

# In situ and laboratory studies on the fate of specific organic compounds in an anaerobic landfill leachate plume, 2. Fate of aromatic and chlorinated aliphatic compounds

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## Abstract

The transformation of specific organic compounds was investigated by in situ and laboratory experiments in an anaerobic landfill leachate pollution plume at four different distances from the landfill. In a previous paper (Part 1, also published in this issue) we described the in situ microcosm and laboratory batch microcosm experiments performed focusing on redox conditions, microbiology and the fate of 7 phenolic compounds. In this paper we present the results on the fate of 8 aromatic compounds and 4 chlorinated aliphatic compounds.

Nitrobenzene was transformed at all distances from the landfill in methanogenic, and Fe(III)- and  $\text{NO}_3^-$ -reducing conditions. Toluene was transformed slowly in one out of three in situ experiments at the distance of 250 m from the landfill in the Fe(III)-reducing part of the plume after a lag phase of  $\sim 3$  months. Benzene, *o*-xylene, *p*-dichlorobenzene, *o*-dichlorobenzene, naphthalene and biphenyl were not transformed at any of the investigated distances from the landfill, neither in in situ nor in laboratory experiments. In the methanogenic part of the aquifer 2 m from the landfill, 1,1,1-trichloroethane, tetrachloromethane and tetrachloroethene were transformed in in situ experiments while trichloroethene was not. Lag phase periods were up to 40 days for 1,1,1-trichloroethane and up to 100 days for tetrachloroethene. No or only short lag phases ( $< 10$  days) were observed for tetrachloromethane. Tetrachloromethane was furthermore transformed at

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distances of up to 250 m from the landfill in Fe(III)-reducing conditions but not in  $\text{NO}_3^-$ -reducing conditions at 350 m from the landfill. Abiotic processes apparently contributed to the transformation of tetrachloromethane. A local variation in the transformation of the chlorinated aliphatic hydrocarbons was observed at 2 m from the landfill. In general, good accordance with respect to compound transformation was observed between in situ and laboratory experiments, but in a few cases more compounds were transformed in in situ experiments than in the corresponding laboratory experiments.

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## 1. Introduction

Landfill leachate contains a variety of specific organic pollutants which may potentially be transported through the sequence of redox zones formed in the aquifer downstream of the landfill. The fate of these compounds in the aquifer is associated with much concern due to their potential health risk (Christensen et al., 1994).

This paper is the second of a series of two papers focusing on the fate of phenolic, aromatic and aliphatic compounds in the leachate plume of Vejen Landfill (Denmark). In Part 1 (Nielsen et al., 1995 published in this issue) the experimental conditions (redox chemistry and microbiology in the aquifer and in the experiments) and the fate of 7 phenolic compounds were reported. In this paper the fate of 8 aromatic and 4 chlorinated aliphatic compounds is reported.

## 2. Materials and methods

The fate study of all the investigated compounds was performed in the same in situ microcosms (ISM's) and laboratory batch microcosms (LBM's) as described in Part 1. Here only a summary is provided.

The fate study was performed in a shallow, unconfined sandy aquifer in the leachate plume downstream Vejen Landfill at four different distances from the landfill. The predominant redox conditions were methanogenic, Fe(III)-reducing and  $\text{NO}_3^-$ -reducing as determined by a combination of chemical and biological studies on groundwater and sediment.

The ISM essentially consists of a 2-L stainless-steel cylinder installed in the aquifer. The ISM is open at the bottom and screened at the top, and allows for loading and sampling of groundwater spiked with a mixture of specific organic compounds. The LBM consists of a 2.5-L glass bottle loaded with sediment and groundwater from the aquifer and spiked with the same mixture of specific organic compounds as the ISM's. ISM's and LBM's were sampled approximately once per week during a period of 80–180 days. For the interpretation of the fate of the aromatic and chlorinated aliphatic compounds the fate curves from LBM experiments were corrected for evaporation to the increasing headspace in accordance with Henry's law assuming that equilibrium was reached between the samplings. The Henry constants used were determined at 10°C by Ashworth et al. (1988) except for naphthalene and nitrobenzene (Montgomery and Welkom, 1990) and biphenyl (Schwarzenbach et al., 1993).

### 3. Results and discussion

Redox conditions and biological conditions were monitored on water samples collected during ISM and LBM experiments and on sediment and groundwater samples collected prior to and after the experiments. The results were discussed in Part 1 and the redox conditions during the experiments are summarized in Table 1 and Table 2.

#### 3.1. Fate curves: examples

Examples of the fate curves determined for the studied aromatic and chlorinated aliphatic hydrocarbons in experiments representing the four distances from the landfill are shown in Fig. 1. In many experiments the compound concentration dropped in the beginning of the experiment. After the initial drop, concentrations of aromatic compounds (except nitrobenzene) remained constant or almost constant throughout the experiments at all distances from the landfill. Nitrobenzene decreased either quickly in the beginning of the experiments or more slowly throughout the experiments. After the

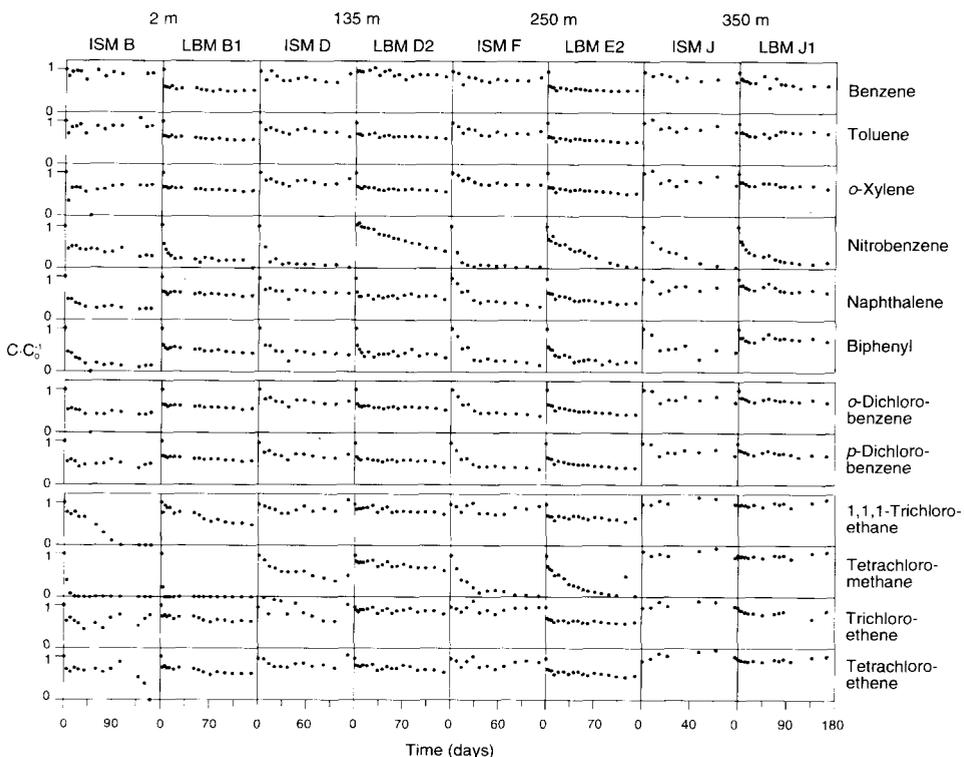


Fig. 1. Concentrations of aromatic and chlorinated aliphatic compounds as function of time in four in situ microcosm experiments (ISM's B, D, F and J) and four laboratory batch microcosm experiments (LBM's B1, D2, E2 and J1) at the four investigated distances from the landfill. All concentrations are normalized to the initial concentration of  $\sim 150 \mu\text{g L}^{-1}$ .

Table 1  
Transformation of aromatic hydrocarbons in an aquifer influenced by landfill leachate at four distances from the landfill as determined by in situ experiments (ISM's) and laboratory batch experiments (LBM's)

Distance from landfill (m)	Location <sup>a</sup>	Governing redox conditions	Benzene	Toluene	<i>o</i> -Xylene	Nitrobenzene	Naphthalene	Biphenyl
2	A	methanogenesis	– <sup>b</sup>	–	–	2? <sup>c</sup>	–	–
	B	methanogenesis	–	–	–	2?	–	–
	C	methanogenesis	–	–	–	2?	–	–
135	D	Fe(III) reduction	–	–	–	2	–	–
	E	Fe(III) reduction	–	–	–	2	–	–
250	F	Fe(III) reduction	–	–	–	2	–	–
	G	Fe(III) reduction	–	I (90) <sup>d</sup>	–	3	–	–
	H	NO <sub>3</sub> <sup>-</sup> reduction	–	–	–	2	–	–
350	I	NO <sub>3</sub> <sup>-</sup> reduction	–	–	–	2	–	–
	J	NO <sub>3</sub> <sup>-</sup> , Mn(IV) reduction	–	–	–	I	–	–

ISM experiments:

LBM experiments:

2	B1	supposedly methanogenesis	-	-	2?	-
	B2	supposedly methanogenesis	-	-	2?	-
	B3	supposedly methanogenesis	-	-	2?	-
135	D1	Fe(III) reduction	-	-	1	-
	D2	Fe(III) reduction	-	-	1	-
250	E1	no processes observable	-	-	1	-
	E2	no processes observable	-	-	1	-
	E3	no processes observable	-	-	1 (20)	-
350	H1	NO <sub>3</sub> <sup>-</sup> reduction	-	-	1	-
	H2	NO <sub>3</sub> <sup>-</sup> reduction	-	-	1	-
	J1	NO <sub>3</sub> <sup>-</sup> , Mn(IV) reduction	-	-	1	-
	J2	NO <sub>3</sub> <sup>-</sup> , Mn(IV) reduction	-	-	1	-

1 = slow transformation (< 80% transformed in 2 months); 2 = fast transformation (> 80% transformed in 2 months); 3 = very fast transformation (> 90% transformed in 10 days).

<sup>a</sup> ISM's were installed at different locations in the aquifer. Aquifer material for LBM experiments was collected adjacent to the ISM's at the same locations.

<sup>b</sup> No transformation observed.

<sup>c</sup> ? indicate that the results did not allow for conclusive statements because of analytical uncertainties.

<sup>d</sup> Lag phases (days) of > 10 days are given in parentheses.

Table 2  
Transformation of chlorinated aromatic and aliphatic hydrocarbons in an aquifer influenced by landfill leachate at four distances from the landfill as determined by in situ experiments (ISM's) and laboratory batch experiments (LBM's)

Distance from landfill (m)	Location <sup>a</sup>	Governing redox conditions	<i>o</i> -Dichloro-benzene	<i>p</i> -Dichloro-benzene	<i>1,1,1</i> -Tri-ethane	Tetrachloro-methane	Trichloro-ethene	Tetrachloro-ethene
2	A	methanogenesis	- <sup>b</sup>	-	2 (40) <sup>c</sup>	3	-	1 (60)
	B	methanogenesis	-	-	2 (40)	2	-	2 (100)
	C	methanogenesis	-	-	1 (30)	2	-	-
135	D	Fe(III) reduction	-	-	-	1	-	-
250	E	Fe(III) reduction	-	-	-	2	-	-
	F	Fe(III) reduction	-	-	-	2	-	-
	G	Fe(III) reduction	-	-	-	3	-	-
350	H	NO <sub>3</sub> <sup>-</sup> reduction	-	-	-	-	-	-
	I	NO <sub>3</sub> <sup>-</sup> reduction	-	-	-	-	-	-
	J	NO <sub>3</sub> <sup>-</sup> , Mn(IV) reduction	-	-	-	-	-	-

LBM experiments:

2	B1	supposedly methanogenesis	–	–	1	3	–
	B2	supposedly methanogenesis	–	–	1	3	–
	B3	supposedly methanogenesis	–	–	1	3	–
135	D2	Fe(III) reduction	–	–	–	–	–
	D3	Fe(III) reduction	–	–	–	–	–
250	E1	no processes observable	–	–	–	1	–
	E2	no processes observable	–	–	–	2	–
	E3	no processes observable	–	–	–	2	–
350	H1	NO <sub>3</sub> <sup>-</sup> reduction	–	–	–	–	–
	H2	NO <sub>3</sub> <sup>-</sup> reduction	–	–	–	–	–
	J1	NO <sub>2</sub> <sup>-</sup> , Mn(IV) reduction	–	–	–	–	–
	J2	NO <sub>3</sub> <sup>-</sup> , Mn(IV) reduction	–	–	–	–	–

1 = slow transformation (< 80% transformed in 2 months); 2 = fast transformation (> 80% transformed in 2 months); 3 = very fast transformation (> 90% transformed in 10 days).

<sup>a</sup> ISM's were installed at different locations in the aquifer. Aquifer material for LBM experiments was collected adjacent to the ISM's at the same locations.

<sup>b</sup> No transformation observed.

<sup>c</sup> Lag phases (days) of > 10 days are given in parentheses.

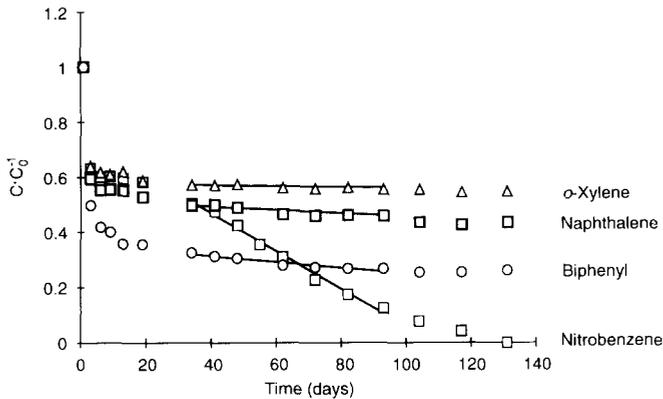


Fig. 2. Concentrations of four aromatic compounds as function of time in a laboratory batch microcosm experiment (LBM E3). Concentrations are corrected for evaporation to headspace during sampling and normalized to the initial concentration. The lines show the compound losses from days 34 to 93 estimated by linear regression.

initial drop, concentrations of the chlorinated aliphatic compounds remained constant in experiments at the more distant part of the plume while the concentrations of some of the compounds, especially tetrachloromethane, decreased significantly in experiments close to the landfill. The concentration of all compounds, except of nitrobenzene and tetrachloromethane, decreased slowly and very similarly in some experiments, especially at 250 m from the landfill.

### 3.2. Identification of compound transformation

The aromatic and chlorinated aliphatic compounds could be influenced by sorption to the sediment, biotransformation and chemical transformation in both ISM and LBM experiments and furthermore evaporation to the increasing headspace during the LBM experiments. For the interpretation of the fate of the volatile aromatic and chlorinated aliphatic compounds the fate curves from LBM experiments were corrected for evaporation to the increasing headspace.

In most experiments the shapes of the fate curves of the aromatic compounds, except nitrobenzene, were very similar as illustrated in Fig. 2. For *o*-xylene, naphthalene and biphenyl an initial drop in concentration was followed by a slow levelling off, while the nitrobenzene concentration continuously decreased throughout the experiment. The initial short-term drop in concentrations of *o*-xylene, naphthalene and biphenyl and the following long-term slow levelling off is evidence for the typical sorption behaviour for specific organic compounds in aquifer materials (e.g., Brusseau and Rao, 1989). A previous investigation of sorption of naphthalene in the same aquifer (Larsen et al., 1992) indicated a long sorption period in the Vejen sediment before sorption equilibrium was reached. Although the sorption period may be long in this study (2–3 months) it is within the range of days to months proposed by Brusseau and Rao (1989) and sorption

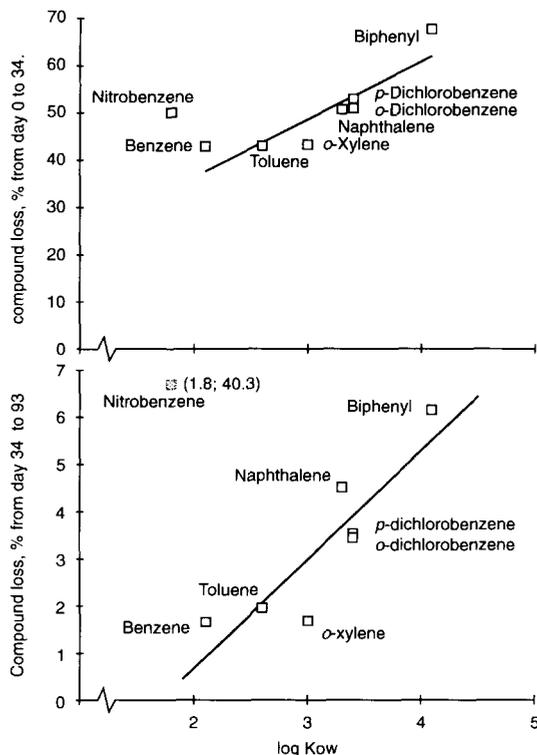


Fig. 3. Compound loss during two periods of a laboratory batch microcosm experiment (LBM E3) as function of the octanol–water partition coefficient,  $\log K_{ow}$  (Hansch and Leo, 1979; Montgomery and Welkom, 1990).

periods up to 100 days observed by Ball and Roberts (1991). Since the compound loss onto the sediment was very small during both the ISM and LBM experiments a mass balance was not a useful tool to determine if transformation or sorption or both caused the compound loss. In addition, it was not possible to make a mass balance on the specific organic compounds after the ISM experiments, as the ISM's were emptied from the spiked groundwater during sampling. Therefore, in order to differentiate between sorption and degradation, the compound loss was compared with the sorption properties of the compounds as exemplified in Fig. 3. The compound loss from day 0 to 34 and the compound loss from day 34 to 93 was plotted as function of the octanol/water partition coefficients ( $\log K_{ow}$ ) of the compounds. The former loss was estimated by the difference in compound concentration at days 0 and 34, while the latter loss was estimated by linear regression ( $r^2 > 0.77$ ) with respect to time. In both periods, the compound losses increased with increasing  $\log K_{ow}$ -values for all the aromatic compounds except for nitrobenzene (days 0 to 34:  $r^2 = 0.79$ ; days 34 to 93:  $r^2 = 0.78$ ). Since the partition coefficient,  $K_d$ , between sediment and water for organic solutes commonly is assumed to increase with increasing  $\log K_{ow}$  (e.g., Schwarzenbach and Westall, 1981) this indicates that the compound loss could be caused by sorption.

Nitrobenzene was, however, presumably transformed during the experiment since it decreased significantly more than the other compounds and since the compound loss was not related to the  $K_{ow}$ -value, see Fig. 3.

The slow levelling off in compound concentration was also observed in the ISM experiments (see Fig. 1) and a similar relation between compound loss and  $K_{ow}$ -values seemed to exist. However, due to more scatter in the ISM observations and the lower number of samples collected this cannot be discussed in the same detail as for the LBM experiments. When the fate curve of a compound differed from the fate curves of the compounds controlled by sorption (e.g., nitrobenzene; Fig. 2), the compound was considered to undergo transformation. Some compounds, for example *1,1,1*-trichloroethane, were transformed after a lag phase. The lag phase was defined as the time period from the beginning of the experiment until  $\sim 10\%$  of the compound had been transformed. The identification of lag phases was complicated by the sorption in the beginning of the experiments and short lag phases ( $< 10$  days) could generally not be determined. Table 1 and Table 2 summarize the transformation of the aromatic and chlorinated aliphatic compounds in all ISM and LBM experiments performed.

### 3.3. Fate of aromatic hydrocarbons

Benzene, *o*-xylene, naphthalene, biphenyl, and *o*- and *p*-dichlorobenzene were not transformed in any experiments at any of the investigated distances from the landfill, while toluene was transformed in one Fe(III)-reducing ISM experiment at 250 m from the landfill; see Table 1. The recalcitrance of benzene and *o*-xylene in the denitrifying experiments 350 m from the landfill is in good agreement with laboratory findings by Hutchins et al. (1991) who found that none of the compounds degraded during a 6-month period. The lack of transformation of aromatic compounds in the  $\text{NO}_3^-$ -reducing part of the aquifer is in accordance with findings by Acton and Barker (1992) who performed ISM experiments under denitrifying conditions. However, Acton and Barker (1992) found transformation of both toluene and *o*-xylene in a methanogenic ISM experiment, which is in accordance to observations reviewed by Grbić-Galić (1990), but not with the findings in this study. The dichlorobenzenes studied were not transformed in any part of the plume. Previous studies reviewed by Grbić-Galić (1990) have shown that chlorobenzenes may be reductively dehalogenated in methanogenic conditions, but that the less chlorinated compounds tend to be the most recalcitrant.

The transformation of toluene in an ISM installed 250 m from the landfill in Fe(III)-reducing redox conditions is illustrated in Fig. 4. The fate of benzene, toluene *o*-xylene and *p*-dichlorobenzene are included in order to show how the transformation of toluene was determined. The fate curve of toluene followed the other aromatic compounds during a 3-month period whereafter the concentration began decreasing more quickly. Although the samples after day 70 are rather few, the decrease of toluene relative to the other compounds most likely was caused by transformation, since analytical uncertainties during sampling, extraction and analysis also would have influenced the other compounds in a similar way. The observation of toluene transformation in the Fe(III)-reducing field experiment 250 m from the landfill is in good accordance with Lovley and Lonergan (1990), who found in laboratory experiments that

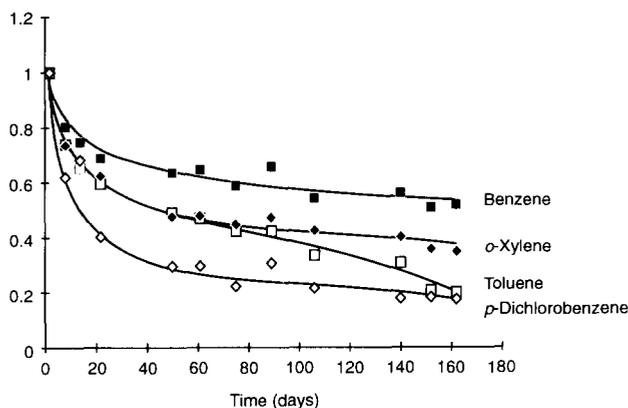


Fig. 4. Concentrations of four aromatic compounds as function of time in an in situ microcosm experiment (ISM G) installed in the plume at 250 m from the landfill in Fe(III)-reducing conditions, illustrating the transformation of toluene. Concentrations are normalized to the initial concentration of  $\sim 150 \mu\text{g L}^{-1}$ .

toluene could be oxidized by a Fe(III)-reducing microorganism (GS-15). Toluene transformation has previously been observed in methanogenic laboratory experiments (e.g., Wilson et al., 1986), under  $\text{NO}_3^-$ -reducing conditions in laboratory experiments (e.g., Hutchins et al., 1991) and in  $\text{NO}_3^-$ -reducing field experiments (e.g., Barbaro et al., 1992). These observations are not in accordance with the lack of toluene transformation in the methanogenic and  $\text{NO}_3^-$ -reducing parts of this aquifer.

Nitrobenzene was transformed at all distance from the landfill, see Table 1. In almost all experiments the remaining concentration of nitrobenzene was  $< 2 \mu\text{g L}^{-1}$  except those performed at 2 m from the landfill. In these experiments the interpretation of gas chromatograms was complicated by the presence of several specific organic compounds originating from the landfill (Lyngkilde and Christensen, 1992) and concentrations of nitrobenzene lower than  $\sim 50 \mu\text{g L}^{-1}$  could not be measured precisely. With only one exception (see Fig. 2) lag phases for nitrobenzene were either short ( $< 10$  days) or absent. In many biologically active experiments and control experiments, nitrobenzene and *o*- and *p*-nitrophenol (see Part 1) behaved similarly. Biological processes or abiotic processes coupled to biological activity seem to be important in the transformation of nitrobenzene throughout the plume while abiotic processes seem to contribute to the transformation in the more reduced part of the plume at distances up to 250 m as was the case also for the nitrophenols. In the reduced environment nitrobenzene may be reduced to aniline (see Macalady et al., 1986).

### 3.4. Fate of chlorinated aliphatic compounds

In ISM's installed 2 m from the landfill in the methanogenic part of the plume, 1,1,1-trichloroethane, tetrachloromethane and tetrachloroethene were transformed, while trichloroethene was not (see Table 2). In LBM experiments, only 1,1,1-trichloroethane and tetrachloromethane were transformed. No chlorinated compounds except tetrachloromethane were transformed in the more distant parts of the plume. 1,1,1-Trichloro-

ethane and tetrachloroethene were often transformed after long lag periods of up to ~ 3 months, while tetrachloromethane was transformed after no or very short lag phases (< 10 days). Chlorinated aliphatic hydrocarbons are commonly assumed to be transformed by reductive dechlorination in anaerobic environments as described by Murray

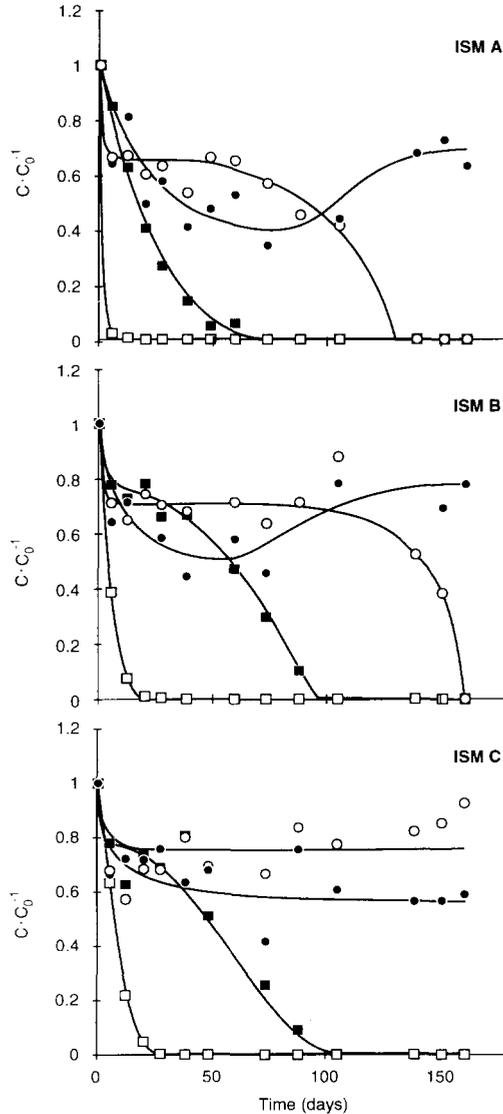


Fig. 5. Concentrations of 1,1,1-trichloroethane (■), tetrachloromethane (□), trichloroethene (●) and tetrachloroethene (○) as function of time in three in situ microcosm experiments (ISM's A, B and C) installed at 2 m from the landfill. Concentrations are normalized to the initial concentration of  $\sim 150 \mu\text{g L}^{-1}$ .

and Richardson (1993). These processes may be responsible for the transformation of the chlorinated compounds in the methanogenic part of this aquifer.

The fate of the investigated chlorinated aliphatic hydrocarbons in the three ISM's installed 2 m from the landfill are shown in Fig. 5. The compounds were transformed at the same sequence at all three locations: (1) tetrachloromethane; (2) 1,1,1-trichloroethane; and (3) tetrachloroethene. The explanation may be that compounds with a high potential to accept electrons tend to be preferred for reductive dechlorination before less electron accepting compounds as discussed by Murray and Richardson (1993). The concentration of trichloroethene increased when the concentration of tetrachloroethene decreased, indicating that tetrachloroethene was dechlorinated to trichloroethene. Reductive dechlorination of tetrachloroethene to trichloroethene has previously been observed in laboratory experiments under methanogenic conditions by Vogel and McCarty (1985).

Tetrachloroethene was transformed after lag phases of 3 and 2 months at locations A and B, respectively, while no transformation was observed within the experimental

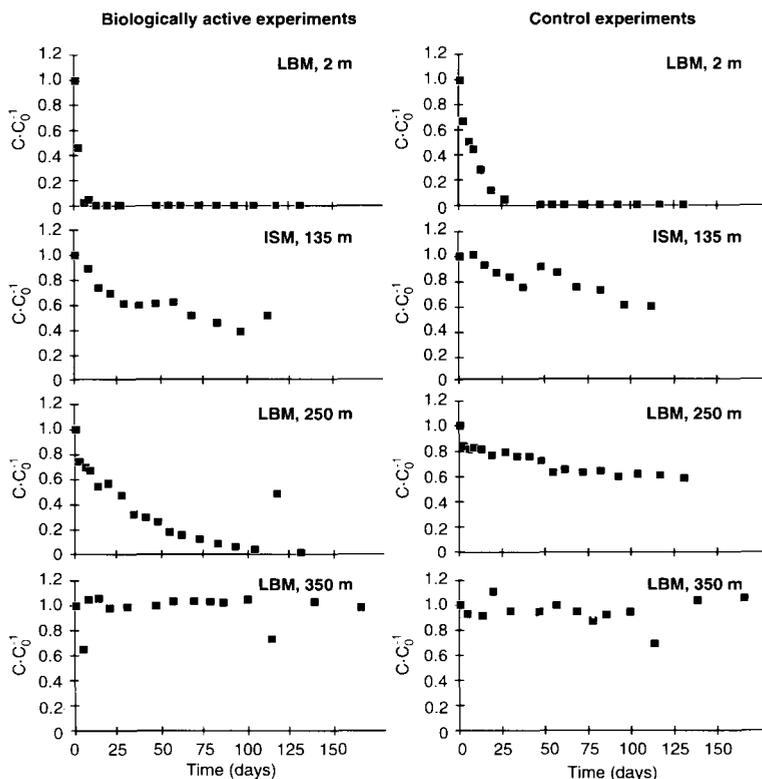


Fig. 6. Concentrations of tetrachloromethane as function of time in biologically active experiments (ISM D, and LBM's B3, E2 and H1) and their respective control experiments at 2, 135, 250 and 350 m distance from the landfill. Concentrations measured in LBM experiments are corrected for evaporation to headspace during sampling and all concentrations are normalized to the initial concentration of  $\sim 150 \mu\text{g L}^{-1}$ .

period at location C. Variation in the transformation of phenolic compounds was observed in the same ISM's (see Part 1) although no correlation was found.

### 3.5. Fate of tetrachloromethane throughout the plume

Tetrachloromethane transformation was observed at all the investigated distances from the landfill except at 350 m in the denitrifying part of the plume. The fate of tetrachloromethane in biologically active and biologically deactivated ISM's and LBM's at 2, 135, 250 and 350 m from the landfill are shown in Fig. 6. The data presented in Fig. 6 originate from both ISM and LBM experiments, because tetrachloromethane was not transformed in LBM experiments at the distance of 135 from the landfill (Table 2) and all ISM control experiments installed 2, 250 and 350 m from the landfill were diluted during the experiments as discussed in Part 1. Since tetrachloromethane is very volatile all data from LBM experiments were corrected for evaporation to the increasing headspace during sampling ( $K_H = 0.015 \text{ atm m}^3 \text{ mol}^{-1}$ ; Ashworth et al., 1988).

In the strongly reduced part of the aquifer at the distance of 2 m from the landfill, the transformation of tetrachloromethane was fast and only slightly inhibited by the addition of the biocide. At the distance of 135 m from the landfill the transformation was slow in the biologically active experiment as well as in the control experiment. At the distance of 250 m from the landfill the transformation was quite fast in the biologically active experiment but very slow in the control experiment. At 350 m from the landfill no transformation appeared in neither biologically active nor control experiments. Laboratory investigations by Kriegman-King and Reinhard (1992,1994) and Doong and Wu (1992) have shown that tetrachloromethane can abiotically be transformed in the presence of sulphide, biotite, vermiculite, Fe(II), and pyrite. Pyrite was present in the aquifer at distances up to 250 m from the landfill (Heron et al., 1994) and Fe(II) was present in all ISM experiments except those installed 350 m from the landfill (see Part 1). The abiotic contribution to the transformation of tetrachloromethane may therefore be caused by the presence of pyrite and/or Fe(II).

The significant biological contribution to the transformation of tetrachloromethane 250 m from the landfill may have been caused by the high biological Fe(III)-reduction activity (see Part 1) in this part of the aquifer. The lack of tetrachloromethane transformation at 350 m from the landfill under  $\text{NO}_3^-$ -reducing conditions is in good agreement with observations by Semprini et al. (1992) who found that transformation of tetrachloromethane was highest when no  $\text{NO}_3^-$  was present.  $\text{NO}_3^-$  may compete with highly halogenated compounds as electron acceptor as discussed by Murray and Richardson (1993) and may limit the transformation of tetrachloromethane.

## 4. Conclusions

In a leachate plume at four different distances (2, 135, 250 and 350 m) from the landfill, the fate of 8 aromatic and 4 chlorinated aliphatic hydrocarbons was studied in situ microcosm (ISM) and laboratory batch microcosm (LBM) experiments. At the four distances from the landfill, the following redox processes were dominant: 2 m, methano-

genesis; 135 and 250 m, Fe(III) reduction; and 350 m,  $\text{NO}_3^-$  reduction, as determined by a combination of chemical and biological studies on sediment and groundwater (see Part 1).

Benzene, *o*-xylene, naphthalene, biphenyl, and *o*- and *p*-dichlorobenzene were not transformed at any of the investigated distances from the landfill during the experimental period of 80–180 days.

Toluene was transformed slowly after a lag phase of  $\sim 3$  months in one of three ISM's installed at the distance of 250 m from the landfill, where Fe(III) reduction was the dominant redox process, but not in any other experiments.

Nitrobenzene was transformed in both ISM and LBM experiments throughout the plume in all of the investigated redox conditions. Generally lag phases prior to transformation were absent or short ( $< 10$  days). At distances up to 250 m in methanogenic and Fe(III)-reducing conditions abiotic transformation apparently contributed to the transformation, while no abiotic transformation was observed at the distance of 350 m under  $\text{NO}_3^-$ -reducing conditions.

*1,1,1*-Trichloroethane, tetrachloromethane and tetrachloroethene were transformed in ISM experiments at the distance of 2 m from the landfill in the methanogenic part of the aquifer while trichloroethene was not. Tetrachloromethane was furthermore transformed at distances up to 250 m from the landfill under Fe(III)-reducing conditions. Lag phases for *1,1,1*-trichloroethane and tetrachloroethene were up to 3 months while no or only short lag phases ( $< 10$  days) were observed for tetrachloromethane. Non-biological processes seemed to contribute to the transformation of tetrachloromethane, but at 250 m from the landfill, where high Fe(III)-reduction activity was observed, also processes directly coupled to microbial activity were apparently of importance.

In general, good accordance with respect to compound transformation was observed between ISM and LBM experiments, however, a few more compounds were transformed in the ISM experiments than in the corresponding LBM experiments.

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## References

- Acton, D.W. and Barker, J.F., 1992. In situ biodegradation potential of aromatic hydrocarbons in anaerobic groundwaters. *J. Contam. Hydrol.*, 9: 325–352.
- Ashworth, R.A., Howe, G.B., Mullins, M.E. and Rogers, T.N., 1988. Air–water partitioning coefficients of organics in dilute aqueous solutions. *J. Hazard. Mater.*, 18: 25–36.
- Ball, W.P. and Roberts, P.V., 1991. Long-term sorption of halogenated organic chemicals by aquifer material, 2. Intraparticle diffusion. *Environ. Sci. Technol.*, 25: 1237–1249.

- Barbaro, J.R., Barker, J.F., Lemon, L.A. and Mayfield, C.I., 1992. Biotransformation of BTEX under anaerobic, denitrifying conditions: Field and laboratory observations. *J. Contam. Hydrol.*, 11: 245–272.
- Brusseau, M.L. and Rao, P.S.C., 1989. Sorption nonideality during organic contaminant transport in porous media. *Crit. Rev. Environ. Control.*, 19: 33–99.
- Christensen, T.H., Kjeldsen, P., Albrechtsen, H.-J., Heron, G., Nielsen, P.H., Bjerg, P.L. and Holm, P.E., 1994. Attenuation of landfill leachate pollutants in aquifers. *Crit. Rev. Environ. Sci. Technol.*, 24: 119–202.
- Doong, R.-A. and Wu, S.-C., 1992. Reductive dechlorination of chlorinated hydrocarbons in aqueous solutions containing ferrous and sulphide ions. *Chemosphere*, 24: 1063–1075.
- Grbić-Galić, D., 1990. Methanogenic transformation of aromatic hydrocarbons and phenols in groundwater aquifers. *Geomicrobiol. J.*, 8: 167–200.
- Hansch, C. and Leo, A., 1979. Substituent Constants for Correlation Analysis in Chemistry and Biology. Wiley, New York, NY.
- Heron, G., Crouzet, C., Bourg, A.C.M. and Christensen, T.H., 1994. Speciation of Fe(II) and Fe(III) in contaminated aquifer sediments using chemical extraction techniques. *Environ. Sci. Technol.*, 28: 1698–1705.
- Hutchins, S.R., Sewell, G.W., Kovacs, D.A. and Smith, G.A., 1991. Biodegradation of aromatic hydrocarbons by aquifer microorganisms under denitrifying conditions. *Environ. Sci. Technol.*, 25: 68–76.
- Kriegman-King, M.R. and Reinhard, M., 1992. Transformation of carbon tetrachloride in the presence of sulphide, biotite and vermiculite. *Environ. Sci. Technol.*, 26: 2198–2206.
- Kriegman-King, M.R. and Reinhard, M., 1994. Transformation of carbon tetrachloride by pyrite in aqueous solution. *Environ. Sci. Technol.*, 28: 692–700.
- Larsen, T., Christensen, T.H. and Brusseau, M.L., 1992. Predicting nonequilibrium transport of naphthalene through aquifer materials using batch determined sorption parameters. *Chemosphere*, 24: 141–153.
- Lovley, D.R. and Lonergan, D.J., 1990. Anaerobic oxidation of toluene, phenol and *p*-cresol by the dissimilatory iron-reduction organism, GS-15. *Appl. Environ. Microbiol.*, 56: 1858–1864.
- Lyngkilde, J. and Christensen, T.H., 1992. Fate of organic contaminants in the redox zones of a landfill leachate pollution plume (Vejen, Denmark). *J. Contam. Hydrol.*, 10: 291–307.
- Macalady, D.L., Tratnyek, P.G. and Grundl, T.J., 1986. Abiotic reduction reactions of anthropogenic organic chemicals in anaerobic systems: A critical review. In: D.L. Macalady (Editor), *Transport and Transformations of Organic Contaminants*. *J. Contam. Hydrol.*, 1: 1–28 (special issue).
- Montgomery, J.H. and Welkom, L.M., 1990. *Groundwater Chemicals Desk Reference*. Lewis, Chelsea, MI, 2nd ed.
- Murray, W.D. and Richardson, M., 1993. Progress toward the biological treatment of C<sub>1</sub> and C<sub>2</sub> halogenated hydrocarbons. *Crit. Rev. Environ. Sci. Technol.*, 23: 195–217.
- Nielsen, P.H., Albrechtsen, H.-J., Heron, G. and Christensen, T.H., 1995. In situ and laboratory studies on the fate of specific organic compounds in an anaerobic landfill leachate plume. 1. Experimental conditions and fate of phenolic compounds. *J. Contam. Hydrol.*, 20: 27–50 (in this issue; in this paper referred to as Part 1).
- Schwarzenbach, R.P. and Westall, J., 1981. Transport of nonpolar organic compounds from surface water to groundwater. Laboratory sorption studies. *Environ. Sci. Technol.*, 15: 1360–1367.
- Schwarzenbach, R.P., Gschwend, P.M. and Imboden, D.M., 1993. *Environmental Organic Chemistry*. Wiley, New York, NY.
- Semprini, L., Hopkins, G.D., McCarty, P.L. and Roberts, P.V., 1992. In-situ transformation of carbon tetrachloride and other halogenated compounds resulting from biostimulation under anoxic conditions. *Environ. Sci. Technol.*, 26: 2454–2461.
- Vogel, T.M. and McCarty, P.L., 1985. Biotransformation of tetrachloroethylene to trichloroethylene, dichloroethylene, vinyl chloride, and carbon dioxide under methanogenic conditions. *Appl. Environ. Microbiol.*, 49: 1080–1083.
- Wilson, B.H., Smith, G.B. and Rees, J.F., 1986. Biotransformations of selected alkylbenzenes and halogenated aliphatic hydrocarbons in methanogenic aquifer material: A microcosm study. *Environ. Sci. Technol.*, 20: 997–1002.