20
0
0 50 100 150 200 250 300 350
Distance from landfill [m]

Fig. 5 presents the observed concentrations of reduced iron (Fe^{2+}) in the groundwater as a function of distance downgradient from the landfill. At every distance with two or three sampling locations, reduced Fe concentrations from the sampling locations with the highest concentration of chloride is presented in Fig. 5. The concentrations of reduced Fe exhibit a dramatic increase ~20 m downgradient of the landfill. This is interpreted as the result of an active Fe-reducing zone in the area 20 m to at least 130 m downgradient of the landfill. This is in general accordance with the redox map developed by Lyngkilde and Christensen (1992). Methanogenic and sulfidogenic conditions are believed to exist within the first 20 m of the leachate plume. The low concentrations of reduced Fe in this zone is supposedly the result of precipitation as sulfides or of depletion of microbiologically reducible oxidized Fe compounds on the aquifer sediment.

Any unambiguous interpretation of the SOC fate patterns in Fig. 4 within the first 20 m is impossible. However, weak indications of degradation of toluene, xylenes and naphthalenes in the methanogenic/sulfidogenic zone may be found. Degradation of all the listed compounds in the ferrogenic zone of the aquifer seems evident from the data provided in Fig. 4. This observation indicates that the ferrogenic zone should obtain much more focus in the future with respect to its degradation potential for xenobiotic organic compounds. Lovley et al. (1989), the only reference found in literature, reported on biological degradation of toluene, phenol and *4*-methylphenol under ferrogenic conditions.

Recent developments in modelling of leachate plumes have taken into account the mixing of the plume, represented by dissolved organic carbon, with oxygen and nitrate from the unpolluted aquifer assuming that degradation is rapid (relative to the flow velocity) and mass transfer limited in the transfer zone between the anaerobic plume and the nitrate- or oxygen-containing zones (e.g., MacQuarrie and Sudicky, 1990). These developments are major steps forward and may be important in the future work on modelling the redox sequence of the plume, but the assumption of the microbial degradation to be focused in the transfer zone between the anaerobic and aerobic plume does not seem justified from the observations at Vejen Landfill. Apparently the major part of the degradation takes place under strictly anaerobic conditions.

Fig. 4. Concentrations of different groups of specific organic compounds (SOC's) in the groundwater downgradient from Vejen Landfill as a function of distance. All concentrations have been corrected for dilution, according to chloride concentrations.

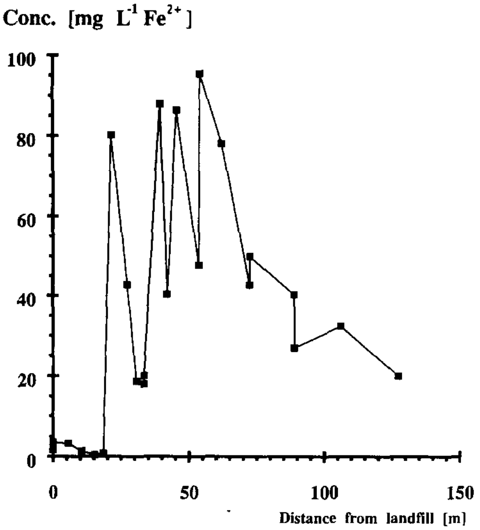

Fig. 5. Concentrations of reduced iron (Fe^{2+}) in the groundwater downgradient of Vejen Landfill as a function of distance.

Intermediary degradation products

The data presented in Figs. 3 and 4 indicate that NVOC and SOC's are being degraded in the anaerobic part of the pollution plume since neither sorption nor dilution can account for the decreasing concentrations as a function of distance from the landfill. Direct proofs of degradation in terms of microbiological activity tests, laboratory batch degradation tests and field degradation of injected SOC's are currently being established, but until the results of these projects are available, indirect evidence of degradation may support the hypothesis of degradation.

Degradation of substituted benzenes and phenols is presumed to lead to intermediary products and end-products of higher polarity (finally carbon dioxide and water) and they will not be detected by the analytical method used. However, the bicyclo compounds have such complex structures that partial oxidation does not necessarily make the compound undetectable by the analytical method used. Two of the bicyclo compounds found in the groundwater (refer to Table 1) are directly related: *1,7,7*-trimethyl-bicyclo[*2.2.1*]-heptane-*2,5*-dione can be an oxidized form of camphor (*1,7,7*-trimethyl-bicyclo[*2.2.1*]-heptane-*2*-one) (Fig. 6). Fig. 7 shows the concentrations of the different bicyclo compounds corrected for dilution, by multiplying by the dilution factor, as a function of distance downgradient from the landfill. As already argued above (p. 303), the accumulated concentrations of bicyclo compounds are diminishing after ~20 m. However, the concentration

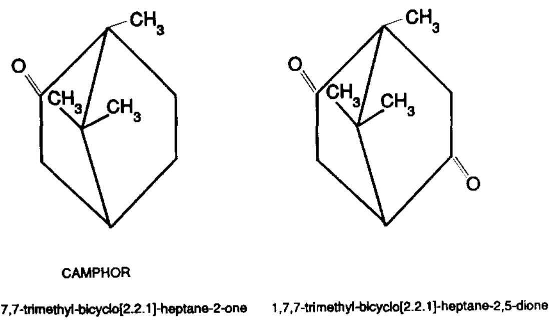

Fig. 6. Structures of camphor and the oxidized derivative *1*,*7*,*7*-trimethyl-bicyclo[*2*, *2*,*1*]-heptane-*2*,*5*-dione.

of *1*,*7*,*7*-trimethyl-bicyclo[*2*.*2*.*1*]-heptane-*2*,*5*-dione rises after this distance and then also declines after ~35 m, indicating its transformation in the aquifer. The actual analytical response factor of the oxidized camphor is not known exactly, but the same response factor as that for camphor was used for calculating concentrations. However, the oxidized camphor is undoubtedly more polar than the camphor itself, so the calculated concentrations of the oxidized camphor compound is underestimated, making a stoichiometric

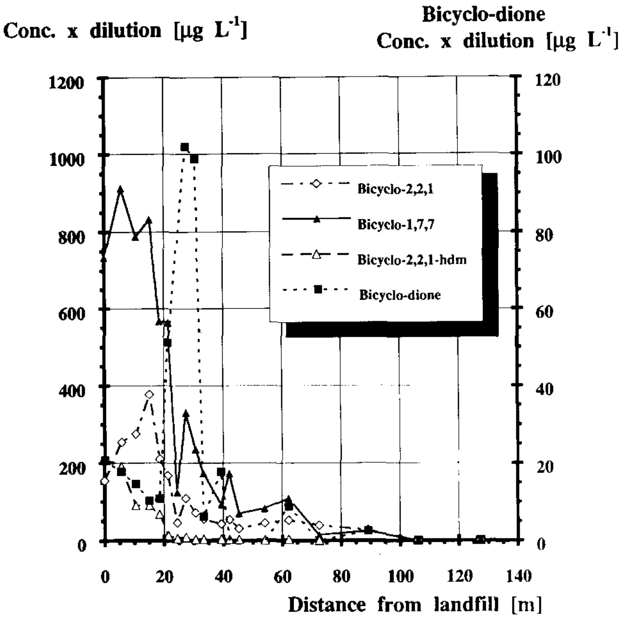

Fig. 7. Concentrations of different bicyclo compounds in the groundwater downgradient of Vejen Landfill as a function of distance. The abbreviations are easily related to the bicyclo compounds listed in Table 1. The sequence of compounds is the same in Table 1 and the legend shown.

comparison of the two compounds impossible. However, even on a qualitative basis the oxidation of camphor supports the assumption that degradation is responsible for the removal of the SOC's from the groundwater.

CONCLUSIONS

The groundwater immediately downgradient of the Vejen Landfill has a high content of dissolved organic carbon (500 mg L^{-1} NVOC) and a wide spectrum of specific organic compounds (SOC's) in varying concentrations.

Within the first 100 m of the leachate pollution plume nearly all SOC's. Only the herbicide Mecoprop® (MCPP) migrates farther downgradient from the landfill ultimately disappearing 250–350 m downgradient in a nitrate-reducing or aerobic zone of the pollution plume. Sorption and dilution cannot explain the compound disappearance. Degradation seems to be the governing process. A concomitant disappearance of NVOC indicates the presence of microbial processes degrading NVOC as well as specific xenobiotic organic compounds. The presence of oxidized intermediary products, as shown in the case of an oxidized camphor compound, supports the hypothesis of degradation being the controlling process.

The investigated leachate pollution plume has probably existed for nearly 15 years. Close to the landfill methanogenic/sulfidogenic environments exist, but apparently the most significant degradation of organic compounds takes place in a ferrogenic zone stretching, in this case, from 20 to 350 m downgradient of the landfill. The substantial self-cleaning capacity of this originally oxidized aquifer with respect to organic compounds perhaps indicates less risk to the groundwater quality and less need for remediation at such landfills. Ferrogenic zones are found to control degradation of organic compounds. With respect to degradation of specific xenobiotic organic compounds this zone has generally been neglected but definitely deserves more attention.

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