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Review

Biogeochemistry of landfill leachate plumes

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Abstract

The literature has been critically reviewed in order to assess the attenuation processes governing contaminants in leachate affected aquifers. Attenuation here refers to dilution, sorption, ion exchange, precipitation, redox reactions and degradation processes. With respect to contaminants, focus is on dissolved organic matter, xenobiotic organic compounds, inorganic macrocomponents as anions and cations, and heavy metals. Laboratory as well as field investigations are included. This review is an up-date of an earlier comprehensive review. The review shows that most leachate contamination plumes are relatively narrow and do not in terms of width exceed the width of the landfill. The concept of redox zones being present in the plume has been confirmed by the reported composition of the leachate contaminated groundwater at several landfills and constitutes an important framework for understanding the behavior of the contaminants in the plume as the leachate migrates away from the landfill. Diverse microbial communities have been identified in leachate plumes and are believed to be responsible for the redox processes. Dissolved organic C in the leachate, although it appears to be only slowly degradable when the volatile organic acids are gone, apparently acts as substrate for the microbial redox processes. Several xenobiotic organic compounds have been found to be degradable in leachate contaminated groundwater, but degradation rates under anaerobic redox conditions have only been determined in a few cases. Apparently, observations in actual plumes indicate more extensive degradation than has been documented in the laboratory. The behavior of cations in leachate plumes is strongly influenced by exchange with the sediment, although the sediment often is very coarse and sandy. Ammonium seems to be subject to anaerobic oxidation, but the mechanisms are not yet understood. Heavy metals do not seem to constitute a significant pollution problem at landfills, partly because the heavy metal concentrations in the leachate often are low, and partly because of strong attenuation by sorption and precipitation. Although complexation of heavy metals with dissolved organic matter is significant, the heavy metals are in most cases still strongly attenuated in leachate-polluted aquifers. The information available on attenuation processes has increased dramatically during the last 15 a, but the number of well-documented full scale leachate plumes are still few and primarily from sandy aquifers. Thus, the diversity of attenuation processes in leachate plumes is probably not yet fully understood. Apparently, the attenuation processes in leachate plumes may for many contaminants provide significant natural remediation, limiting the effects of the leachate on the groundwater to an area usually not exceeding 1000 m from the landfill. © 2001 Elsevier Science Ltd. All rights reserved.

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Contents

1. Introduction	661
2. Landfill leachate	661
2.1. Dissolved organic matter	662
2.2. Inorganic macrocomponents	663
2.3. Heavy metals	664
2.4. Xenobiotic organic compounds (XOCs)	664
3. Dilution	664
3.1. Leachate and groundwater flow	664
3.2. Dispersion	668
3.3. Observed leachate plumes	668
3.4. Conclusion: dilution	669
4. Redox environments and processes	669
4.1. Overall redox sequence	669
4.2. Redox buffering	671
4.3. Fe minerals in redox buffering	672
4.4. Observed redox environments in leachate plumes	674
4.5. Redox characterization of the Grindsted Landfill (DK) plume	674
4.6. Conclusions: redox environments	676
5. Microbiology	676
5.1. Presence of microorganisms	678
5.2. Microbial redox processes in leachate plumes	680
5.3. Conclusion: microbiology	683
6. Dissolved organic matter	683
6.1. Sorption	683
6.2. Degradation	685
6.3. Field evidence	685
6.4. Conclusion: dissolved organic matter	687
7. Inorganic macrocomponents	687
7.1. Anions	687
7.2. Cations	689
7.3. Ammonium	691
7.4. Fe and Mn	691
7.5. Conclusion: inorganic macrocomponents	693
8. Heavy metals	693
8.1. Heavy metal species in leachate plumes	693
8.2. Sorption	695
8.3. Precipitation	696
8.4. Experimental evidence	697
8.5. Conclusion: heavy metals	699
9. Xenobiotic organic compounds (XOCs)	699
9.1. Sorption	700
9.2. Degradation overview	701
9.3. Microcosm studies	702
9.4. Field injection experiments	704
9.5. Detailed monitoring in plumes	705
9.6. Overall degradation patterns	707
9.7. XOC-associated toxicity	708
9.8. Conclusions: XOCs	709
10. Conclusion	709
Acknowledgements	710
References	710

1. Introduction

The large number of cases of groundwater pollution at landfills (Arneeth et al., 1989) and the substantial resources spent in remediation suggest that landfill leachate is a significant source of groundwater pollution.

Understanding the natural attenuation of leachate pollutants in aquifers is mandatory for evaluation of environmental risks associated with leachate entering the groundwater, for coherent interpretation of groundwater samples from monitoring wells, and for determining appropriate remedial action, including monitored natural attenuation. Attenuation is here used as a common term for processes reducing the concentrations of dissolved contaminants in the leachate plume, including physical (e.g. dilution), physico-chemical (e.g. sorption, ion exchange), chemical (e.g. precipitation) and microbial (e.g. degradation) processes.

Christensen et al. (1994) reviewed the information available before 1993 about processes important in attenuation of landfill leachate plumes. The purpose of this review is to provide an update of the 1994-review with emphasis on literature published since 1993. Most of the classical landfill leachate studies reviewed by Christensen et al. (1994) are also included in this current review, but general literature about attenuation processes have been excluded. This should make the current review fully up-dated and comprehensive with respect to landfill leachate plumes, but full appreciation of the information reviewed may require that the reader has some understanding of contaminant geochemistry in general.

As an introduction to this complex area of biogeochemistry, a summary of leachate composition and characteristics is presented. This is followed by a description of the physical (dilution), geochemical (redox zones) and microbial frameworks for the attenuation processes in leachate plumes. The biogeochemical processes are discussed in detail for the various contaminants under the terms: dissolved organic matter, inorganic macrocomponents (cations and anions), heavy metals and xenobiotic organic compounds (XOCs).

The review focuses on aquifers contaminated by leachate. Leachate is described as a water based solution of compounds from the waste. Only where large amounts of chemicals are disposed of will organic compounds possibly appear as free phases (e.g. non-aqueous phase liquids as solvents). However, free phase transport in aquifers and diffusive pollutant migration in clay and aquitards are not included in this review.

2. Landfill leachate

Landfill leachate is generated by excess rainwater percolating through the waste layers. Combined physical, chemical and microbial processes in the waste transfer

pollutants from the waste material to the percolating water (e.g. Christensen and Kjeldsen, 1989). Focusing on the common type of landfill receiving a mixture of municipal, commercial and mixed industrial waste, but excluding significant amounts of concentrated specific chemical waste, landfill leachate may be characterized as a water based solution of four groups of pollutants (Christensen et al., 1994).

- Dissolved organic matter, expressed as Chemical Oxygen Demand (COD) or Total Organic C (TOC), including CH₄, volatile fatty acids (in particular in the acid phase of the waste stabilization, Christensen and Kjeldsen, 1989) and more refractory compounds for example, fulvic-like and humic-like compounds.
- Inorganic macrocomponents: Ca, Mg, Na, K, NH₄⁺, Fe, Mn, Cl, SO₄²⁺ and HCO₃⁻.
- Heavy metals: Cd, Cr, Cu, Pb, Ni and Zn.
- Xenobiotic organic compounds (XOCs) originating from household or industrial chemicals and present in relatively low concentrations in the leachate (usually less than 1 mg/l of individual compounds). These compounds include among others a variety of aromatic hydrocarbons, phenols and chlorinated aliphatics.

Other compounds may be found in leachate from landfills: e.g. B, As, Se, Ba, Li, Hg and Co. But in general, these compounds are found in very low concentrations and are only of secondary importance.

Leachate composition varies significantly among landfills depending on waste composition, waste age and landfilling technology. Leachate sampling methods and sample handling routines may also influence the measured leachate quality.

Colloids have high affinity for heavy metals (Goumaris et al., 1993), and thus the concentration of heavy metals measured in a leachate sample may depend strongly on the amount of colloidal matter present in the sample and the handling of the sample. No standard protocols for sampling, filtration, and storage of leachate samples exist. Sampling and sample handling may explain part of the variation seen among landfills with respect to the heavy metal concentration in leachates.

Leachate analysis for XOCs may be biased by loss of pollutants due to volatilization or uptake in sampling equipment. However, recent studies have shown that the quality of leachate analysis for XOCs is seriously jeopardized only if very poor sampling protocols are used (see review by Parker, 1994).

Table 2.1 presents ranges of general leachate parameters compiled from data reported in the literature. The table is based mainly on data originating from newer landfills. Data from older uncontrolled landfills may exhibit lower values than the minimum values given in the table (Assmuth and Strandberg, 1993;

Kjeldsen and Christophersen, 2000). In general landfill leachates may contain very high concentrations of dissolved organic matter and inorganic macrocomponents. The concentrations of these components may typically be up to a factor 1000–5000 higher than groundwater concentrations.

Several parameters change dramatically as the landfill stabilizes. During the initial acid phase, the leachate may show low pH-values and high concentrations of many compounds, in particular high concentrations of easily degradable organic compounds as volatile fatty acids. In the later methanogenic phase, when CH₄ production is significant in the landfill, pH increases and the BOD₅/COD-ratio, reflecting the degradability of the organic C (biological O₂ demand measured over 5 days divided by chemical O₂ demand), is lowered dramatically (Ehrig, 1988). This again affects many of the inorganic parameters as illustrated in Table 2.2, where data are presented for acid phase leachate and methanogenic leachate. For parameters not significantly affected by landfill stabilization only average values are given.

The data given in Tables 2.1 and 2.2 are based on leachate sampled from landfills of less than 25 a of age, and the values are difficult to extrapolate beyond the first 25 a of a landfill's life. Belevi and Baccini (1992) estimated by use of leaching tests on municipal solid waste that leachate from landfills would contain significant concentrations of several compounds for centuries. Especially the N content (and the organic C content) will be significant for several centuries.

In addition to the time-wise changes in leachate composition as the landfill changes from acid to methanogenic phase, short-term variations in leachate quality may also appear. Seasonal variations in leachate composition have been observed in several cases. Åkesson and Nilsson (1997) observed lower leachate concentrations in a Swedish landfill test cell in the wet season. Similar observations were found by Chu et al. (1994) in a Hong Kong landfill.

Investigations on leachate composition have often been based on only one or a few leachate samples from each landfill. This may suffice if the leachate collection system averages the leachate from different sections of the landfill and the leachate is pumped out of the landfill for treatment. But in the context of groundwater pollution, the spatial distribution of the leachate quality must be appreciated, and this would require a large number of sampling points. Only few such studies exist. Pronounced irregular spatial variation in leachate composition was found at four old Finnish landfills (Assmuth, 1992). Significant spatial variability in leachate concentrations was also observed in wells at the 10 ha large old Grindsted Landfill (DK) (Kjeldsen et al., 1998a). Very low concentrations of almost all parameters (including XOCs) were found in areas covering about 60–70% of the landfill. A “hot spot”, occupying about 10% of the

Table 2.1
Composition of landfill leachate^a

Parameter	Range
pH	4.5–9
Specific conductivity (μS cm ⁻¹)	2500–35 000
Total solids	2000–60 000
<i>Organic matter</i>	
Total organic carbon (TOC)	30–29 000
Biological oxygen demand (BOD ₅)	20–57 000
Chemical oxygen demand (COD)	140–152 000
BOD ₅ /COD (ratio)	0.02–0.80
Organic nitrogen	14–2500
<i>Inorganic macrocomponents</i>	
Total phosphorous	0.1–23
Chloride	150–4500
Sulphate	8–7750
Hydrogencarbonate	610–7320
Sodium	70–7700
Potassium	50–3700
Ammonium-N	50–2200
Calcium	10–7200
Magnesium	30–15 000
Iron	3–5500
Manganese	0.03–1400
Silica	4–70 ^b
<i>Inorganic trace elements</i>	
Arsenic	0.01–1
Cadmium	0.0001–0.4
Chromium	0.02–1.5
Cobolt	0.005–1.5
Copper	0.005–10
Lead	0.001–5
Mercury	0.00005–0.16
Nickel	0.015–13
Zinc	0.03–1000

^a The ranges are based on Andreottola and Cannas (1992), Chu et al. (1994), Robinson (1995), Ehrig (1980, 1983, 1988), Garland and Mosher (1975), Johansen and Carlson (1976), Karstensen (1989), Krug and Ham (1997), Lu et al. (1985), Naturvårdsverket (1989), Owen and Manning (1997), and Robinson and Maris (1979). Values in mg/l if nothing else stated.

^b Values based on Owen and Manning (1997).

landfill area, was found with concentrations 20–1000 times higher than in the low concentration area. Especially for large landfills, information on spatial variability in leachate concentrations is very important as a basis for locating the main sources of the groundwater pollution plume and for selection of cost-effective remedial actions.

2.1. Dissolved organic matter

Dissolved organic matter in leachate is a bulk parameter covering a variety of organic degradation products

Table 2.2

Leachate composition in terms of average values and ranges for parameters with differences between acid and methanogenic phase (Ehrig, 1988) and average values for parameters with no observed differences between acid and methanogenic phase (Ehrig, 1983), all values in mg/l except pH and BOD₅/COD

Parameter	Acid phase		Methanogenic phase		Average
	Average	Range	Average	Range	
pH	6.1	4.5–7.5	8	7.5–9	
Biological oxygen demand (BOD ₅)	13 000	4000–40 000	180	20–550	
Chemical oxygen demand (COD)	22 000	6000–60 000	3000	500–4500	
BOD ₅ /COD (ratio)	0.58		0.06		
Sulfate	500	70–1750	80	10–420	
Calcium	1200	10–2500	60	20–600	
Magnesium	470	50–1150	180	40–350	
Iron	780	20–2100	15	3–280	
Manganese	25	0.3–65	0.7	0.03–45	
Ammonia-N					741
Chloride					2120
Potassium					1085
Sodium					1340
Total phosphorus					6
Cadmium					0.005
Chromium					0.28
Cobalt					0.05
Copper					0.065
Lead					0.09
Nickel					0.17
Zinc	5	0.1–120	0.6	0.03–4	

ranging from small volatile acids to refractory fulvic and humic like compounds (Chian and DeWalle, 1977). Discussion of attenuation processes in aquifers is difficult without specifying the organic compound in question. Unfortunately, there is generally very little information on the composition of dissolved organic matter in landfill leachate. However a few investigations concerning DOC in landfill leachate are available.

Harmsen (1983) analyzed an acid-phase leachate and a methanogenic-phase leachate. In the acid-phase leachate, more than 95% of the DOC content of 20 000 mg/l consisted of volatile fatty acids and only 1.3% of the DOC consisted of high molecular weight (MW) compounds (MW > 1000). Also, volatile amines and alcohols were detected. In the methanogenic-phase leachate, however, no volatile acids, amines or alcohols were detected, and 32% of the DOC (2100 mg/l) consisted of high molecular weight compounds (MW > 1000). In a methanogenic-phase leachate Artiola-Fortuny and Fuller (1982) described more than 60% of the DOC content as humic-like material. Investigating anaerobic and aerobic leachates and leachates which have passed a model aquifer Frimmel and Weis (1991) found that only 6–30% of the DOC could be described as fulvic acids.

More detailed characterization of the DOC in leachate and leachate polluted groundwater is based on isolation and purification of the DOC. These procedures

may potentially change the properties of the organic matter but it is necessary to purify the material in order to obtain results. Weis et al. (1989) compared fulvic acids from landfill leachates with those from soil and bog lake water. The fulvic acids isolated from landfill leachate had higher C, H, and S content, lower quantities of phenolic groups, lower complexation capacities for Cu and lower molecular weight. Christensen et al. (1998a) characterized 82% of the DOC in leachate-polluted groundwater sampled less than 10 m downgradient from the Vejen Landfill (DK) and found 49% fulvic acids, 8% humic acids and 25% hydrophilic fraction. Based on molecular weight (around 2000 MW), elemental composition and acidity, the fulvic acid fraction and the hydrophilic fraction resembled fulvic acids from other origins, where as the humic acid had rather low molecular weight.

2.2. Inorganic macrocomponents

The concentrations of some of the inorganic macrocomponents in leachate depend, as in the case of the dissolved organic matter, on the stabilization processes in the landfill. Table 2.2 shows that the cations Ca, Mg, Fe and Mn are lowest in the methanogenic phase leachate, due to a higher pH (enhancing sorption and precipitation) and lower content of dissolved organic matter, which may complex the cations. Sulfate concentrations

are also lower in the methanogenic phase due to microbial reduction of SO_4^{2-} to S^{2-} .

Table 2.2 also presents average values for parameters with no observed difference between acid and methanogenic phase. These are the macro components, Cl^- , Na and K, which only to a minor extent are governed by sorption, complexation and precipitation. Decreasing trends in concentration with time of these pollutants could be due to wash out by the leaching, but Ehrig (1983, 1988) did not observe any decrease in concentration for these parameters for up to 20 a of leaching.

Table 2.2 is based on detailed studies performed by Ehrig (1983, 1988) on a large number of landfills in Germany. Similar findings are presented in a study of 13 sanitary landfills in Wisconsin, USA (Krug and Ham, 1997), where equivalent concentration ranges and time dependency of the selected parameters were found.

Many investigations report concentrations of $\text{NH}_4\text{-N}$ in the range of 500–2000 mg/l, and no decreasing trend in concentration with time. Ammonia is released from the waste mainly by decomposition of proteins.

2.3. Heavy metals

The concentrations of heavy metals can be exemplified by the averages of methanogenic phase leachates from 20 German landfills as shown in Table 2.2 (Ehrig, 1983). In general the concentrations of the heavy metals in leachates from different landfills (see Table 2.1) show major variations. The average metal concentrations, however, are fairly low. A survey of 106 old Danish landfills (Kjeldsen and Christophersen, 2000) showed that metal concentrations for old landfills are also low: 0.006 mg Cd/l, 0.13 mg Ni/l, 0.67 mg Zn/l, 0.07 mg Cu/l, 0.07 mg Pb/l and 0.08 mg Cr/l. Metals like Hg and Co are rare in leachates and, together with the metalloid As, are not dealt with in this context. Iron and Mn are usually not considered heavy metals and are dealt with in the section on inorganic macrocomponents.

Laboratory techniques have been used to divide the heavy metal content in landfill leachates into different species. Several investigations have determined Cd species in landfill leachate and found that free divalent Cd^{2+} only made up a small fraction of the total Cd content (between a few per cent and 1/3 of the total content; Lun and Christensen, 1989; Bolton and Evans, 1991, Holm et al., 1995b). The complexes were both organic and inorganic. The proportion of the two groups of complexes very much depended on the composition of the leachate (Bolton and Evans, 1991). Most of the complexed fraction was characterized as labile complexes that were easily redistributed. Investigations also showed that a significant, but highly varying, part of the heavy metals was associated with the colloid content of leachate (Jensen and Christensen, 1999; Gounaris et al., 1993; Klein and Niessner, 1996). In all three investigations,

comparison of the distribution of organic matter and heavy metals between the size fractions indicated that the heavy metals in the colloidal fractions were not simply related to organic matter, even though the colloidal humic substances are suspected to play a major role with respect to the speciation of the heavy metals.

2.4. Xenobiotic organic compounds (XOCs)

Table 2.3 presents concentration ranges of the most frequently found xenobiotic organic compounds (XOCs) in landfill leachate. The table is based on landfills with leachate collection systems. Very broad ranges are observed, reflecting differences in co-disposal practices, general waste composition, landfill technologies, and waste age. The most frequently found XOCs are the aromatic hydrocarbons (benzene, toluene, ethylbenzene, and xylenes) and halogenated hydrocarbons like tetrachloroethylene and trichloroethylene. These pollutants are also the ones found in the highest concentrations. Another major group of newly identified compounds in leachates is the phenoxyalkanoic acid herbicides. Especially MCPP (or Mecoprop) has frequently been observed (Schultz and Kjeldsen, 1986; Gintautas et al., 1992; Kjeldsen, 1993; Öman and Hynning, 1993).

The concentration of XOCs in landfill leachate is expected to decrease over time, depending for each compound on its degradation in the landfill and its volatilization with the landfill gas (Kjeldsen and Christensen, 2000). However, the time aspects of this are hard to evaluate. Ravi et al. (1998) found, as shown in Fig. 2.1, highly varying concentrations of Cl^- , benzene and 1,1-DCA just downgradient from the West KL Landfill (USA) for a 15 a period.

3. Dilution

All compounds in leachate entering an aquifer will be subject to dilution as the leachate mixes with the groundwater. For non-reactive components, of which Cl^- is the dominant component, dilution is the only attenuation mechanism.

3.1. Leachate and groundwater flow

Dilution is the interaction of the leachate flow in the aquifer with the flow of groundwater. As such, it is mandatory to understand the processes governing the flow of water in an aquifer, but a discussion of these processes is beyond the scope of this review (refer e.g. to Freeze and Cherry, 1979). However, it should be emphasized that leachate migration should be seen in terms of a 3-dimensional plume developing in a 3-dimensional geological structure, where gradients, permeabilities and physical boundaries (geological strata,

Table 2.3

The most frequently observed xenobiotic organic compounds (XOCs) in landfill leachates. Only pollutants that have been observed in more than three independent investigations are included

Compound	Range ($\mu\text{g/l}$)	References ^d
<i>Aromatic hydrocarbons</i>		
Benzene	1–1630	a,b,d,f,h,i,k,l,m,n,o,p,q
Toluene	1–12300	a,b,d,f,h,i,k,l,m,n,o,p,q
Xylenes	4–3500	a,b,d,f,h,i,k,l,m,n,o,p,q
Ethylbenzene	1–1280	a,b,d,f,m,n,o,p,q
Trimethylbenzenes	4–250	b,f,o,p
Naphthalene	0.1–260	c,d,f,m,n,o,p
<i>Halogenated hydrocarbons</i>		
Chlorobenzene	0.1–110	a,d,f,m,o
1,2-Dichlorobenzene	0.1–32	a,c,d,f,o
1,4-Dichlorobenzene	0.1–16	a,c,d,f,m
1,1,1-Trichloroethane	0.1–3810	a,b,d,f,m,o,p,q
Trichloroethylene	0.7–750	a,b,d,f,l,m,n,o,p
Tetrachloroethylene	0.1–250	a,b,f,i,l,m,n,o,p,q
Methylene chloride	1.0–64	a,b,d,k,m
Chloroform	1.0–70	a,b,d,h,i,k,o,p,q
<i>Phenols</i>		
Phenol	1–1200	c,f,g,k,m,n
Cresols	1–2100	c,g,j,k,l,m,n
<i>Pesticides</i>		
Mecoprop ^a	2.0–90	c,e,l,n
<i>Miscellaneous</i>		
Acetone	6–4400	a,i,k,o
Diethylphthalate	10–660	c,g,j,m
Di- <i>n</i> -butylphthalate	5.0–15	c,g,i,j,m
Tetrahydrofuran	9–430	a,i,k,o
Tri- <i>n</i> -butylphosphate	1.2–360	c,f,j,l,m
Camphor ^b	1 ^c	c,f,j,n

^a 2-(2-methyl-4-chlorophenoxy)propionic acid (MCPP).

^b 1,7,7-trimethyl-bicyclo[2.2.1]-heptane-2-one.

^c I: Identified.

^d The references are: (a) Sabel and Clark (1984), (b) Först et al. (1989), (c) Öman and Hynning (1993), (d) Harkov et al. (1985), (e) Gintautas et al. (1992), (f) Reinhard et al. (1984), (g) Albaiges et al. (1986), (h) Khare and Dondero (1977), (i) DeWalle and Chian (1981), (j) Dunlap et al. (1976), (k) Sawhney and Kozloski (1984), (l) Schultz and Kjeldsen (1986), (m) Karstensen (1989), (n) Kjeldsen (1993), (o) Barker et al. (1987a), (p) Barker et al. (1987b), (q) Krug and Ham (1997).

infiltration, rivers, abstraction wells etc.) determine the position and migration velocity of the plume. However, the flow of leachate may physically differ from the flow of groundwater at least with respect to the following three aspects.

Local water table gradients below and around the landfill will most likely differ from the general gradients because the landfill will usually have a different hydrogeology than the surrounding area. This was observed especially in the spring and summer at the Borden

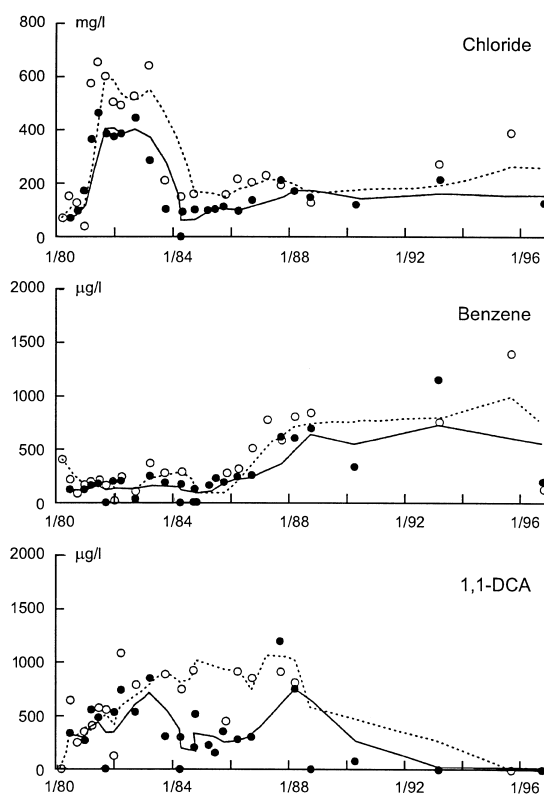


Fig. 2.1. Temporal variations (15 a) in leachate quality monitored in two wells (○ and ●) just downgradient from the KL Landfill in Michigan (USA) with respect to Cl^- , benzene and 1,1-DCA (after Ravi et al., 1998, with permission).

Landfill (CAN) (MacFarlane et al., 1983). Local water table mounds have been observed at the Vejen Landfill (DK) (Kjeldsen, 1993), the Noordwijk Landfill (NL) (Duijvenbooden and Kooper, 1981) and the Grindsted Landfill (DK) (Kjeldsen et al., 1998b). The groundwater table in the area of the Grindsted landfill site was monitored by 150 piezometers on eight different occasions within a $2\frac{1}{2}$ a period. A significant water table mound beneath and just upgradient the landfill was observed in the winter and spring season (Fig. 3.1). The isopotential maps reveal significant seasonal variations with respect to flow directions from different areas of the landfill and depending on the season. The reasons for water mounds in general are not fully understood, but at least three aspects may be important: (1) Higher infiltration in the landfill area due to “poor” top cover or different vegetation, (2) lower hydraulic conductivity below the landfill, or (3) higher infiltration at the borders of the mounding area due to interflow in the waste or surface runoff from the sloping cover. Lower hydraulic conductivities may be likely as landfills often have been placed on land of marginal value (e.g. seasonally water-logged), but also bacterial growth, precipitates or production of gaseous

bubbles of CH_4 and CO_2 can lead to reduced pore space, and thereby reduce the hydraulic conductivity. It should be emphasized that identification of a water table mound may demand isopotential maps representing different seasons and involve piezometers also within the landfill site. The effects of local mounding are (1) enhanced lateral spreading of the leachate plume, and (2) downward directed hydraulic gradients in the groundwater zone beneath the landfill. The latter can cause an unexpected spreading pattern despite homogeneous aquifer conditions and limited density difference between leachate and the ambient groundwater. The enhanced lateral spreading of the plume may increase the volume of contaminated groundwater, but provides increased dilution of contaminants. Furthermore, the spreading pattern may depend on the actual season, which may influence temporal data from monitoring wells in the outskirts of the plume.

The viscosity of the leachate may differ from the viscosity of the groundwater. A higher viscosity would theoretically lead to lower flow velocities, which could influence the dilution of the leachate plume. Very few data exist on leachate viscosity. Christensen et al. (1985) reported on the viscosity of 13 Danish leachate samples and concluded that the effect of the leachate viscosity was marginal (1–15% increase relative to water at equal temperatures). Kimmel and Braids (1980) stated that the change in viscosity due to temperature changes and to changes in solid concentration was also insignificant.

The density of the leachate is a function of the temperature and the concentration of dissolved solids. Leachate with a total dissolved solids concentration of 20 000 mg/l is not uncommon (see Table 2.1), corresponding to a density that is over 1% higher than the groundwater density (a density of 1.014 g cm^{-3} at 10°C , assuming that the leachate is similar to a NaCl solution,

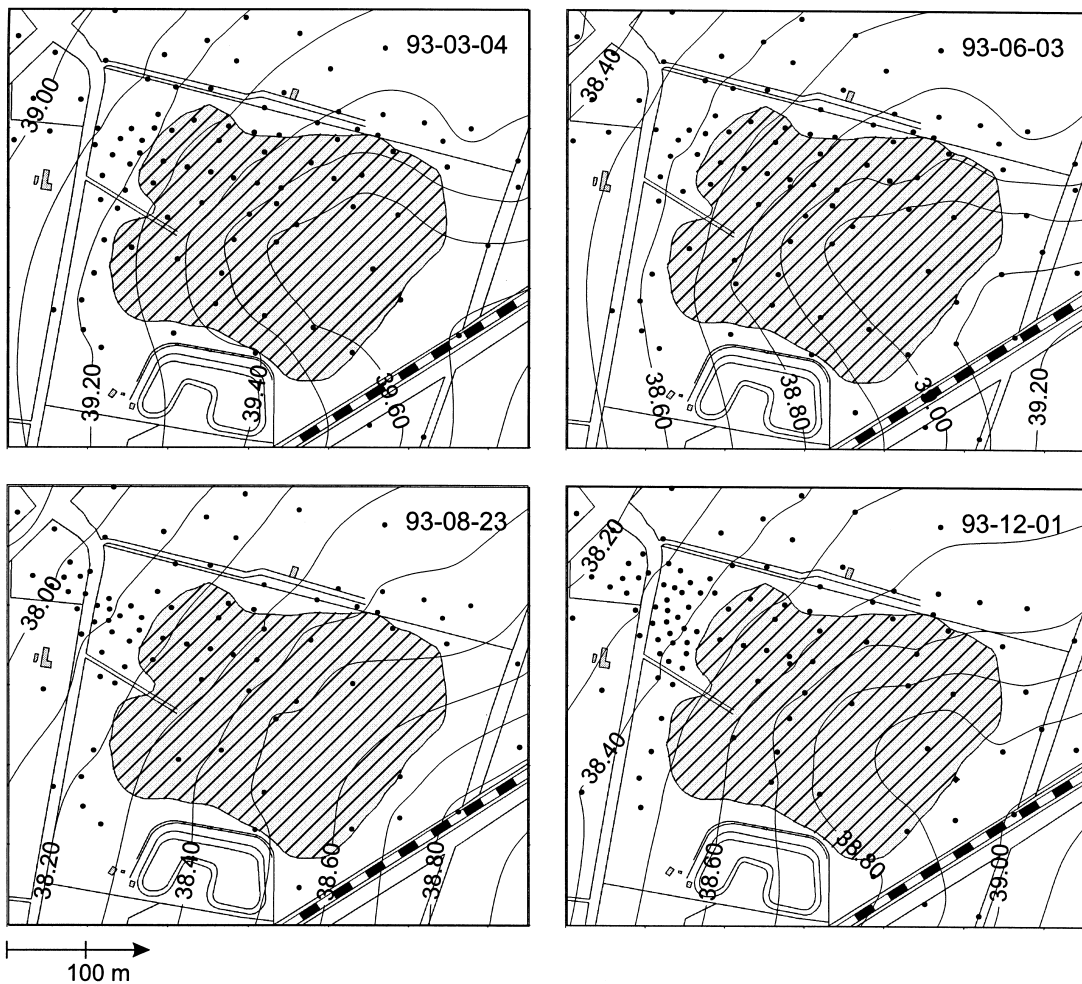


Fig. 3.1. Mounding of the leachate-groundwater table below Grindsted Landfill (DK) shown as isopotential contours for the landfill (shaded) and surrounding area at four different events during a 9 month period (from Kjeldsen et al., 1998a, with permission).

Kimmel and Braids, 1980). Christensen et al. (1985) measured densities of 13 different leachates and found a good correlation with the specific conductivity of the leachates (coefficient of correlation, $R^2=0.98$). This investigation indicates that it is mainly the salt content which contributes to the density increase. The regression equation was:

$$\text{Density (in g cm}^{-3}\text{)} = 6.87 \times 10^{-6} \times \text{Specific Conductivity (in mS m}^{-1}\text{)} + 0.9982 \text{ g cm}^{-3}$$

Temperatures elevated by up to 10°C in leachate plumes have been reported by several authors (Exler, 1972; Kimmel and Braids, 1980; MacFarlane et al., 1983; Kjeldsen et al., 1998b). However, the effect on the density of an increase in temperature by 10°C is insignificant compared to the effect caused by the content of dissolved solids (Kimmel and Braids, 1980).

The effect of higher density on the downward movement of leachates entering an aquifer has been studied in the laboratory by downflow column experiments with different soils (Kjeldsen, 1986). The leachate had a density of 1.008 g cm⁻³ (at 10°C) compared to the initial pore water of the columns having a density of 1.000 g cm⁻³. In columns with medium and coarse sands the initial Cl⁻ breakthrough curves showed increased mixing due to density effects as compared to columns with sandy and clayey loam (soil with much lower hydraulic conductivity). Experiments with artificial leachate in a small tank filled with groundwater-saturated sand (Schincariol and Schwartz, 1990) showed significant density effects even at solute concentration of 1000 mg/l (corresponding to a density difference of 0.08%). At a solute concentration of 10 000 mg/l a drastic effect was seen with unstable “fingering” of the leachate plume.

Density differences may significantly affect the vertical positioning of the plume just below the landfill. In field situations it is often difficult to separate the effect of local water table mounds from the effect of the higher density of the leachate on observed downward movement of the plume. At the Borden Landfill (CAN) the two causes of downward movement were compared (MacFarlane et al., 1983). It was found that in the spring and early summer the driving force due to density was small in comparison to the downward hydraulic gradient caused by mounding of the water table beneath the landfill. During the rest of the year, the density force was of the same magnitude or greater than the downward component of the hydraulic gradient. At the Babylon Landfill (USA) and the Islip Landfill (USA) studied by Kimmel and Braids (1974, 1980) no mounds were observed. However, significant density effects were observed since high leachate concentrations were observed at the bottom of the aquifers (23 and 54 m of thickness, respectively). At the Grindsted Landfill (DK), leachate density and Cl⁻ have been measured in a ver-

tical transect following an approximate flow line beneath the landfill and 120 m downgradient as shown on Fig. 3.2 (Jensen, 1994; Kjeldsen et al., 1998b). The densities of the leachate contaminated groundwater was in the range of 1.0021–1.0070 g cm⁻³. The results showed that the water samples with the highest density and highest Cl⁻ concentrations were found in the deepest parts of the plume outside the landfill. This was due to vertical gradients (see previous discussion in relation to Fig. 3.1), density gradients, and also to infiltration of rainwater on top of the contaminated groundwater. Duijvenbooden and Kooper (1981) found high leachate concentrations (50% diluted) at a fresh/salt water transition zone 35–41 m below the bottom of the Noordwijk Landfill (NL). They also observed a mound in the landfill, but by use of simple models the downward movement of the leachate was explained by density effects.

A better understanding of the effects of higher leachate densities in field situations is needed, because density effects could be the major cause of vertical leachate spreading in aquifers as “normal” vertical dispersion is usually very small (see next section).

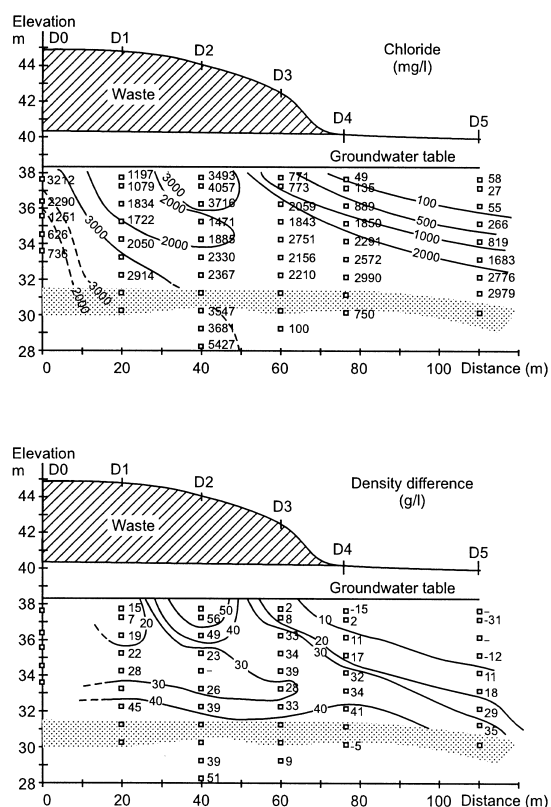


Fig. 3.2. Profiles of groundwater Cl⁻ (mg/l) and density difference ($\Delta\rho$ in g/l above background water density) along a flow-line below the Grindsted Landfill (DK). Based on data by Kjeldsen et al. (1998b), and Jensen (1994).

3.2. Dispersion

Dispersion is the mathematical term in the solute transport equation (see Freeze and Cherry, 1979) accounting for dilution or mixing according to concentration gradients. The hydrodynamic dispersion coefficient D (L^2T^{-1}) is often represented by the product of the pore flow velocity V (LT^{-1}) and the dispersivity α (L) neglecting the contribution of the molecular diffusion coefficient.

The dispersivity, α , has a longitudinal component (in the flow direction), a vertical component and a horizontal, transverse component. The dispersivity is difficult to measure in field situations, and often α has been used as a calibration parameter accounting for insufficient information on the spatial distribution of the hydraulic conductivity. Gelhar et al. (1992) reviewed dispersivity observations from 59 different field sites. The field sites were classified in three reliability classes. The high reliability data (from tests with well controlled physics of the system and appropriate data analysis) showed low longitudinal dispersivities in a range from 0.4 to 3 m for a scale between 15 and 250 m. Later published field injection studies have confirmed the low dispersivities (Adams and Gelhar, 1992; Jensen et al., 1993; Rügge et al., 1999a,b). The variations in dispersivity reflect the influence of different degrees of aquifer heterogeneity at different sites. The longitudinal dispersivity is important only for the concentrations in the front of leachate plumes. Of much more interest is the magnitude of the transverse dispersivities, which govern the transverse spreading of the

plume. The data presented by Gelhar et al. (1992) on transverse dispersivities are much more limited. The high and intermediate reliability data showed values of the horizontal transverse dispersivity in the range of 0.01–1 m (lowest for the very few high reliability data). This has been confirmed in detailed field mapping of various plumes from petroleum hydrocarbons and chlorinated solvent. However, detailed horizontal delineation of landfill leachate plumes have not been presented since the early field data from Borden landfill (Fig. 3.3). The review data from Gelhar et al. (1992) also indicates that vertical transverse dispersivities are extremely small, which means very limited vertical mixing due to dispersion alone. This has been confirmed in a number of landfill studies (e.g. Nicholson et al., 1983; Barker et al., 1986; Lyngkilde and Christensen, 1992b; Bjerg et al., 1995), where very sharp vertical concentration gradients of Cl^- have been observed (see also Fig. 3.4).

The mixing of a leachate plume with the surrounding groundwater is primarily due to local heterogeneities with respect to hydraulic conductivity. This means that dilution is limited in homogeneous aquifers. However, most aquifers contain substantial small-scale heterogeneities and will usually provide significant mixing, not necessarily accounted for by a large dispersivity coefficient but by the actual configuration of the hydrogeological heterogeneities. This complicates reliable prediction of local plume movement, which typically is in a length scale of a few hundred meters to 1 km, while readily available hydrogeological data usually are of a larger length scale. This would call for a substantial effort in mapping the local hydrogeology.

Dilution may also be caused by seasonal variations in flow direction, for example due to changing infiltration (MacFarlane et al., 1983) or water abstraction patterns (Baedecker and Apgar, 1984). This would correspond to a larger dispersion of the pollutants, but the variations may have a systematic pattern that makes it unaccountable just by increasing the dispersivity in the solute transport equation.

3.3. Observed leachate plumes

The development of an actual plume is the result of all the above-mentioned aspects and to give an appreciation of actual plumes, Fig. 3.3 (Borden Landfill, CAN) and 3.4 (Vejen Landfill, DK) contain examples of plumes reported in the literature. Table 3.1 characterizes the plumes reported in the literature with respect to landfill age, landfill size, plume size, contaminants measured, etc. These plumes, which are all located in sandy aquifers, will be further discussed in the following sections.

Most plumes have lengths less than 1000 m, and very few exceed 2000 m, probably due to dilution of the contaminants. Some plumes may have reached a stationary stage, i.e. the Cl^- plume does not develop any

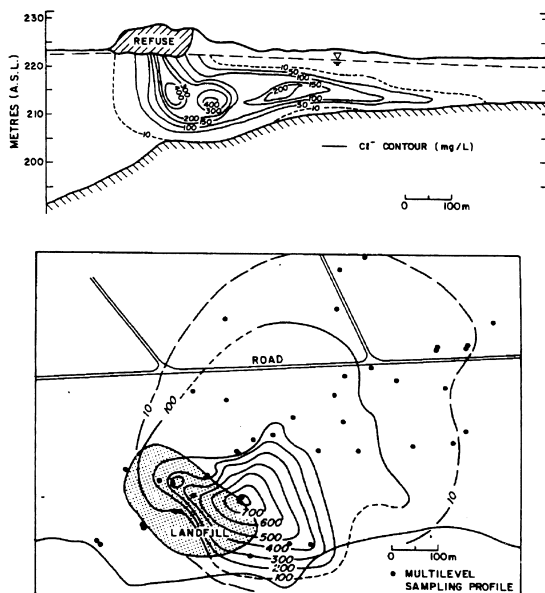


Fig. 3.3. Horizontal and vertical transect contours of Cl^- (mg/l) in the Borden Landfill (CAN) plume (from MacFarlane et al., 1983, with permission).

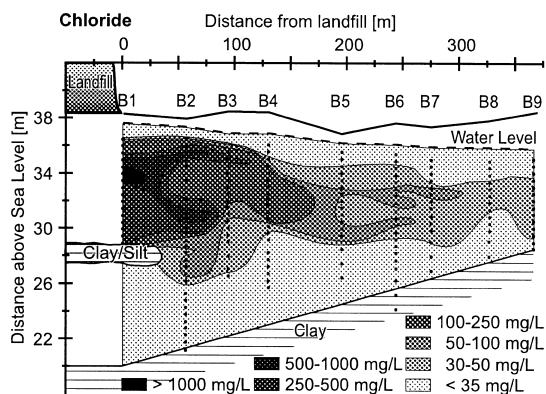


Fig. 3.4. Vertical transect contours of Cl^- (mg/l) in the Vejen Landfill (DK) plume (from Lyngkilde and Christensen, 1992b, with permission).

further. Many of the plumes show very little lateral, horizontal mixing as illustrated by the limited plume widths. An exception is the plume at the Borden Landfill (CAN) which according to the Cl^- contours, is much wider (~1600 m) than the landfill. This apparent horizontal mixing is supposedly due to seasonal variations in flow directions.

The information on dispersion available from observed leachate pollution plumes is rather uncertain as compared to information from controlled tracer experiments as described by Gelhar et al. (1992). This must be ascribed to larger scale, lower observation well density and inadequate information on leachate release pattern and history.

3.4. Conclusion: dilution

All leachate pollutants will be subject to dilution as the leachate in the aquifer mixes with the groundwater. Local groundwater table mounds, caused by the deviating hydrogeology of the landfill, and the higher density of the leachate, caused by the high salt content, may lead to an initial sinking of the leachate plume. Local groundwater table mounds may lead to vertical transport beneath the landfill, enhanced spreading of the leachate plume and/or seasonal variations in flow directions. The interaction between density driven transport and vertical transport due to vertical gradients is very complicated, and often both processes are important.

Reports of leachate plumes at actual full-scale landfills have been found in the literature (17 cases identified). Usually, the plumes are narrow (not much wider than the landfill) and have not been detected beyond 2000 m from the landfill. These narrow plumes indicate limited lateral or transverse mixing, which is in accordance with the current acceptance of the transverse dispersivities being very small. This also means that the mixing and dilution of leachate with groundwater is primarily gov-

erned by local variations in the hydrogeology. Thus, the hydrogeological conditions need to be characterized in detail at a relevant scale in order to understand the spreading of a leachate plume properly.

The landfill leachate plumes studied are all located in relatively homogeneous sandy aquifers. Many landfills are found in such geological settings, but the lack of reports on leachate plumes in geological settings with till deposits and fractured consolidated sediments is probably due to the technical complications and vast demands for economic resources associated with such studies.

4. Redox environments and processes

The entry of strongly reduced landfill leachate into a pristine, often oxidized, aquifer, leads to the creation of very complex redox environments. Important processes include organic matter biodegradation, abiotic redox processes, dissolution/precipitation of minerals, complexation, ion exchange, and sorption. The resulting redox environments strongly influence both the inorganic and organic biogeochemistry of the aquifer, and create the chemical framework for understanding the attenuation processes in the plume. In the following, the redox environments observed in landfill leachate plumes are presented, based on the simplified presentation of redox zonations as given in Fig. 4.1. Later in this section it is shown that actual redox conditions may be somewhat more complex.

4.1. Overall redox sequence

The sequence of redox zones as simplified in Fig. 4.1 was suggested by Baedecker and Back (1979a,b), Champ et al. (1979) and Nicholson et al. (1983), and verified by detailed monitoring in leachate plumes (Lyngkilde et al., 1992b; Bjerg et al., 1995). In an aquifer with a continuous leachate release, a methanogenic zone evolves close to the landfill. Within this zone and downgradient from it, SO_4^{2-} reduction may take place. Iron reduction takes place further downgradient as conditions become less reducing. Zones of Mn and NO_3^- reduction have been observed, sometimes overlapping the Fe reducing zone. Finally, aerobic conditions may exist in the outskirts of the reduced plume, if the pristine aquifer is oxidized and contains significant amounts of dissolved O_2 (> 1 mg/l).

Along the streamline given in Fig. 4.1, the content of reduced species (organic matter and NH_4) in the water decreases. The redox potential increases with distance. Close to the landfill, dissolved electron acceptors such as O_2 , NO_3^- and SO_4^{2-} are depleted or lowered in concentration. S may be present due to SO_4^{2-} reducing processes. At some distances, the content of reduced

Table 3.1
 Characteristics of landfill leachate plumes described in the literature (partly based on Christensen et al., 1994)

Name	Landfill area (ha) ^a	Landfilling period	Type of aquifer	Length of plume (m)	Width of plume (m)	Number of samples for delineation (approx.)	Compounds addressed
Borden, Canada ^b	4.5	1940–1976	Sand	~700	~600	600	Inorganics Redox pairs Organic matter
North Bay, Canada ^c	28	1962–?	Silt	~400	~100	300	Inorganics Redox pairs Organic matter XOCs
Woolwich, Canada ^d	3.5	1965–?	–	~600	–	500	Chloride Organic matter XOCs
Grindsted, Denmark ^e	10	1936–1972	Sand	~400 More plumes ?	~400 ?	350	Inorganics Redox pairs Organic matter XOCs
Vejen, Denmark ^f	6	1962–1981	Sand	~400	~100	160	Inorganics Redox pairs Heavy metals Organic matter XOCs
Augsburg-Nord, Germany ^g	26	1955–1990?	Sand, gravel	800?	500?	38	Inorganics Redox pairs Heavy metals XOCs
Unnamed, Germany ^h	15	1954–1970	Coarse sand	~3000	~500	20	Inorganics Organic matter
Noordwijk, Netherlands ⁱ	~6	1960–1973	Coarse sand	–	–	22	Inorganics XOCs
Army Creek, Delaware, USA ^j	24	1960–1968	Sand	~700	–	20	Inorganics Redox pairs Organic matter XOCs
Babylon, Connecticut, USA ^k	10	1947–1975	Coarse sand	3000	600	120	Inorganic
Bristol (mun.), Vermont, USA ^l	3	1968?–> 1992	Sand, gravel	200	150	30	Inorganics Redox pairs XOCs
Bristol (priv.), Vermont, USA ^m	4	1968–1995?	Sand, gravel	100	100	30	Inorganics Redox pairs XOCs
Islip, Connecticut, USA ⁿ	7	1960–1973	Coarse sand	1500	400	75	Inorganics
KL, Michigan USA ^o	27	1960–1979	Sand	1600	–	60	Inorganics Redox pairs Organic matter XOCs
Norman, Oklahoma, USA ^p	19	1920?–1985	Sand	> 225	400?	> 50	Inorganics Redox pairs Hydrogen Organic matter XOCs

(continued on next page)

Table 3.1 (continued)

Name	Landfill area (ha) ^a	Landfilling period	Type of aquifer	Length of plume (m)	Width of plume (m)	Number of samples for delineation (approx.)	Compounds addressed
Reno County, Kansas, USA ^q	55	1960?–1987	Sand	600	–	–	Inorganics Redox pairs
Shelby County, Tennessee, USA ^r	–	1968–1988	Sand	< 200	–	30	Inorganics Redox pairs Heavy metals XOCs
Unmaned, USA ^s	4	1956–1977	Sandy silt/gravel	+ 800	200 g	16	Inorganics Redox pairs Organic matter XOCs

^a 1 ha, hectare equals 10 000 m².

^b MacFarlane et al. (1983), Nicholson et al. (1983).

^c Barker et al. (1986), Reinhard et al. (1984).

^d Reinhard et al. (1984).

^e Bjerg et al. (1995), Rügge et al. (1995), Holm et al. (1995a), Kjeldsen et al. (1998a,b).

^f Andersen et al. (1991), Lyngkilde and Christensen (1992a,b), Kjeldsen (1993).

^g Baumann et al. (1993).

^h Exler (1972).

ⁱ Duijvenboden and Kooper (1981).

^j Baedecker and Apgar (1984), DeWalle and Chian (1981).

^k Kimmel and Braids (1974), Kimmel and Braids (1980).

^l Mack (1995).

^m Mack (1995).

ⁿ Kimmel and Braids (1974, 1980).

^o Kehew and Passero (1990), Ravi et al. (1998).

^p Christenson et al. (1999), Cozzarelli et al. (1999), Harris et al. (1999), Eganhouse et al. (1999).

^q Heck et al. (1992).

^r Parks and Mirecki (1992).

^s Eberle et al. (1997).

dissolved species such as S²⁻, Fe(II) and Mn peak as a result of redox processes. Also the composition of the solid minerals changes with distance, as discussed below. Overall, the pollutants leaving the landfill will, unless removed from the water, migrate through a series of redox zones, and over time migrate into more oxidizing environments.

The model presented in Fig. 4.1 is simplified. The redox zonation may be affected by several hydrological and geochemical factors such as water table fluctuations (smearing the redox zones vertically), changing groundwater flow directions (broadening and shortening the zones), and natural spatial variations in redox conditions associated with the aquifer sediment. One example, from the Grindsted Landfill (DK) leachate plume, is that local organic-rich deposits within the alluvial aquifer created a localized reducing zone within the oxic aquifer, which could easily have been mistaken for a reducing zone created by leaching from the landfill (Heron et al., 1998).

4.2. Redox buffering

The formation of the different redox environments is best described by the concept of redox buffering (Scott and Morgan, 1990; Barcelona and Holm, 1991; Heron, 1994). Leachate from landfills typically is strongly reduced, rich in organic matter and NH₄, and may be seen as infiltrating water with a great capacity for donating electrons (reduction capacity, RDC) during redox reactions (examples of reactions are given in Table 4.1). The produced electrons must be accepted by dissolved or solid aquifer electron acceptors (examples given in Table 4.2). The chemical changes in the aquifer can be understood as a series of redox titrations, depleting the aquifer close to the source of electron acceptors, as these are reduced. The titrator is the leachate, the titrant is the aquifer. The capacity of the aquifer to accept electrons is denoted the oxidation capacity (OXC, Scott and Morgan, 1990, Heron et al., 1994a).

The set of reactions that creates the complex redox environments consists of combinations of two half-reactions, one oxidation half reaction and one reduction half reaction. Table 4.3 presents the most prominent overall redox reactions, along with their calculated Gibbs free energy change at standard conditions [$\Delta G_0(W)$]. The lower (numerically higher) the $\Delta G_0(W)$, the more energy is gained, and the more willingly the reaction will proceed. Considering the processes of organic matter oxidation, it is evident that when all

electron acceptors are present, O_2 will be used first, followed by NO_3^- , Mn, Fe, and SO_4^{2-} . Finally, methanogenesis and fermentation reactions dominate, when the most favorable electron acceptors are depleted. This explains the overall redox zonation proposed in Fig. 4.1.

Table 4.1 shows that for typical leachates, the organic matter dominates the reduction capacity. Ammonium and CH_4 may also contribute significantly, showing that the fate of these inorganic compounds in the aquifer may also affect the formation of redox environments.

4.3. Fe minerals in redox buffering

An example of measured redox buffering capacity of aquifer solids along a streamline in the Vejen Landfill (DK) leachate plume is given in Fig. 4.2. The oxidation capacity, dominated by Fe oxides, was depleted in the reduced zones of the plume, as supported by detailed Fe speciation analysis by chemical extraction and scanning electron microscopy (Heron et al., 1994b). Increased reduction capacity of the solids was observed in the methanogenic, SO_4^{2-} reducing and Fe reducing zones. This increase was explained by reduced inorganic precipitates such as iron sulfide (FeS), pyrite (FeS_2), iron carbonate ($FeCO_3$), and generally by the presence of Fe(II) on mineral surfaces and in silicates (Heron et al., 1994b; Heron and Christensen, 1995). Such ferrous Fe forms may be important for reductive transformation of nitro-aromatic and chlorinated XOCs, as shown for the Grindsted Landfill (DK) plume (Rügge et al., 1998).

The aquifer oxidation capacity may be dominated by Fe oxides, when calculated for an aquifer volume including aquifer material and groundwater (Table 4.2). This is caused by the limited aqueous solubility of O_2 , and the relatively low NO_3^- and SO_4^{2-} contents in aquifers. Where dilution of the leachate is not significant, the amount and reactivity of the Fe and Mn oxides will govern the formation of the reduced plume (Heron and Christensen, 1995). Also solid Mn oxides contribute to the OXC, as they can be reduced into dissolved Mn. However, when long-term aquifer changes are in question,

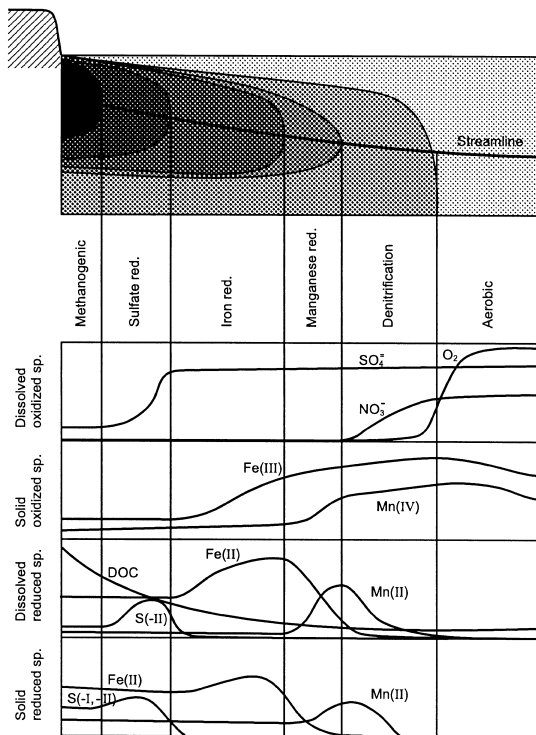


Fig. 4.1. Schematic redox zonation in an originally aerobic aquifer downgradient from a landfill, and the distribution of redox-sensitive species along a streamline in the plume. The value axes are not to scale.

Table 4.1

Reduction capacity (RDC, milliequivalent per liter of leachate) calculated for main pollutants in leachate from acid-phase and methanogenic phase landfills. The calculations are based on the shown typical composition of landfill leachate and possible oxidation half reactions

Species	Oxidation half reaction	Acid phase		Methanogenic phase	
		Concentration (mg/l)	RDC (m-equiv/l)	Concentration (mg/l)	RDC (m-equiv/l)
DOC	$CH_2O + H_2O \rightarrow CO_2 + 4H^+ + 4e^-$	5000	1670	250	85
XOCs	$CH + 2H_2O \rightarrow CO_2 + 5H^+ + 5e^-$	—	—	5	2
CH_4	$CH_4 + 2H_2O \rightarrow CO_2 + 8H^+ + 8e^-$	5	3	20	10
NH_4^+	$NH_4^+ + 3H_2O \rightarrow NO_3^- + 10H^+ + 8e^-$	60	30	100	45
Fe^{2+}	$Fe^{2+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ + e^-$	800	15	15	0

Table 4.2

Oxidation capacity (OXC, milliequivalent per liter of aquifer) calculated for oxidized species in two aerobic aquifers. The calculations are based on the shown contents of oxidized species, the proposed reduction half reactions, and assumed physical parameters: Porosities of 0.35 and bulk densities of 1.6 kg/l. Modified from Heron et al. (1994a) and Barcelona and Holm (1991). The potential contributions from CO₂ and natural organic matter were not evaluated

Species	Reduction half reaction	Vejen (DK)		Sand Ridge (Illinois, USA)	
		Content	OXC (m-equiv/l)	Content	OXC (m-equiv/l)
O ₂	O ₂ + 4H ⁺ + 4e ⁻ → 2H ₂ O	10 mg/l	0.44	9 mg/l	0.39
NO ₃ ⁻	NO ₃ ⁻ + 6H ⁺ + 5e ⁻ → 1/2N ₂ + 3H ₂ O	15 mg/l	1.9	0.95 mg/l	0.12
Mn(IV) (sediment)	MnO ₂ + 4H ⁺ + 2e ⁻ → Mn ²⁺ + 2H ₂ O	0.1 mg/g	6	0.39 mg/g	23
Fe(III) (sediment)	FeOOH + 3H ⁺ + e ⁻ → Fe ²⁺ + 3H ₂ O	2 mg/g	60	6.8 mg/g	200
SO ₄ ²⁻	SO ₄ ²⁻ + 9H ⁺ + 8e ⁻ → HS ⁻ + 4H ₂ O	40 mg/l	1.2	36 mg/l	1.1

Table 4.3

Most prominent redox reactions in landfill leachate plumes. Dissolved organic matter is represented by the model compound CH₂O. Gibbs free-energy changes at pH 7 are taken from Champ et al. (1979). OMO is short for the reaction Organic Matter Oxidation

Reaction	Process	ΔG ₀ (W) kcal/mol
Methanogenic/fermentative organic matter mineralization	2CH ₂ O → CH ₃ COOH → CH ₄ + CO ₂	-22
Sulfate reduction/OMO	2CH ₂ O + SO ₄ ²⁻ + H ⁺ → 2CO ₂ + HS ⁻ + 2H ₂ O	-25
Iron reduction/OMO	CH ₂ O + 4Fe(OH) ₃ + 8H ⁺ → CO ₂ + 4Fe ²⁺ + 11H ₂ O	-28
Manganese reduction/OMO	CH ₂ O + 2MnO ₂ + 4H ⁺ → CO ₂ + 2Mn ²⁺ + 3H ₂ O	-81
Denitrification/OMO	5CH ₂ O + 4NO ₃ ⁻ + 4H ⁺ → CO ₂ + 2N ₂ + 7H ₂ O	-114
Aerobic respiration/OMO	CH ₂ O + O ₂ → CO ₂ + H ₂ O	-120
CO ₂ reduction	HCO ₃ ⁻ + H ⁺ + 4H ₂ → CH ₄ + 3H ₂ O	-55 ^a
Ammonium oxidation	NH ₄ ⁺ + 2O ₂ → NO ₃ ⁻ + 2H ⁺ + H ₂ O	-72 ^a
Methane oxidation	CH ₄ + 2O ₂ → HCO ₃ ⁻ + H ⁺ + H ₂ O	-196 ^a

^a Calculated from standard Gibbs free energy of formation of the compounds in the reaction (values from Stumm and Morgan, 1996).

Fe reduction is likely to dominate, since Fe concentrations typically are 20–50 times higher than Mn concentrations in aerobic glacio-fluvial sediments.

Not all Fe oxides are available for reduction. Some Fe minerals are solid crystals or even entire Fe grains, which makes them resistant to e.g. microbial reduction (Lovley, 1991; Postma, 1993; Heron et al., 1994b). Other Fe oxides or hydroxides are amorphous and readily reducible. Over time, even some crystalline minerals such as goethite and hematite may be reduced in the complex environment of leachate plumes, as evidenced by the absence of such minerals in the Vejen Landfill (DK) leachate plume (Heron and Christensen, 1995). Albrechtsen et al. (1995) showed that the microbial Fe reduction rate in the Vejen Landfill (DK) leachate plume was controlled by the Fe oxide availability close to landfill and by the availability of the organic C source in the outskirts of the Fe-reducing zone. Amendment with a readily degradable C source or amorphous Fe hydroxide led to increased Fe-reduction rates, respectively. Heron and Christensen (1995) found in the Vejen Landfill (DK) plume that less than 50% of the total Fe in aquifer solids were available for reduction. This indicates that the importance of Fe as a redox

buffer controlling the size of plumes is not given just by the amount of Fe oxides present. The composition and availability of Fe for reduction are key parameters.

Methods for detailed speciation of Fe and S minerals in aquifer solids from leachate plumes were developed and tested by Heron et al. (1994a,b), Kennedy et al. (1998) and Amirbaham et al. (1998). These chemical extraction techniques provided a speciation of the total Fe content into Fe(II) and Fe(III) sub-categories. Although labor intensive, these methods are useful for understanding plume geochemistry and for characterizing the redox conditions during microcosm experiments (e.g. Albrechtsen et al., 1995; Nielsen et al., 1995a).

The reduction of Fe oxides and precipitation of the reduced metals as carbonates or sulfides changes the composition of the solids along a flow-line (Fig. 4.1). Overall, Fe oxides are reduced into Fe(II), which partly precipitates and partly migrates downgradient into more oxidized zones. When meeting O₂, and maybe also Mn oxides, Fe(II) is oxidized and precipitates as amorphous Fe hydroxides. The newly precipitated hydroxides form a very reactive and accessible electron acceptor. The migrating part of the reduced Fe thus contributes to a regeneration of oxidation capacity further away from

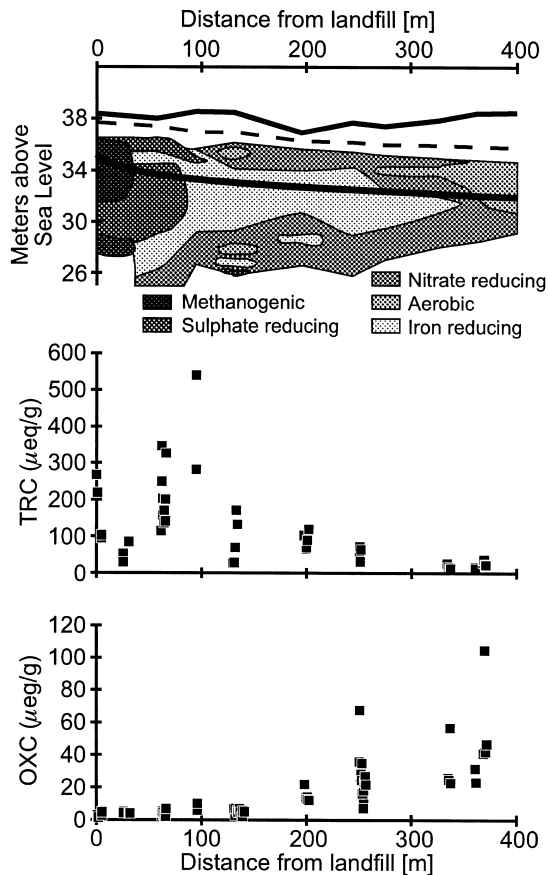


Fig. 4.2. Redox zones identified from water samples (upper) and the content of sediment reduction capacity (RDC, dominated by Fe(II) and sulfide precipitates) and oxidation capacity (OXC, dominated by Fe oxides) along a central streamline in the Vejen Landfill leachate plume (modified from Heron and Christensen, 1995).

the landfill. This may be essential in controlling the size of the reduced zones, especially if the plume expands. The substantial buffering by Fe oxides, thus, is related to consumption of oxidation capacity and the build-up of reduced species in the strongly reduced part of the plume. Overall, Fe acts to minimize the size of the plume by the redox buffering reactions, thus greatly retarding the migration of the reduced leachate and associated problematic compounds (Heron, 1994).

4.4. Observed redox environments in leachate plumes

Investigations of leachate plumes seldom directly address the existence of redox zones (Christensen et al., 1994). Based on the reported data on organic and inorganic species, the authors evaluated the redox processes in several leachate plumes (Table 4.4). Generally, the greater the detail of the investigations, the more redox

zones or environments were found. This suggests that most of the discussed redox environments develop at most sites. However, there are some exceptions to the general rule of redox sequences.

- In fractured rock such as limestone, plumes may migrate very far, with limited retardation by redox buffering reactions, as evidenced by the landfill at Kohl Springs, Missouri (Murray et al., 1981). In such systems, Fe reduction may be insignificant due to leachate flow in open fractures, and NO_3^- reduction and aerobic respiration may be limited due to limited mixing with the ambient water.
- Sulfate reduction is sometimes insignificant. Lyngkilde and Christensen (1992b) found evidence of SO_4^{2-} reduction in one out of two investigations in the same leachate plume, suggesting seasonal variations in the SO_4^{2-} reducing activity. Absence of SO_4^{2-} in the aquifer and leachate excludes SO_4^{2-} reduction (Kimmel and Braids, 1980; Ludvigsen et al., 1998).
- Iron reduction seems to occur in all the glaciofluvial aquifers examined. However, direct evidence has been established only in three cases, since Fe solubility is limited, Fe geochemistry is complicated, and careful solid sampling and analysis is required (Heron et al., 1994b).
- Recent results of aquifer material incubations suggest that several groups of different redox-active bacteria may be present and active in the same sample (Ludvigsen et al., 1998). This indicates that redox zones overlap to a greater extent than shown in Fig. 4.1.

In the following, the results from the Grindsted Landfill (DK) plume are presented in greater detail, since this recent investigation is the most extensive investigation reported and has shed light on several important redox processes.

4.5. Redox characterization of the Grindsted Landfill (DK) plume

At the Grindsted Landfill site, the redox environments were addressed in terms of dissolved redox-sensitive species (Bjerg et al., 1995), aquifer solid compositions (Heron et al., 1998), activity of microorganisms performing each electron accepting reaction (Ludvigsen et al., 1997), and the concentration of dissolved H_2 in the groundwater (Jakobsen et al., 1998).

The distribution of dissolved redox-sensitive species (example given in Fig. 4.3) showed that the redox zones were somewhat different in two parallel vertical transects, separated by only 30 m (Fig. 4.4). The overall sequence was consistent with the one depicted in Fig. 4.1, although the water chemistry of the Grindsted Landfill

Table 4.4
Redox environments found in landfill leachate plumes (+: observed, (+): indications,-: not observed). Modified from Christensen et al. (1994) and Heron (1994)

Landfill	Studied plume length (m)	Leachate RDC (m-equiv/l)	Aquifer type	Methanogenic	Sulfate reducing	Iron/manganese reducing	Nitrate reducing	Aerobic	References
Vejen, Denmark	400	150	Oxidized alluvial sand	+	+/- ^a	+	+	+	Lyngkilde and Christensen (1992b), Heron and Christensen (1995)
Borden, Ontario	700	30	Oxidized glaciofluvial sand	NE ^b	+	+	(+) ^c	(+)	Nicholson et al. (1983)
North Bay, Ontario	700	200	Oxidized glacio-fluvial sand and silt	+	NE	NE	NE	NE	Cherry (1983), Barker et al. (1986)
KL, Michigan	700	500	Sand and silt/clays	+	+	(+)	NE	NE	Kehew and Passero (1990)
Islip, Connecticut	1500	–	Oxidized sand and gravel	NE	–	(+)	NE	NE	Kimmel and Braids (1974, 1975, 1980)
Babylon, Connecticut	3000	–	Oxidized sand and gravel	NE	+	(+)	+	NE	Kimmel and Braids (1974, 1975, 1980)
Army Creek, Delaware	700	300–1500	Oxidized confined sand	+	–	(+)	NE	NE	Baedecker and Back (1979a), Baedecker and Apgar (1984)
Kohl Springs; Missouri	1500	2000	Oxidized fractured limestone	+	+	(+)	NE	NE	Murray et al. (1981)
Grindsted, Denmark	320	50–100	Oxidized sand and fine sands, layering	+	+	+	+	+	Bjerg et al. (1995), Ludvigsen et al. (1998), Jakobsen et al. (1998), Heron et al. (1998)

^a Found once out of two investigations.

^b NE, not evaluated (insufficient data).

^c Probable, but not documented by data.

(DK) leachate plume suggested that several of the redox zones overlapped. Methanogenic and SO_4^{2-} reducing zones overlapped (Fig. 4.4). Iron, Mn and NO_3^- reducing zones overlapped in some cases, and were separate in others. Also, the sizes of the zones varied considerably between neighboring transects, which is interesting in light of the conclusions drawn earlier for sites with much less data. In this plume CH_4 and NH_4 migrate further than dissolved organic matter (Fig. 4.3), and thus are the dominant reductants at distances above 100–150 m from the landfill.

Detailed geological and geochemical description of the aquifer sediment resulted in an enhanced understanding of the distribution of Fe species in the plume (Heron et al., 1998). The majority of the aquifer consisted of mineral-poor fine sands, low in organic matter and Fe oxides. It was concluded that Fe and Mn reduction was less important than at the Vejen Landfill (DK) located in the same geographical area, even though very high concentrations of dissolved Fe^{2+} and Mn^{2+} were observed in the Grindsted Landfill (DK) leachate plume. Both a lower initial Fe oxide content and a different Fe mineralogy (presumably solid grains of crystal Fe oxides) indicated lower Fe reactivity.

Bioassays (microbially active, unamended incubations of aquifer solids and groundwater, Ludvigsen et al., 1998) monitored all the redox processes that occurred and allowed for estimating rates of the individual redox processes as shown in Fig. 4.5. The rates were fairly low for many of the redox processes. The bioassays also showed that in several samples, more than one redox process was significant. However, in most cases one electron acceptor dominated in terms of equivalent rates of organic matter oxidation, and altogether the rates balance fairly well the degradation of dissolved organic C observed in the plume. However, the rates determined for denitrification exceeded the dissolved C available in that part of the plume suggesting that other electron donors also played a role here, maybe NH_4 . It was furthermore demonstrated that geological heterogeneities can lead to unexpected redox activities, exemplified by the high SO_4 reduction activity 170 m from the landfill. This was caused by localized, SO_4^{2-} and organic matter rich deposits, not by the leachate from the landfill.

Measurements of dissolved H_2 have been used to characterize redox levels according to distinct criteria based on competitive exclusion of terminal electron acceptors for H_2 oxidation (Lovley and Goodwin, 1988; Chapelle et al., 1995). In the Grindsted Landfill plume, the variations in H_2 concentrations (52 sampling points) were limited, and the values were low (0.004–0.88 nmol/l) indicating, according to previous criteria, Fe reducing conditions in most of the anaerobic part of the plume (Jakobsen et al., 1998). This was surprising as the microbial assays and the geochemistry have revealed more active redox processes in the plume (see above). This suggests a need for refining the use of H_2 in identifying

terminal electron acceptors in complex plumes. The H_2 measurements were used along with the measurements of groundwater chemistry in thermodynamic calculations of free energies of the redox reactions at the actual temperature of the plume (11°C). These calculations showed that both SO_4^{2-} reduction and Fe reduction could occur in the plume, since ΔG_r values were below a proposed threshold value of -7 kJ/mol of H_2 in several places for each reaction. Methanogenesis (by CO_2 reduction) showed in all samples higher ΔG_r values, suggesting that methanogenesis only occurred in stagnant pore water, where more reducing conditions may prevail. The small differences in calculated ΔG_r values actually suggested that SO_4^{2-} reduction and Fe reduction could take place simultaneously in the same sample.

Overall, this refined use of H_2 concentrations supported the results of the bioassays and the complex system of redox zones observed from the distribution of dissolved redox-sensitive species. The Grindsted Landfill (DK) plume is host to all of the proposed redox reactions, but also to secondary oxidation–reduction reactions involving NH_4 , CH_4 , Mn oxides, Fe(II) and sulfides.

4.6. Conclusions: redox environments

Recent, detailed investigations into redox processes in landfill leachate plumes have added significantly to the understanding of redox zones in landfill sites. The findings indicate that the zonation proposed in Fig. 4.1 generally holds in terms of the overall redox gradient: methanogenic conditions close to the landfill, through SO_4^{2-} , Fe, Mn and NO_3^- reducing conditions to aerobic conditions furthest away from the landfill. But recent investigations have also shown that each redox process is not found in an individual, distinct and separate zone. Redox zones seems to overlap, allowing more simultaneous redox processes, although one process may dominate in terms of actual rates. Microbial and sediment analysis has greatly enhanced our understanding of redox zones, and unamended bioassays and H_2 measurements have proven useful in determining on-going redox processes. Geological heterogeneities may lead to erroneous conclusions on redox reactions in the plume, since naturally reduced sediments may be mistaken for sediments that have been reduced during processes involving leachate pollutants. Solid Fe oxides may be the dominant electron acceptor in many leachate plumes, buffering the reduced species in the leachate through reduction to Fe(II), but the Fe availability is a key factor.

5. Microbiology

Most uncontaminated aerobic aquifers are oligotrophic and entry of landfill leachate, reduced and rich in dissolved organic matter, will dramatically change the

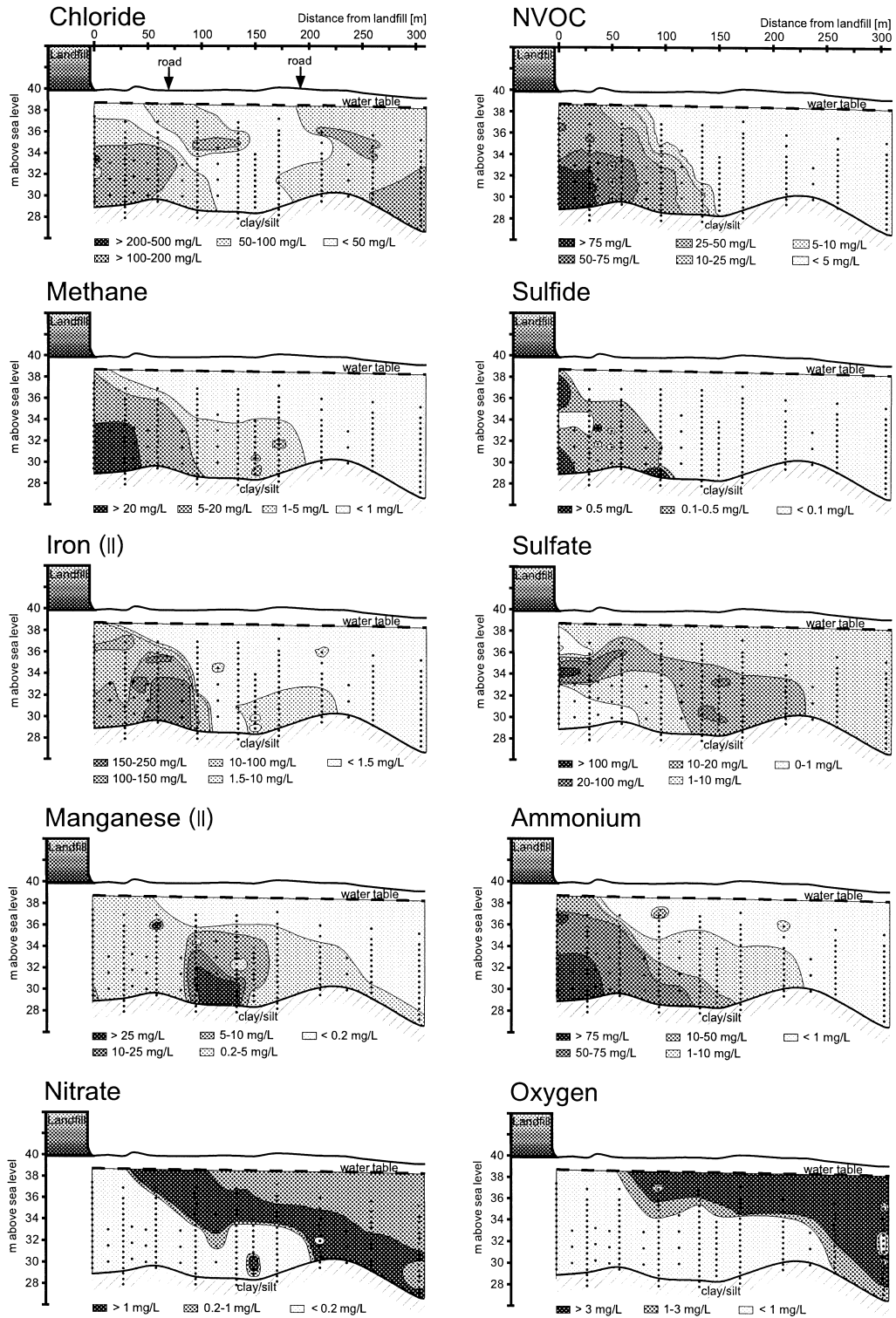


Fig. 4.3. Distribution of Cl^- and dissolved redox-sensitive compounds in Transect 1 downgradient of Grindsted Landfill (DK). Non-Volatile Organic Carbon (NVOC) is given as mg C/l, NO_3^- and NH_4^+ as mg N/l, and sulfide and SO_4^{2-} are given as mg S/l (from Bjerg et al., 1995, with permission).

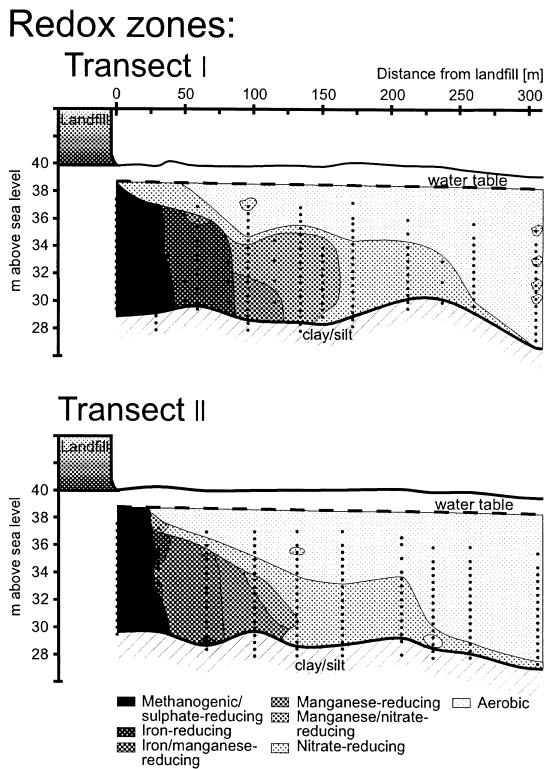


Fig. 4.4. Redox zone distribution in two parallel transects downgradient of Grindsted Landfill (DK), based on the observed groundwater chemistry. The upper transect is the one represented in Fig. 4.3 (from Bjerg et al., 1995, with permission).

composition of the original microbial population. A general review of the microbial ecology of the terrestrial subsurface, contaminated as well as uncontaminated, has been presented by e.g. Ghiorse and Wilson (1988), Dobbins et al. (1992), Chapelle (1993), and Lovley and Chapelle (1995); but these authors paid only little attention to aquifers affected by landfill leachate.

The microbial populations in landfill leachate contaminated aquifers are dominated by bacteria (eubacteria and archaea), as shown by analysis of the PLFAs (Phospho Lipid Fatty Acids) (Ludvigsen et al., 1999). Microscopic investigations of aquifer samples after acridine orange staining of the microorganisms, unsuccessful attempts to grow protozoas and the absence of PLFA-indicators for protozoas in samples from the Grindsted Landfill (DK) plume suggest the absence of protozoas and, hence, support the dominance of bacteria in landfill leachate contaminated aquifers (Ludvigsen et al., 1999).

5.1. Presence of microorganisms

The number of bacteria in leachate contaminated aquifers is relatively high compared to the number of

bacteria usually found in pristine aquifers. Table 5.1 summarizes the reported numbers determined by direct counting (cells) or spread plate technique [colony forming units (CFU)]: $0.04\text{--}1470 \times 10^6$ cells g^{-1} dry weight (dw) or $0.06\text{--}20000 \times 10^3$ CFU g^{-1} dw. The reported numbers originate from investigations of unconsolidated (sandy) as well as consolidated (limestone or sandstone) aquifers, and the large variation between different samples and different reports may be due to geochemical or hydrogeological differences, different methods used, inappropriate media for plate counts, and the impossibility of creating a single medium appropriate for all the bacteria to be enumerated by direct counting. A simple comparison of reported numbers from different sites is therefore not meaningful, but it can be concluded that relatively high numbers of bacteria are present in leachate plumes.

The total number of bacteria (measured by direct counting) in the aquifer downgradient from the Grindsted Landfill (DK) was fairly constant with the distance from the landfill (Ludvigsen et al., 1999). However, by this method it is not possible to distinguish between living and dead cells, and as an estimate of living bacteria, the PLFA concentration was higher close to the landfill than further away from the landfill, whereas ATP showed no significant trend. From the measurements of ATP and PLFA the viable biomass was estimated to range from $10^4\text{--}10^6$ viable cells/g dw (Ludvigsen et al., 1999) clearly demonstrating the presence of a significant viable population. In a controlled, 100 m long artificial leachate contaminated aquifer, the bacterial numbers were about two orders of magnitude higher close to the leachate inlet than in an unaffected section (Diekmann, 1991). The bacterial biomass (in terms of ATP content and cell numbers) and electron transport system (ETS)-activity was the highest adjacent to the leachate inlet, but decreased to less than a third of that value within the first few meters of the artificial aquifer. These investigations indicate higher and more active microbial populations close to the landfill in plumes under development (represented by the experimental aquifer), whereas the microbial populations apparently show less gradients in older plumes [represented by the 25 a old plume at the Grindsted Landfill (DK)].

The fraction of individual PLFAs of the total content of PLFA can be used as an indicator for the composition of the microbial community, and it is evident that it changes with distance from the landfill (Ludvigsen et al., 1999). Ratios between selected PLFAs can also be used as indicators for the metabolic status and stress of the investigated microbial population. For example, the ratio of membrane cyclopropyl fatty acids to their monoenoic precursors reflects the physiological status of Gram-negative bacterial populations (Knivett and Cullen, 1965), and Gram-negative bacterial populations produce more *trans* fatty acids than *cis* fatty acids in the

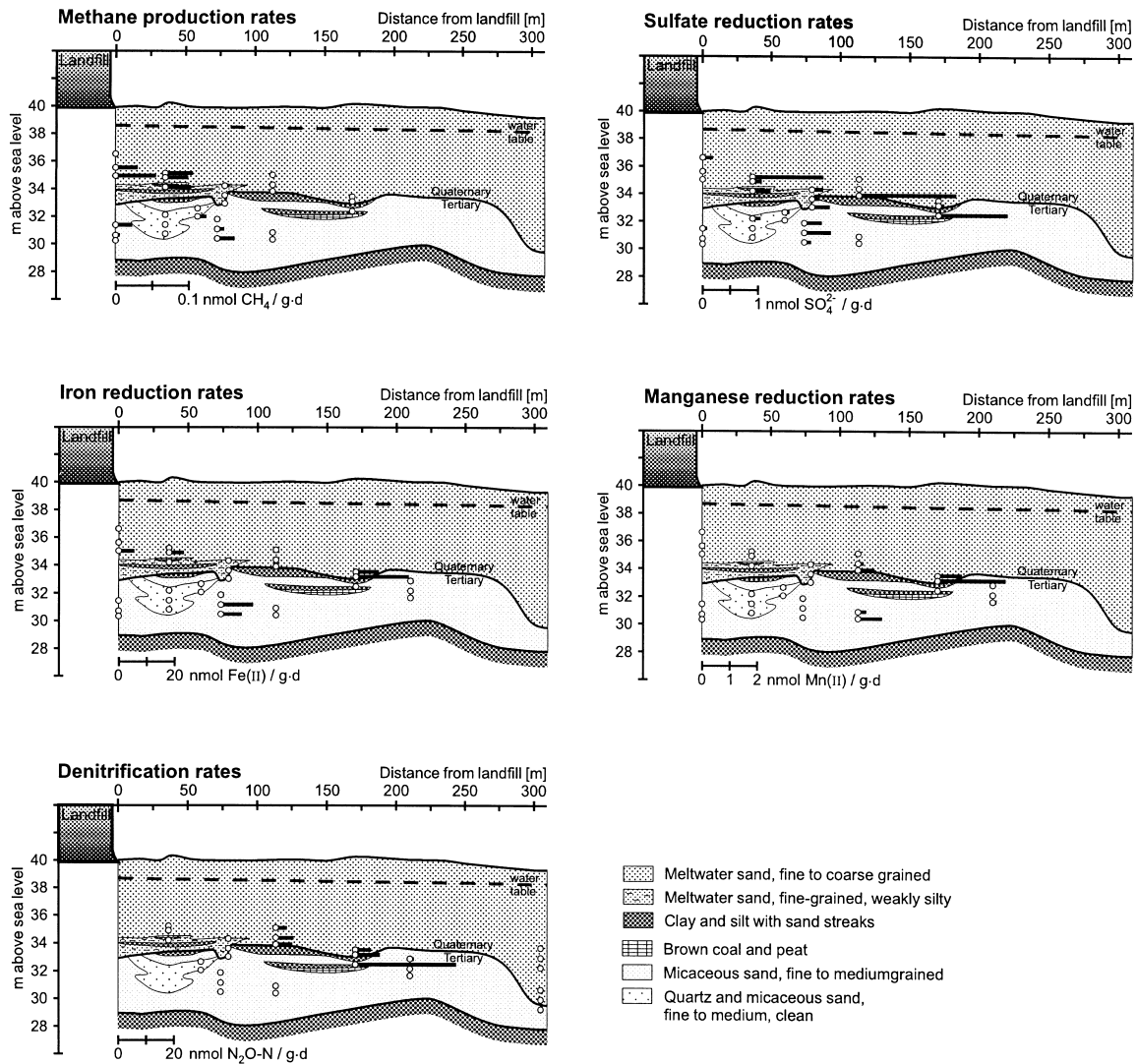


Fig. 4.5. Rates observed by unamended bioassays for individual redox processes at several locations in the Grindsted Landfill (DK) plume. Note that Fe reduction rates may be underestimated due to the high detection limit of the method (from Ludvigsen et al., 1998, with permission).

modification of the cell membrane, often in response to exposure to e.g. a toxic pollutant (Heipieper et al., 1992) or to starvation (Hedrick et al., 1991). Despite the mature age of the plume at the Grindsted Landfill (DK) such investigations of the microbial populations revealed that closest to the landfill a higher proportion of the microorganism was active and responded to the presence of the pollutant (Ludvigsen et al., 1999). Similar results were observed at the Vejen landfill site (Albrechtsen et al., 1995). In addition to the effect of the changes in substrate concentrations, the leachate may contain toxic compounds, but very little information exists on possible toxic effects of leachate in terms of changes in PLFAs.

The composition of the microbial population also reflects the redox conditions in the plume as discussed later.

Most of the aquifer bacteria are associated with particle surfaces (see Table 5.1). The sediment associated bacteria in leachate affected aquifers are metabolically active and are especially associated with surfaces of the finer sediment fractions (clay and silt) (Albrechtsen, 1994). The sediment attached bacteria are also important for the degradation of anthropogenic organic compounds as the degradation potential (in terms of how many compounds were degradable) was larger and the maximum degradation rates were faster in experiments inoculated with both sediment and groundwater than in experiments with groundwater only (Holm et al., 1992; Albrechtsen et al.,

Table 5.1
Number of bacteria observed in landfill leachate contaminated aquifers

Location	Aquifer type	Microscopic, direct countings $\times 10^6$		Plate countings $\times 10^3$		ATP pmol/g dw	PLFA pmol/g dw	References
		Groundwater cells ml ⁻¹	Sediment cells g ⁻¹ dw	Groundwater CFU ml ⁻¹	Sediment CFU g ⁻¹ dw			
Grindsted, Denmark	Glacio-fluvial sand	–	5–53	–	–	0.1–2.9	0.7–33	Ludvigsen et al. (1999)
Vejen, Denmark	Glacio-fluvial sand	0.1–8.1	17–1470	–	–	0.2–0.7	0.3–22	Albrechtsen et al. (1995), Nielsen et al. (1995a)
Artificial aquifer, Germany	Sand	1–100	0.6–50	–	–	–	–	Diekmann (1991)
Unnamed, Germany	N.I. ^a	– ^b	–	0.4–450	100–10 000	–	–	Farkasdi et al. (1969)
Burntstump, Nottinghamshire, UK	Sandstone	–	<0.01–100 ^c	–	–	–	–	Blakey and Towler (1988)
Ingham, Suffolk, UK	Chalk	–	0.04–190 ^c	–	0.06–1400 ^c	–	–	Towler et al. (1985)
Norman, OK, USA	Unconfined alluvial sand	–	17–112	–	–	–	–	Beeman and Suffita (1987), Beeman and Suffita (1990)

^a N.I.: No information.

^b Not measured.

^c Per gram wet weight.

1996, 1997). The degree of attachment of bacteria to aquifer material is not constant, but may be affected by pH and by the presence of Fe, Mn and Al oxyhydroxides (Scholl and Harvey, 1992). An increase of the level of contamination (measured as DOC and specific conductance) may reduce (Harvey and Barber, 1992) or increase the sorption of bacteria (Lindqvist and Bengtsson, 1991).

Though present in relatively high numbers, and associated with sediment surfaces, the abundance of bacteria in polluted aquifer material is probably too low to create a complete and continuous coverage of the solid particles. Thus, the biofilm concept is believed inappropriate for aquifers (Baveye et al., 1992).

5.2. Microbial redox processes in leachate plumes

As early as 1969, Farkasdi et al. (1969) distinguished between reduction, transition and oxidation zones in leachate plumes at German landfills, and enumerated SO_4^{2-} and NO_3^- reducing and denitrifying bacteria in all three zones. This indicated that the observed zones were related to microbial activity. Investigations of redox related microbiology can be carried out in two ways: by enumerating the bacteria in terms of different metabolic types (denitrifiers, Mn reducers, Fe reducers, SO_4^{2-} redu-

cers, methanogens, etc.) or by investigating the specific processes (e.g. SO_4^{2-} reduction, denitrification etc.).

Different physiological groups (utilizing different substrates) of SO_4^{2-} reducers and methanogens were observed in the Norman Landfill (USA) leachate-contaminated aquifer (Beeman and Suffita, 1987, 1990). The microbial population changed in composition throughout the plume at the Grindsted landfill (DK). Methanogens and SO_4^{2-} reducers were abundant close to the landfill, but their numbers decreased in the more distant parts of the plume (Fig. 5.1, Ludvigsen et al., 1999). The Fe-, Mn-, and NO_3^- -reducers occurred in surprisingly high numbers compared to the total cell numbers and varied only little with distance, when enumerated with the Most Probable Number (MPN) technique, which counts all the bacteria that can perform the redox processes investigated. A multivariate statistical analysis of the relation between the PLFA profile and different microbial processes and redox conditions revealed that the PLFA approach has limited ability to identify more specific microbial populations (Ludvigsen et al., 1997). Nevertheless, some specific lipid biomarkers indicated that the proportion of SO_4^{2-} and Fe-reducing bacteria was greater closest to the landfill (Ludvigsen et al., 1999).

With techniques such as in situ columns, Acton and Barker (1992) have shown the potential for different

microbially mediated redox processes in methanogenic sediment in the North Bay Landfill (CAN) leachate plume. After enrichment with different electron acceptors, they observed CH₄-production, SO₄²⁻-reduction or denitrification. In various unamended in situ columns installed in the plume at the Vejen Landfill (DK), Nielsen et al. (1995a) observed weak CH₄ production, but evident Fe- and Mn-reduction, and denitrification. Performance of bioassays with unamended groundwater and sediment samples verified the presence of the following metabolic activities in the Grindsted Landfill (DK) plume (Ludvigsen et al., 1998): denitrification (accumulation of N₂O after acetylene blockage), Fe-reduction (accumulation of Fe(II) during incubation), Mn-reduction (accumulation of Mn(II) during incubation), SO₄²⁻-reduction (³⁵S²⁻ evolution from ³⁵SO₄²⁻), and CH₄ production. Examples of these bioassays are shown in Fig. 5.2. Similar results were obtained from the Vejen Landfill plume (DK) (Christensen et al., 1997; Albrechtsen and Christensen, 1994). The unamended bioassays for different processes, but set up with material from the same sample, also revealed the concomitant occurrence of several different microbially mediated redox processes in the same sample (Ludvigsen et al., 1998, see also Fig. 4.5

showing the estimated rates of the various redox processes). This shows that microbially mediated redox processes do not exclude each other at least on a sample size of several grams. However in terms of mineralized organic matter (assuming oxidation level zero of the C in the organic matter) to CO₂ calculated from the measured rates of the electron-accepting processes, one electron-accepting process clearly dominated each sample accounting for more than 70% of the equivalent C conversion (Ludvigsen et al., 1998). This suggests that the concept of redox zones does make sense in terms of dominating redox levels, but that other redox processes may also be taking place simultaneously. This may have further implications for the potential of the redox zone to degrade trace amounts of organic chemicals.

Although present or detectable under optimum growth conditions, the different redox specific bacteria (SO₄²⁻ reducers, denitrifiers ect.) are not necessarily active in situ, and no significant correlation has been found between the abundance of any of the different redox specific bacteria measured by MPN or estimated from specific PLFA biomarkers and quantitative measurements of redox processes (Ludvigsen et al., 1999).

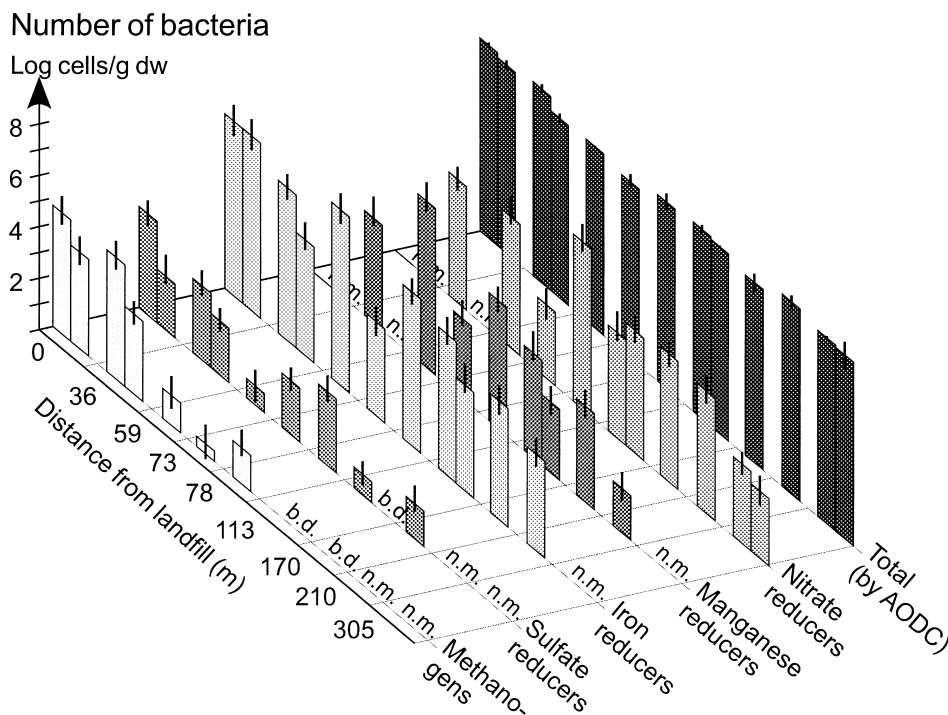


Fig. 5.1. The log number of methanogens (Archaea), SO₄²⁻, Fe-, Mn- and NO₃⁻-reducing bacteria as measured by MPN enumeration as well as AODC counts of aquifer sediments at different locations in the Grindsted Landfill (DK) plume (95% confidence limits shown). Samples were pooled in sets of two or three per distance. When more than one set of samples were collected per distance 2 bars are shown. 'b.d.' indicates below detection limits, 'n.m.' indicates not measured (modified from Ludvigsen et al., 1999, with permission).

Different parameters influence redox processes. For example, as little as 19 mg/l SO_4^{2-} can inhibit methanogenesis in freshwater sediments (Winfrey and Zeikus, 1977), whereas at the North Bay Landfill (CAN) high SO_4^{2-} levels (300–850 mg/l SO_4^{2-}) did not inhibit CH_4 production (Acton and Barker, 1992). Sulfate reduction in unpolluted aquifers has, on the other hand, been shown to be excluded by Fe reduction, which maintained concentrations of dissolved H_2 (approx. 1.0 nM), formate (approx. 2.0 mM), and acetate (approx. 1 mM) lower than thresholds required by SO_4^{2-} reducing bacteria (Chapelle and Lovley, 1992).

At the Norman Landfill (USA), at a location in the plume with high concentrations of organic matter (325–1100 mg/l DOC) and low concentrations of SO_4^{2-} (0–230 mg/l) methanogenesis dominated over SO_4^{2-} reduction. At another location in the same plume, where organic matter concentrations were lower (80–160 mg/l DOC) and SO_4^{2-} concentrations higher (52–537 mg/l), SO_4^{2-} reduction dominated over methanogenesis (Beeman and Suffita, 1987). Detailed laboratory investigations of this plume showed that the CH_4 production rates from endogenous substrates had an optimum at pH 8 at all temperatures and was severely inhibited at temperatures

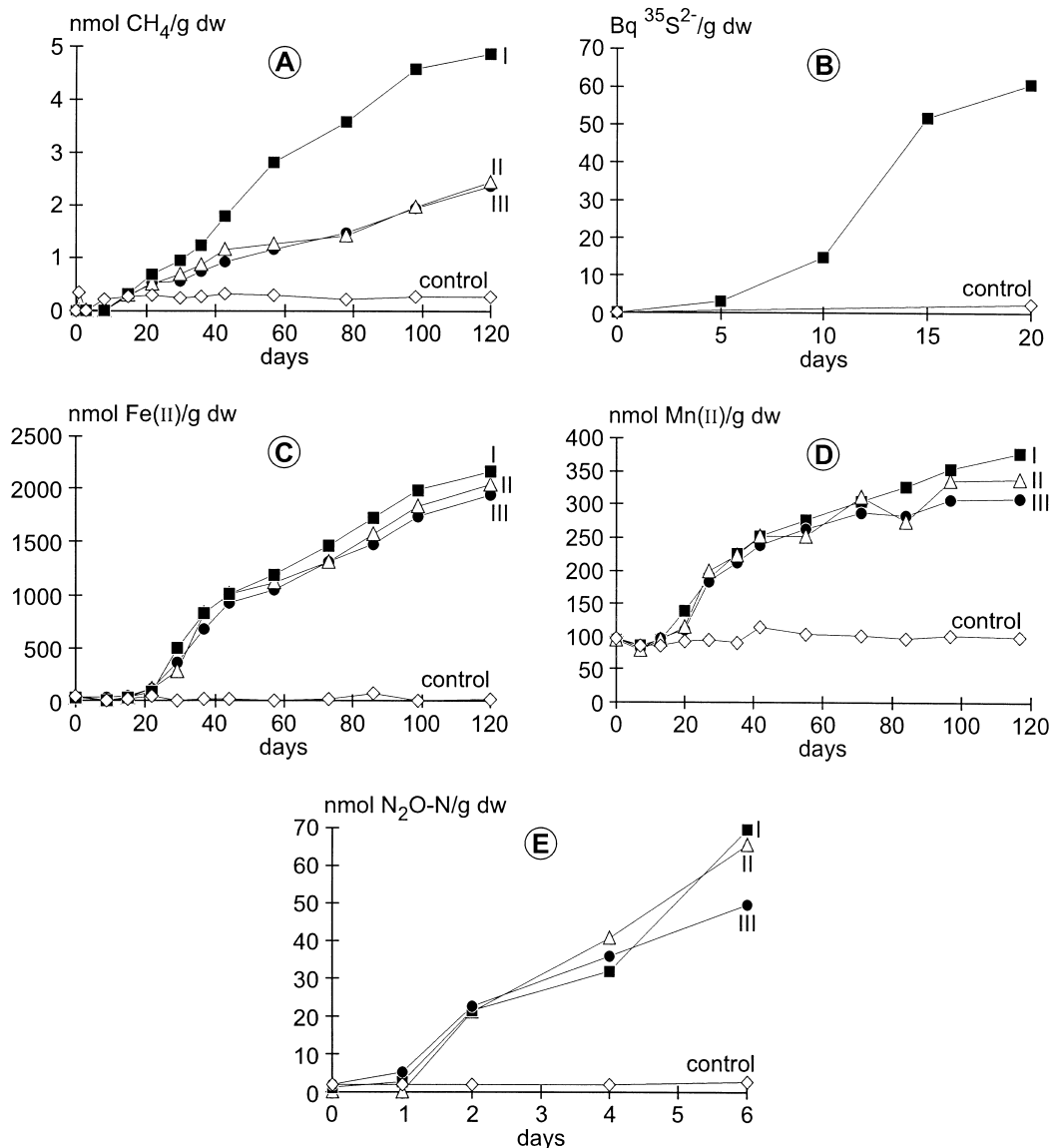


Fig. 5.2. Unamended bioassays showing evidence of each redox reaction at different distances from the Grindsted Landfill (DK): (A) methanogenesis, (B) SO_4^{2-} -reduction, (C) Fe-reduction, (D) Mn-reduction, and (E) Denitrification. Curves I, II and III were biologically active, the controls were inhibited by chemical agents (from Ludvigsen et al., 1998, with permission).

< 13°C or by pH values < 7 (Beeman and Suffita, 1990). In some cases the absence of methanogenesis could not be explained by low pH, low temperature, or the presence of SO_4^{2-} . One explanation might be that different microbial populations at different locations utilized different substrates, since methanol and trimethylamine was utilized by methanogens but not by SO_4^{2-} reducers. The occurrence of different volatile fatty acids differed between the sites, and this may also have influenced the competition between SO_4^{2-} -reduction and CH_4 production. Organic matter present in leachate and leachate contaminated groundwater seemed in a long-term laboratory investigation (several months) to be nearly recalcitrant under methanogenic/ SO_4 reducing, Fe reducing and denitrifying conditions (Albrechtsen et al., 1994).

Controlling factors for microbial Fe-reduction may be the availability of Fe(III) close to the landfill and of the dissolved organic matter furthest away from the landfill. Sediment samples taken from the Fe reducing zone of the Vejen Landfill (DK) plume showed that close to the landfill the potential for Fe-reduction was evident after the samples were enriched with acetate and amorphous Fe(III), whereas very little, if any, Fe-reduction occurred in unamended samples that were stimulated by addition of acetate alone. In the samples collected more distant from the landfill, addition of acetate alone stimulated Fe reduction, but the addition of amorphous Fe(III) alone had no effect. These results are illustrated in Fig. 5.3. This demonstrated that close to the landfill the availability of dissolved organic C has been sufficient for the Fe-reducing bacteria to reduce all of the available Fe(III) in the sediment, but more distant from the landfill the supply and availability of dissolved organic C has been too small to reduce all the Fe(III) in the sediment (Albrechtsen et al., 1995).

It is also important to be aware of the natural variation in a leachate plume. Even within a short horizontal distance of 1.8 m Adrian et al. (1994) observed variations in CH_4 production rates from 40 to 10 500 $\mu\text{mol CH}_4/\text{m}^2/\text{day}$ (Fig. 5.4) in the Norman Landfill (USA) plume, but found no explanation for this variation. Part of the variation could be caused by heterogeneities in the geological settings as observed at the Grindsted Landfill (DK) (Ludvigsen et al., 1998), where samples collected from layers with silt and clay showed SO_4^{2-} and Fe-reduction rates that probably were independent of the leachate pollution. If only few samples are investigated to characterize the redox conditions of a plume, such local geological heterogeneities may prevent a correct and coherent identification of the redox zones in the leachate plume.

Although not yet studied and understood in detail, bacteria abundance and bacterial activity observed in leachate plumes support the proposed processes creating different redox zones in the plume and confirm that the

processes are microbially mediated. Some of these processes occur simultaneously in the same sample. Other metabolic pathways might be possible and at least one metabolic activity — fermentation — which could be important in the context of landfill leachate, is poorly investigated in landfill leachate plumes.

5.3. Conclusion: microbiology

Significant numbers of bacteria, detected with several different approaches, are present in landfill leachate plumes. Methanogens, SO_4^{2-} -reducers, Fe-reducers, Mn-reducers and denitrifiers are believed to be widespread in leachate plumes. In the Grindsted Landfill plume redox-specific bacteria were identified also outside the zones of the dominant redox process, suggesting that the presence of bacteria is not a limiting factor in old leachate plumes.

Microbial activity seems to occur throughout leachate plumes although the actual rates (as measured by ATP, PLFA, and redox processes) are fairly modest. Several redox processes can take place in the same samples adding additional diversity to the concept of redox zones. The microbial measurements at the Grindsted Landfill (DK) plume support the overall redox gradient away from the landfill, but have also identified concomitant redox processes and substantial local variability. It has been demonstrated how the availability of Fe oxides and dissolved organic C may change through the Fe reducing zone. This emphasizes the fact that our understanding of the parameters controlling these redox processes (C-source, competition, inhibition, availability of the electron acceptor, etc.) is still rudimentary.

6. Dissolved organic matter

Attenuation of dissolved organic matter (e.g. expressed as Total Organic C, Dissolved Organic C, Non-Volatile Organic C or Chemical O_2 Demand) in the leachate plume, besides dilution, is caused by sorption and degradation.

6.1. Sorption

Sorption of leachate organic matter onto aquifer material seems to be only of minor significance based on column experiments that showed relative solute velocities of 0.7–1.0 for COD of acid phase as well as of CH_4 phase leachate (Hoeks et al., 1979; Farquhar and Sykes, 1982; Kjeldsen and Christensen, 1984; Kjeldsen, 1986). The generally low sorption observed means that the dissolved organic C in the leachate practically moves with the water or is just slightly retarded. Thus, sorption cannot be viewed as a significant attenuation mechanism for DOC in aquifers. However, no field observations are available on the retardation of organic matter.

Kjeldsen (1986) observed two acid subsoils, where methanogenic leachate caused a substantial rise in the pH of the soil columns, that for a short time period the soils released COD, increasing the solute COD to levels

substantially above the COD content of the leachate. The significance of this additional, dissolved organic matter is not known, but apparently this has been observed only under dramatic pH changes, and will

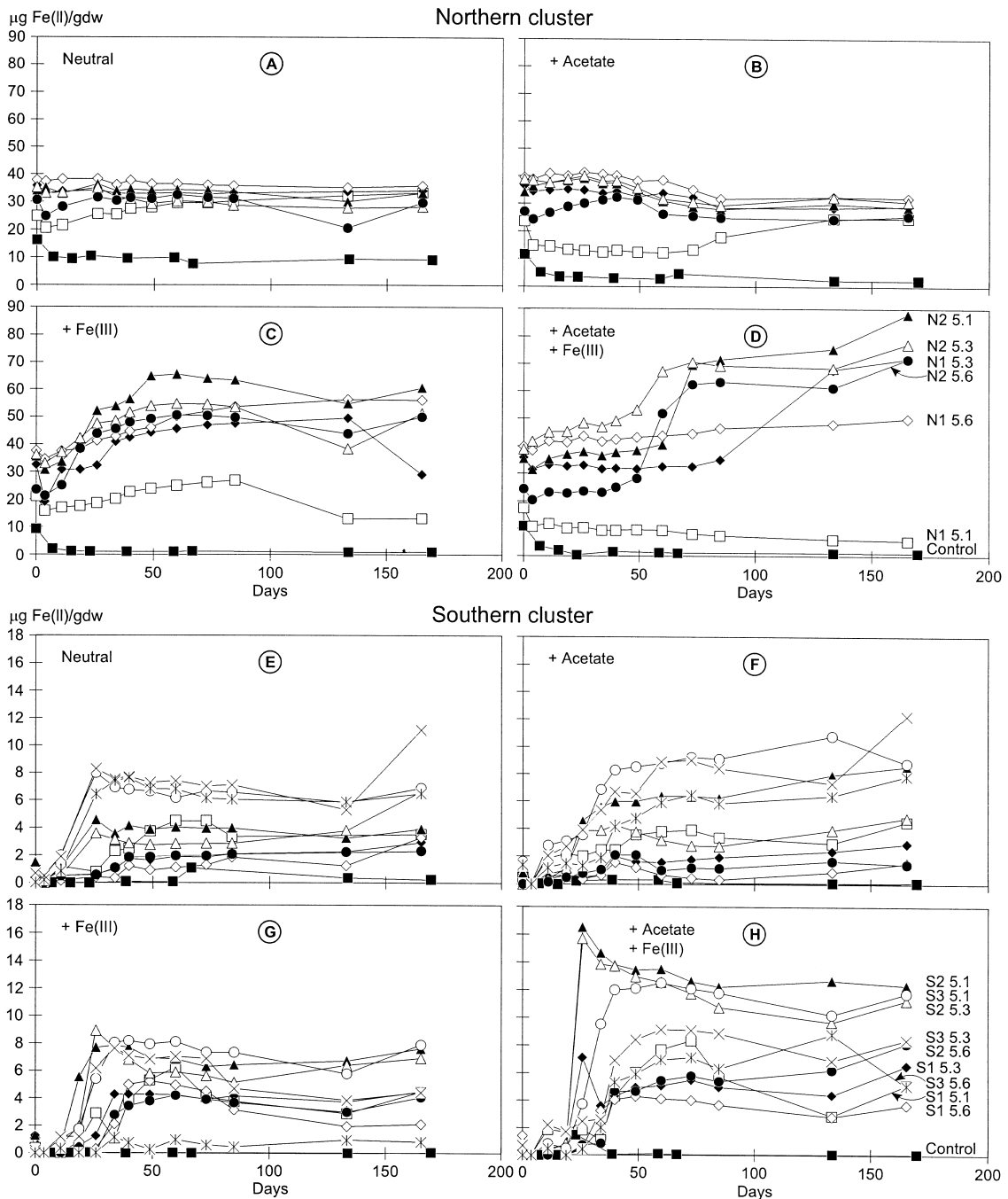


Fig. 5.3. Unamended (neutral) and amended (+ acetate, + Fe(III)) bioassays with sediment from the Fe reducing zone of the Vejen Landfill (DK) plume illustrating limiting availability of Fe and dissolved organic matter. The Northern cluster (Samples marked N1-2 and the sampling depth) is closest to the landfill and the Southern cluster (Samples marked S1-3 and the sampling depth) is furthest away from the landfill (from Albrechtsen et al., 1995, with permission).

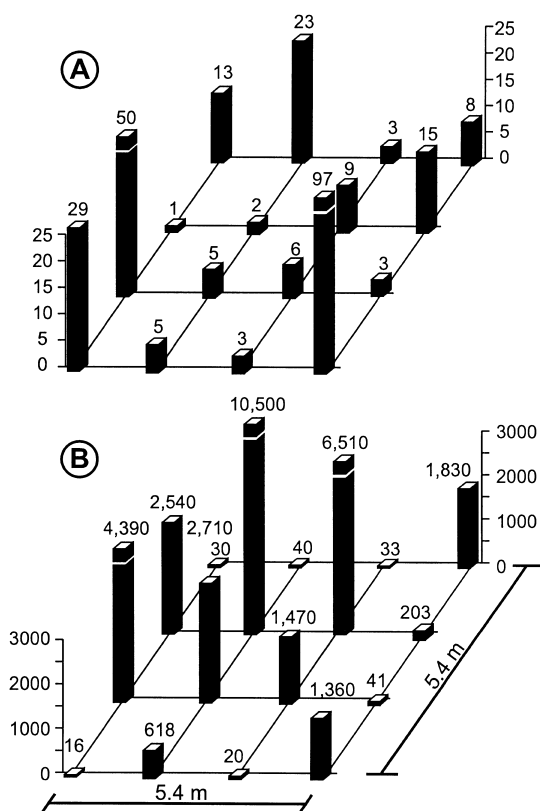


Fig. 5.4. Spatial plot demonstrating extreme variability of the CH₄ production rates for two locations in the Norman Landfill (USA) plume. The columns represent the mean CH₄ production rate observed during the study period with the actual rate above each column. The horizontal distance between the boreholes were 1.8 m and the CH₄ rate is reported in µmoles CH₄/m²/day (from Adrian et al., 1994, with permission).

likely only apply to the first entrance of high-pH leachate into an aquifer.

6.2. Degradation

Degradation of leachate organic matter has been studied in several column studies, where leachate has been loaded under anoxic conditions onto soil columns.

For acid phase leachate, Table 6.1 lists reported experimental results in terms of half-life values in days assuming a steady state first order kinetic reaction. The reported results show substantial degradation of leachate COD for the acid phase leachate. Half-life values range from 5–10 days (20°C) to 30–100 days (10°C). The reported column studies confirm that volatile fatty acids dominating the COD content of acid phase leachate are relatively easily converted under anaerobic conditions. Hoeks and Borst (1982) observed a total breakdown of volatile fatty acids in leachates (740–6470 mg/l of acetic

acid equivalents) loaded to sandy loam columns with retention times of 18–40 days. Investigations into the behavior of the different fatty acids demonstrated the conversion patterns of fatty acids: larger fatty acids are converted to smaller ones by sequential removal of fragments of two C-atoms from the acids until only acetic acid remains. For example, an increase in acetic acid concentration was caused by a decrease in butyric acid concentration (one butyric acid molecule is converted to two acetic acid molecules). Only when the original acid has an odd number of C-atoms the final fragment is propionic acid. Finally, propionic acid is converted to acetic acid.

For methanogenic leachate the reports on degradation of dissolved organic matter are few and negative. Hoeks et al. (1984) found no measurable COD degradation during experimental retention times of 19–25 days and Kjeldsen (1986) found no degradation for retention times up to 240 days, except what could be attributed to volatile fatty acids making up a small part of the methanogenic leachate. Albrechtsen et al. (1994) took groundwater from different redox environments in the Vejen Landfill (DK) leachate plume and added the groundwater to reactors with sediment representing environments of slightly higher redox status in order to evaluate the substrate value of the organic matter in the plume. During a 150-day period only minor increases in microbial populations were observed, suggesting that the organic matter in the leachate plume was very poorly degradable.

In general, the redox conditions have not been adequately described in many of the laboratory experiments, probably because transient conditions have been dominating upon loading of strongly reduced leachate onto aerobic soil columns. Because the time frame usually is very limited for such experiments (e.g. corresponding to 10 pore volumes or maybe 200 days) adequate time may not have been available for stable environments to develop. However, the experiments do indicate that methanogenic leachate COD is not readily degraded under anaerobic conditions in unadapted environments.

6.3. Field evidence

The distribution of dissolved organic matter measured as non-volatile organic C along a vertical transect stretching downgradient from the Grindsted Landfill (DK) was measured by Rügge et al. (1995) as shown in Fig. 4.3. Close to the landfill the NVOC content was nearly 100 mg/l, but it decreased to less than 5 mg C/l within a distance of 150 m from the landfill. In the lower part of the plume the pore flow velocity was of the order of 10 m/a suggesting retention times of 15 a in the lower part of the aquifer. This suggests a half-life of the order of a few years. The NVOC plume was found in redox

Table 6.1

Experimental results of COD degradation in acid landfill leachate reported in the literature

Material	Hydraulic retention time (days)	Inlet COD (mg/l)	Relative outlet concentration	Temperature (°C)	$T_{1/2}$ (days)	Reference
Sand	23	29 600	0.92	20	190	a
Sandy soil	17	6640	0.08	20	4.6	a ^a
Sandy soil	40	6640	0.04	20	8.7	a
Sandy soil	20	7750	0.01	20	5.3	a
Sandy soil	9.3	5700	0.14	?	3.3	b
Sandy soil	7.7	7400	0.91	10	60	c
Sandy soil	7.4	7400	0.95	10	100	c
Loamy sand	7.3	7400	0.87	10	36	c
Loamy sand	9.6	7400	0.78	10	27	c

^a (a) Hoeks et al. (1979), (b) Soyupak (1979), (c) Kjeldsen and Christensen (1984).

environments ranging from methanogenic (close to the landfill) to Mn-reducing and maybe NO_3^- -reducing conditions. The influence of dilution was difficult to account for in the Grindsted Landfill leachate plume because Cl^- from road de-icing also entered the groundwater.

Fig. 6.1 shows a plot of dissolved organic C in the Vejen Landfill (DK) leachate plume as a function of distance from the landfill (Lyngkilde and Christensen, 1992a). The NVOC concentrations are corrected for dilution according to Cl^- concentration in samples and in unpolluted groundwater. The decreasing curve indicates a strong degradation of organic matter in the plume; the majority of the dissolved organic C is degraded within the first 100 m of the plume (retention time on the order of half 0.5 suggesting a half-life on the order of 1 a) and at a distance of 300 m the organic C concentration just slightly exceeds the background value which is of the order of 2 mg C/l. Some of the degradation took place in the methanogenic/ SO_4^{2-} -reducing zone, but the major degradation of NVOC was under Fe-reducing conditions. The interpretation of Fig. 6.1 assumes that the organic matter does not significantly sorb onto the aquifer material and that the organic matter to Cl^- ratio has been constant in the infiltrating leachate during the period in question. The first assumption seems acceptable, according to the previous discussion on sorption, while the second assumption is more questionable (cf. Barker et al., 1986). However, if the focus is on methanogenic leachate and the aim is to observe degradation on an “order of magnitude level”, comparison of organic matter concentration and Cl^- concentration seems reasonable.

Only a few other reports exist on the fate of dissolved organic matter in leachate plumes. DeWalle and Chian (1981) found at the Army Creek Landfill (USA) that in a plume stretching about 700 m with regard to Cl^- , the majority of dissolved C (as COD) was degraded within the first few hundred m from the landfill. This was sup-

ported by observations by Baedecker and Apgar (1984) who showed that DOC in the plume had decreased in the period from 1977 to 1981. Barker et al. (1986) found that the North Bay Landfill (CAN) had contaminated the groundwater throughout the 700 m flow system from the landfill to a discharge zone at a creek. The plume was anaerobic showing elevated concentrations of dissolved organic matter as far as 500–600 m down-gradient of the landfill. DOC concentrations corrected for dispersion by the Cl^- values showed no substantial degradation of the bulk DOC. However, significant changes in organic matter composition along the flow

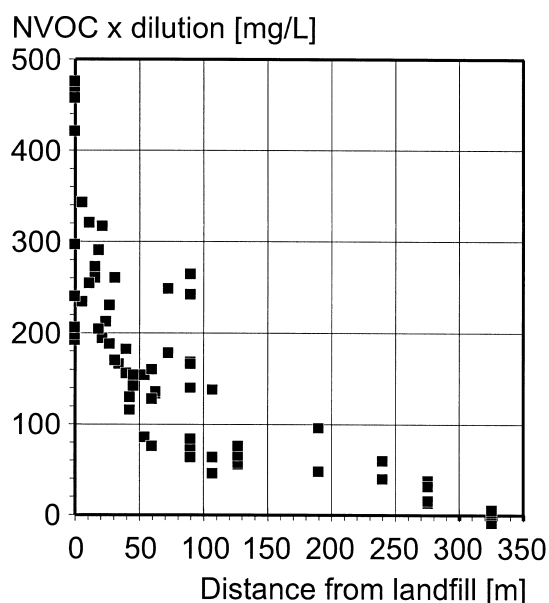


Fig. 6.1. Concentration of dissolved organic matter (Non-Volatile Organic Carbon, NVOC) in the Vejen Landfill (DK) plume as a function of distance from the landfill. Concentrations are corrected for dilution according to Cl^- content (from Lyngkilde and Christensen, 1992a, with permission).

path indicated transformation of organic matter in the plume (Barker et al., 1986).

Several other investigations of leachate plumes have identified dissolved organic matter at substantial distances from landfills (several hundred meters). In some of these investigations, attenuation, besides dilution, has been observed [e.g. Woolwich Landfill (CAN) by Reinhard et al., 1984, Islip and Babylon Landfills (USA) by Kimmel and Braids, 1980 and Kohl Spring Landfill (USA) by Murray et al., 1981]. However, in these cases the data are too scarce or complicated to distinguish the attenuation mechanisms involved.

The attenuation of dissolved CH_4 in leachate polluted groundwater constitutes a unique case, because CH_4 is highly volatile and therefore may escape to the unsaturated zone above the plume. Barber et al. (1990) observed release of CH_4 from leachate polluted groundwater to the unsaturated zone. The release of CH_4 may be so significant that determination of CH_4 in the soil gas can be used for delineation of plumes, but no information is available evaluating this volatilization loss relative to the CH_4 content of the plume. CH_4 may also be microbially oxidized, but the documentation of the significance of such processes in leachate plumes is lacking. Kjeldsen et al (1995) measured CO_2 but found no CH_4 in the shallow unsaturated zone above the leachate plume at the Grindsted Landfill (DK), suggesting that oxidation converts most of the CH_4 that volatilizes from this plume.

6.4. Conclusion: dissolved organic matter

Volatile fatty acids constituting a substantial fraction of the dissolved organic C in acid phase leachate are easily degraded according to reported laboratory studies. The dissolved organic matter dominating the methanogenic leachate does not sorb to any substantial degree onto aquifer material and seems fairly recalcitrant with respect to microbial degradation as seen in laboratory experiments. However, with respect to degradation of rather recalcitrant organic matter, laboratory experiments with short retention times, most likely unstable redox conditions and limited time for microbial adaptation may fail to simulate the conditions in a leachate polluted aquifer. Observations of actual leachate plumes are usually too limited to provide insight into the fate of the dissolved organic matter. One exception is the report by Lyngkilde and Christensen (1992a) demonstrating substantial degradation of dissolved organic matter in the anaerobic part of an old leachate plume. The observations by DeWalle and Chian (1981) and Rügge et al. (1995) may support this, indicating that dissolved organic matter in methanogenic leachate is degradable to a large extent although not very easily. Preliminary estimates of half-life suggest 1–3 a for DOC in anaerobic leachate plumes.

7. Inorganic macrocomponents

The term macrocomponents refers here to inorganic constituents present at elevated concentrations (several mg per liter in leachate and contaminated groundwater) and includes the anions, Cl^- , HCO_3^- and SO_4^{2-} , and the cations, Ca^{2+} , Mg^{2+} , K^+ , Na^+ , NH_4^+ , Fe and Mn. Aluminum is a significant cation only at very low pH-values ($< \text{pH } 5$, Appelo and Postma, 1996) and will not be further addressed in this context.

These inorganic macrocomponents usually do not constitute a severe groundwater pollution problem. However, drinking water quality standards usually include most of these macrocomponents, and their concentrations in leachate often exceed the standards significantly. In addition, some of these components are important in controlling redox environments and attenuation of heavy metals. Ammonium may constitute a separate problem since it is a nutrient that is toxic to fish and expected to be present in high concentrations in leachates ($> 100 \text{ mg/l}$) for decades.

Besides being diluted, the macrocomponents may be attenuated by redox processes, ion exchange and precipitation. In the heavily contaminated part of the pollution plume, complexation may also occur decreasing the attenuation by increasing component solubility and mobility. Component concentrations may also increase by dissolution of solids present naturally in the aquifer. The most likely processes of importance for the behavior of macrocomponents in leachate plumes are summarized in Table 7.1.

7.1. Anions

Chloride is not considered to undergo any chemical or physico-chemical reactions in the aquifers and as such is considered inert or conservative. For this reason, Cl^- was used in the previous discussion on dispersion.

Bicarbonate (alkalinity) and CO_2 pressure are usually high in leachates due to the decomposition and dissolution processes in the landfill (see e.g. Christensen and Kjeldsen, 1989). The importance of HCO_3^- and CO_3^{2-} in the plume is to form complexes with Ca, Mg, Na, Fe and Mn and to form precipitates with Ca, Mg, Fe, Mn and maybe some heavy metals. The significance of these processes depends on the concentrations of the species and pH. An important aspect of the HCO_3^- is the buffering of pH in the landfill leachate plume. In the methanogenic phase of landfill stabilization, which is by far the longest and most important phase, the leachate often has a pH around or slightly above neutral. As a consequence of this, leachate plumes usually have increased alkalinity compared to the uncontaminated groundwater. If the aquifer is acidic, the leachate alkalinity will act as a buffer, increasing pH in the center of the plume (Lyngkilde and Christensen, 1992b; Bjerg et

al., 1995), and if the aquifer is neutral and contains carbonate minerals, for example calcite, the carbonates will be dissolved upon exposure to leachate CO_2 resulting in increased dissolved alkalinity, Ca and Mg (Kehew and Passero, 1990). Several of the terminal electron accepting processes, in particular reduction of sediment-associated Fe oxides, also produce alkalinity. This implies that the high alkalinity often observed in leachate plumes is due to the alkalinity of the leachate, the dissolution of calcite by the CO_2 in the leachate and the alkalinity produced by the reductive dissolution of primarily Fe oxides. The determination of alkalinity in landfill leachate can be affected by volatile fatty acids (anions), since the volatile fatty acids will accept protons during titration (Baedecker and Back, 1979a; Kehew and Passero, 1990). This means, unless great care is taken, that alkalinity values can be dubious for determination of inorganic C needed for speciation calculations. In the absence of volatile fatty acids, alkalinity in the leachate plume is practically equivalent to HCO_3^- .

Sulfate has been detected at elevated concentrations in landfill leachate plumes (e.g. Kimmel and Braids, 1980; Murray et al., 1981; Nicholson et al., 1983; Robinson and Lucas, 1985), but low concentrations as reported by Baedecker and Back (1979a,b) and Barker et al. (1986) supposedly are more common in leachate plumes. Presumably, SO_4^{2-} will be reduced to S^{2-} in an active, methanogenic landfill or in the methanogenic and SO_4^{2-} reducing zone in the leachate plume as demonstrated in the field (Murray et al., 1981; Robinson and Lucas, 1985) and in laboratory soil columns (Hoeks et al., 1979, 1984; Loch et al., 1981; Bisdorf et al., 1983). However, as discussed by Kimmel and Braids (1980), Nicholson et al. (1983) and Beeman and Suffita (1987), landfill cells rich in demolition waste or ashes may release leachate with high SO_4^{2-} concentrations. This has

also been observed at the Grindsted landfill site, where very high concentrations of SO_4^{2-} have been found in the leachate in some areas supposedly due to disposal of plaster boards (gypsum, CaSO_4) in the landfill (Kjeldsen et al., 1998a). After mixing beneath the landfill, SO_4^{2-} may be detectable in the plume, or if the mixing is modest a very uneven distribution of SO_4^{2-} may be observed (Bjerg et al., 1995).

The S buffer system consists of S^{2-} , HS^- , and H_2S , where HS^- and H_2S are the dominant species at neutral pH values. Usually sulfide measurements are given as total dissolved sulfide, which should be taken into account when the results are evaluated. Sulfide generated in areas with free metal ions (e.g. ferro ion or heavy metals) will possibly lead to precipitation of sulfides as FeS or FeS_2 . These reactions accumulate black precipitates and lower dissolved S^{2-} concentrations in the leachate and the plume. Precipitation of mono S has been indicated by calculations of saturation indices (Kimmel and Braids, 1980; Nicholson et al., 1983; Kehew and Passero, 1990; Bjerg et al., 1995). Significant precipitates of pyrite have been observed on aquifer sediments from the anaerobic part of the Vejen Landfill (DK) leachate plume (Heron and Christensen, 1995).

Sulfate has in some cases (Kimmel and Braids, 1980; Nicholson et al., 1983; Bjerg et al., 1995) been shown to persist in leachate plumes at elevated concentrations. The persistence of SO_4^{2-} in the reduced environments might be due to slow kinetics of SO_4^{2-} reduction, allowing the SO_4^{2-} to migrate into zones of higher redox potentials where SO_4^{2-} reduction may be unfavorable. This is most likely in plumes with substantial redox buffering by Fe oxides limiting the extent of the more reduced environments in the plume.

Anion exchange sites on the aquifer material are few (much less exchange sites for anions than for cations)

Table 7.1

Summary of processes affecting macrocomponent behaviour in leachate plumes (+: important, (+): usually of minor importance, -: not important)

Process	Anions			Cations						
	Cl^-	$\text{HCO}_3^-/\text{CO}_3^{2-}$	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+	Fe^a	Mn^a
Dilution	+	+	+	+	+	+	+	+		+
Complexation ^b	- ^c	+	(+)	+	+	- ^d	- ^d	-	(+)	(+)
Redox processes	-	-	+	-	-	-	-	(+) ^e	+	+
Ion exchange	-	-	(+) ^f	+	+	+	+	+	+	+
Precipitation/dissolution	+	+	- ^g	+	+	-	-	-	+	+

^a Fe as Fe^{2+} or Fe^{3+} , Mn as Mn^{2+} or Mn^{4+} .

^b Complexation is not an attenuation process, since complexation results in increased solubility and mobility.

^c Chloride does form many dissolved complexes, primarily with heavy metals and Ca^{2+} and Mg^{2+} , but usually only a small part of the total Cl^- concentrations is complexed.

^d Complexes of Na^+ and K^+ are usually not important but may appear in the leachate.

^e Ammonium may be oxidized under aerobic and maybe also anaerobic (mechanism not identified) conditions.

^f Anion exchange is usually of only minor importance.

^g Usually not very likely.

but may contain small amounts of SO_4^{2-} (Wood, 1978). Exposure of aquifer sediment to leachate rich in other anions (primarily Cl^- and HCO_3^-) may, in addition to decreasing the anion exchange capacity by increasing pH and reducing oxide contents of the solids, expel SO_4^{2-} from the anion exchange sites. Release of SO_4^{2-} from aquifer material has been observed in laboratory column studies by Kjeldsen (1986). Expulsion of SO_4^{2-} is believed to be important only at the front of the plume.

7.2. Cations

The behavior of cations in leachate plumes are governed by dilution, cation exchange and precipitation/dissolution processes (Table 7.1). In addition, NH_4 , Fe and Mn may be subject to redox processes as discussed in separate sections.

Cation exchange processes are often neglected with reference to the low cation exchange capacity of aquifer materials, however, as shown later in the case of the Vejen Landfill (DK) leachate plume, the attenuation of cations may still be substantial (Fig. 7.1). Aquifer material usually has a cation exchange capacity (CEC) of the order of 0.2–5 m-equiv per 100 g (Reardon et al., 1983; Leuchs, 1985; Dahmke et al., 1986; Bjerg and Christensen, 1993; Christiansen et al., 1998; Heron et al., 1998), which is low compared to top soils and sediments with higher contents of clay and organic matter. However, the exchange capacity is still very significant: In pristine aquifers, cations associated with the exchange sites typically make up 80% of the total amount of cations per volume of aquifer, while in the central part of a leachate plume the corresponding value is of the order of 40% [Calculations made for the Borden Landfill (CAN) aquifer on the basis of data published by Nicholson et al., 1983].

Several equations exist describing cation exchange, usually employing a selectivity coefficient expressing the relative affinity of the two cations in question for the exchange sites. The common cation exchange equations (see e.g. Harmsen, 1979) show that the retardation of a cation by exchange onto sediment is related not only to the selectivity coefficients but also to the actual concentrations of the cations in the solute, to the relative ratio of the cations competing for exchange sites and to the CEC. Thus, relative migration velocities estimated from soil column studies can be used for general ranking of the cation migration, but is valid only for that specific combination of leachate and aquifer material. In a full scale plume, the apparent retardation of a cation due to ion exchange will be more significant in the dilute part of the plume than in the concentrated part of the plume (Bjerg and Christensen, 1993).

The term cation exchange implies that when a cation associates with an exchange site another cation is being expelled. In many aquifers, the cation exchange sites are

dominated by Ca, Mg and, at low pH, by protons. In saline soils, Na will dominate. Upon exposure to leachate, having a higher ionic strength and different relative cationic composition than the natural groundwater, extensive exchange reactions will take place. In a leachate plume several cations will be present at the same time, having different affinities for the exchange sites and in different concentrations. This creates a complex system of traveling fronts and peaks in the plume as the plume composition changes due to ion exchange. Fig. 7.2 shows effluent breakthrough curves for several cations in laboratory soil columns exposed to leachate (Kjeldsen and Christensen, 1984). The saturating cation (Ca) was expelled and moved with the leachate front in concentrations in excess of the leachate concentrations. This is often referred to as the “Hardness Halo” and has often been reported in the literature (e.g. Anderson and Dornbush, 1967; Campbell et al., 1983; Nicholson et al., 1983; Kehew et al., 1984). Only a few extensive field studies have mapped the distribution of cations in a leachate plume (Nicholson et al., 1983; Bjerg et al., 1995). Fig. 7.1 presents the Vejen Landfill (DK) plume concentration contours for Cl^- (as a reference), K, NH_4 , Na and Fe (to be discussed later).

Potassium, K^+ has a high affinity for ion exchange and will typically be the most retarded of the cations in the leachate plume as clearly seen in Fig. 7.1. Absorption into crystal lattices of e.g. illite and vermiculite may constitute an additional attenuation mechanism (Bolt and Bruggenwert, 1976).

Sodium, Na^+ is considered to have the least affinity of the relevant cations for ion exchange and will only be slightly retarded in the plume (Fig. 7.1). This is confirmed by Kimmel and Braids (1980), who showed a linear relationship between Cl^- concentrations and Na concentrations in water samples obtained in a leachate plume at different distances from a landfill.

Calcium, Ca^{2+} has a high affinity for exchange sites, but since Ca typically is the dominating base saturating ion, Ca will often move with the leachate front. Attenuation may take place behind the front depending on the selectivity coefficients and plume composition. Ca may also be heavily involved in complex formation (e.g. with HCO_3^+ and DOC) and in dissolution/precipitation reactions e.g. involving calcite (CaCO_3) and maybe siderite (FeCO_3). The precipitation and dissolution processes are closely linked to the dissolved carbonate compounds. It should be mentioned that supersaturation with respect to calcite has been reported (Nicholson et al., 1983; Kehew and Passero, 1990; Bjerg et al., 1995) and calcite has also been detected on aquifer material from leachate plumes (Heron and Christensen, 1995; Heron et al., 1998).

Magnesium, Mg^{2+} resembles in many ways Ca, although its affinity for ion exchange, occurrence as base saturation ion and likelihood for forming precipitates is slightly less than for Ca.

Proton, H^+ , expressed through pH, is involved in many reactions, but mentioned here because of its high affinity for ion exchange sites at low to moderate pH. This is often an overlooked aspect and very little data are available describing proton exchange onto

aquifer material. Models (Appelo, 1994) have included protons in the description of ion exchange in pristine aquifers. However, no attempts have been made yet with respect to landfill leachate plumes, making prediction of cation transport involving pH changes, as

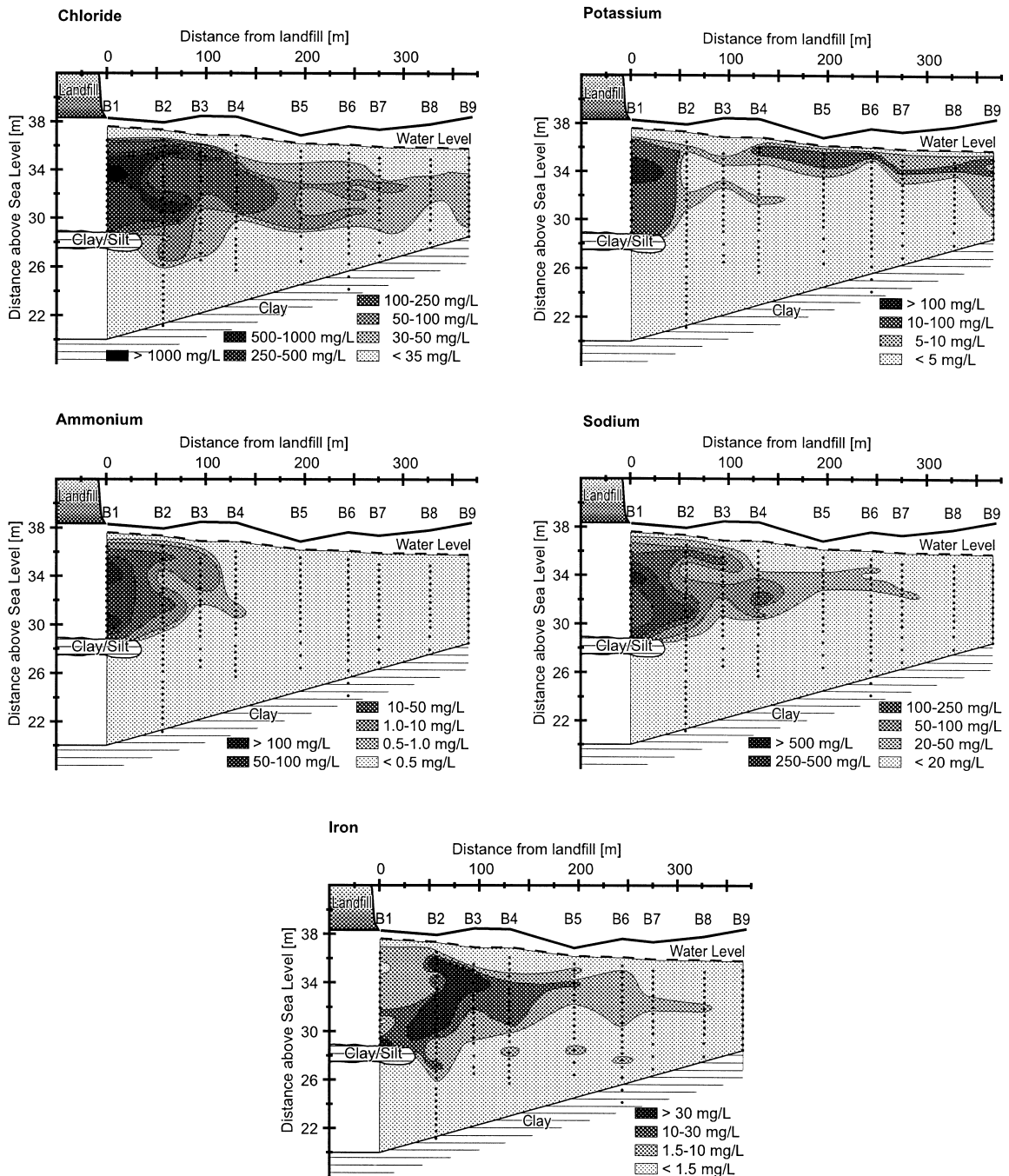


Fig. 7.1. Distribution of selected macro-ions in the Vejen Landfill (DK) leachate plume: Cl^- , K, NH_4 , Na and Fe. Partly based on data from Lyngkilde and Christensen (1992a).

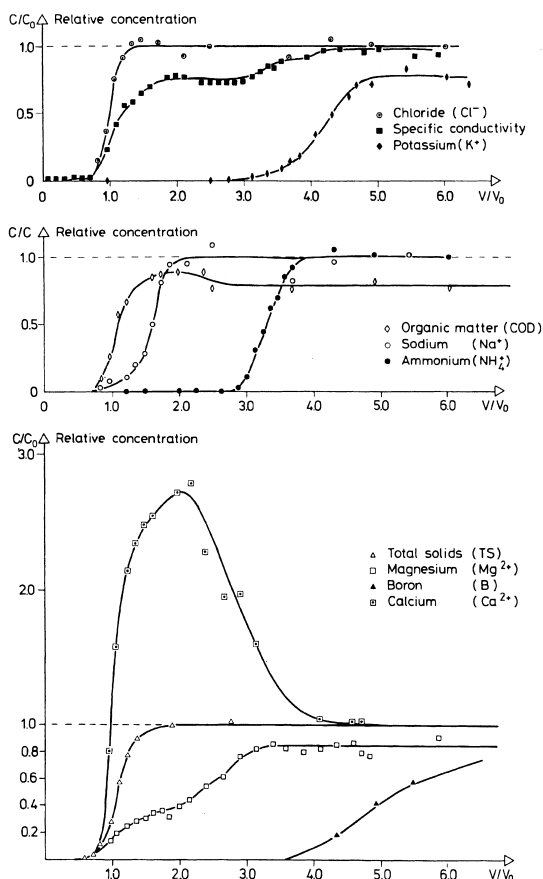


Fig. 7.2. Solute breakthrough curves (C/C_0) illustrating macro-ion migration in a sandy soil column exposed to landfill leachate. V/V_0 expresses the number of pore volumes of leachate that has passed the column (from Kjeldsen and Christensen, 1984, with permission).

they often appear in the outskirts of leachate plumes, a difficult task.

7.3. Ammonium

Ammonium, NH_4^+ , deserves special attention since it is a major reducing agent in landfill leachates, probably constitutes a critical long term pollutant, is an important nutrient in surface water and water supplies and furthermore potentially participates in complex redox reactions.

Ammonium exhibits a high affinity for ion exchange and will be retarded in leachate plumes, as observed in the Vejen Landfill (DK) leachate plume (Fig. 7.1). Ammonium may also partly become incorporated into crystal lattices of clay minerals. Dissociation of NH_4^+ to free ammonia ($\text{NH}_4^+ \rightarrow \text{NH}_3 + \text{H}^+$) is not very likely in aquifers ($\text{p}K_a = 9.3$, Stumm and Morgan, 1996).

Kimmel and Braids (1980) suggested that NH_4 , when migrating into aerobic zones, would be oxidized resulting in elevated NO_3^- concentrations. However, no clear field evidence was presented. Detailed mapping of NH_4 , N_2O and NO_3^- in the Grindsted Landfill (DK) leachate plume showed that NH_4 was strongly attenuated, not only by ion exchange but apparently also by anaerobic oxidation. Nitrate and also N_2O were found in zones convoluting the NH_4 plume, as shown in Fig. 7.3, but were present in only very low concentrations further away from the landfill. The disappearance of NH_4 coincided with increased Mn concentrations in the plume, but the processes involved are not understood (Ludvigsen et al., 1998). With respect to long term aspects of leachate attenuation, understanding attenuation of NH_4 may become crucial and should be further researched.

7.4. Fe and Mn

Fe and Mn are treated separately because they, in contrast to the alkali and alkali earth cations, are subject to redox processes. Reduction of solid Fe and Mn oxides may lead to a substantial input of reduced Fe and Mn to the groundwater, creating Fe and Mn rich areas (see e.g. Fig. 4.2, 4.3 and 7.1). Fe and Mn concentrations in the aquifer are governed by dilution, redox processes, abiotic dissolution of sediment minerals, ion exchange, precipitation and maybe complexation with dissolved organic C.

In aerobic aquifers, Fe and Mn are associated with the sediment as solid oxides and hydroxides (in the oxidized state Fe(III) and Mn(IV)) and in clay minerals. As shown in the section on redox processes, Fe may be the dominant redox buffer in aerobic aquifers, when it is reduced to the more soluble Fe(II) state. Elevated concentrations of dissolved Fe and Mn not originating from the landfill have been demonstrated for the plumes at the Borden Landfill (CAN) (Nicholson et al., 1983), the Vejen Landfill (DK) (Lyngkilde and Christensen, 1992b; Albrechtsen and Christensen, 1994) and the Grindsted Landfill (DK) (Fig. 4.3; Bjerg et al., 1995). These elevated concentrations of Fe and Mn originate from the sediment as discussed in Section 4 (Redox Environments and Processes).

Several other phenomena are responsible for Fe^{2+} and Mn^{2+} input to leachate plumes. Landfill leachate typically contains high (100 mg/l range) levels of Fe, derived from weathering of the waste. This results in elevated concentrations close to the landfill (Kimmel and Braids, 1974, 1980; Baedecker and Back, 1979a; Cherry, 1983; Nicholson et al., 1983; Barker et al., 1986; Kehew and Passero, 1990; Bjerg et al., 1995). Dissolved Fe and Mn are especially high in leachate during the acid phase and moderate in the methanogenic phase (Table 2.2). Abiotic dissolution of solid minerals also leads to Fe input to the plume. Presumably, abiotic dis-

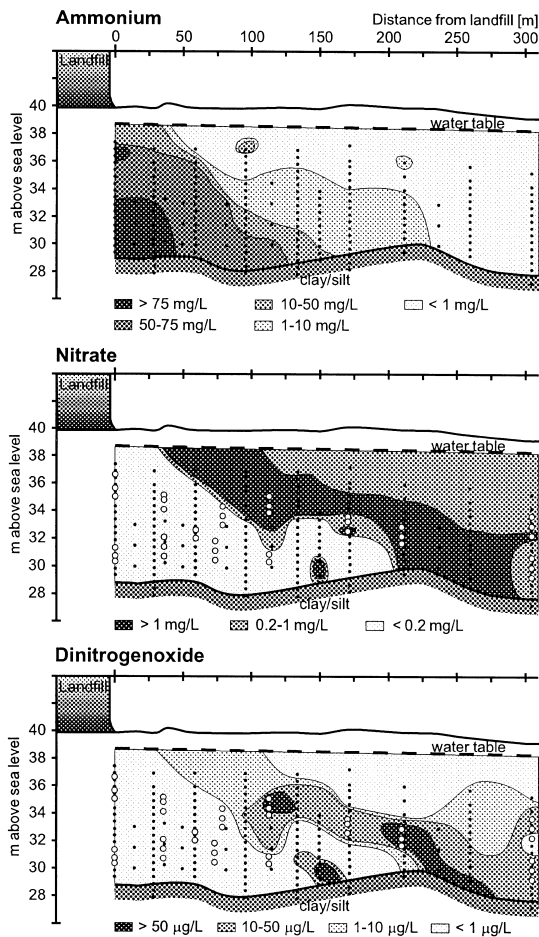


Fig. 7.3. Distribution of NH_4 , NO_3^- and N_2O in the Grindsted Landfill (DK) leachate plume (from Christensen et al., 2000b, with permission).

solution is caused by acetate, oxalate, aromatics, catechols and chelators present in the leachate (Cartwright et al., 1977). However, pH buffering reactions (dissolution of carbonate minerals due to CO_2 in the leachate) may also lead to dissolution of e.g. Fe containing carbonates (siderite, dolomite).

Once reduced and solubilized, Fe(II) and Mn(II) are attenuated by precipitation, ion exchange, and dilution.

Fe(II) and Mn(II) removal by precipitation has been demonstrated by direct identification of the minerals (Heron et al., 1994b, 1998), and indirectly by mineral saturation-index calculations. Field studies have shown supersaturation with respect to iron sulfide, FeS (Kimmel and Braids, 1980; Nicholson et al., 1983; Kehew and Passero, 1990; Bjerg et al., 1995) and siderite, FeCO_3 (Cherry, 1983; Nicholson et al., 1983; Barker et al., 1986; Bjerg et al., 1995). Siderite precipitation may especially be important in Fe reducing zones, as evidenced by solid phase extraction and scanning electron

microscopy of sediments from reduced plumes (Heron and Christensen, 1995; Heron et al., 1994b, 1998). If dissolved Fe migrates to oxidized parts of the plume, precipitation of ferrihydrite, $\text{Fe}(\text{OH})_3$, may take place as indicated by supersaturation at the plume front (Nicholson et al., 1983), and shown by an increased Fe(III) content on the aquifer solids downgradient from the Fe reducing zone (Heron and Christensen, 1995). As discussed in the section on redox processes, this Fe cycling may dominate the development of reducing zones and partly control the overall size of the plume.

The ion exchange properties of Fe and Mn are expected to be similar to Ca considering their valencies and hydrated ion radii. Significant amounts of Fe (up to 30% of the CEC) have been detected on the cation exchange complex in the anaerobic part of the Vejen Landfill (DK) leachate plume (Unpublished data; Heron and Christensen, 1995). Therefore the distribution of Fe and Mn should be seen in the context of the other macrocations.

Complexation of Fe^{2+} and Mn^{2+} with organic ligands was indicated in field studies by Barker et al. (1986). Calculations showed, however, that precipitation of siderite, ferric oxides and manganous carbonate might diminish the amount of organically complexed Fe and Mn. Complexation of Fe and Mn was also indicated in column studies (Knox and Jones, 1979; Hoeks et al., 1984; Kjeldsen, 1986). Fe was found to be kept in solution by complexation with short chain carboxylic acids and the $> 10\ 000$ MW fraction of leachate (Knox and Jones, 1979). In a related study, Theis and Singer (1974) showed that complexation of Fe^{2+} with organics such as tannic acid effectively retarded the oxidation of Fe^{2+} in aerobic solutions. This indicates that complexation of Fe^{2+} in plumes might facilitate its transport downgradient of the landfill. In addition, if a substantial part of Fe and Mn was complexed by dissolved organic matter and account of this was not made in calculation of saturation indices, supersaturation could erroneously be suggested. However, in a recent detailed study it was shown that dissolved Fe and Mn in leachate plumes may primarily be dissolved free ionic species (Jensen et al., 1998). In the Grindsted Landfill (DK) leachate plume, which contains high concentrations of Fe(II) (up to 166 mg/l) and Mn(II) (up to 38 mg/l), dissolved Fe(II) and Mn(II) were divided into different species by size fractionation and a subsequent resin-ion-exchange method for the truly dissolved fraction (< 1 nm). The main species were Fe^{2+} and Mn^{2+} accounting for 59–73% and 64–82% of the total Fe(II) and Mn(II), respectively, whereas the colloidal fractions constituted only a small fraction (Fe(II): 0–22%; Mn(II): 0–13%) and the organic, complexed fractions were insignificant (Fe(II): $< 1\%$; Mn(II): 0–4%). The fact that about 2/3 of the high Fe(II) and Mn(II) concentrations found in the leachate plume was Fe^{2+} and Mn^{2+} suggests, according to geochemical model spe-

ciation by MINTEQA2 (Allison et al., 1991) that Fe(II) and Mn(II) in the leachate plume were supersaturated with respect to siderite and rhodochrosite, respectively (Jensen et al., 1998). This has apparently also been observed in other leachate plumes (e.g. Baedecker and Back, 1979a; Nichol森 et al., 1983). The often observed supersaturation with respect to siderite and rhodochrosite is probably due to extremely slow precipitation kinetics for these two minerals, as shown in laboratory experiments (Jensen et al., 1999a).

7.5. Conclusion: inorganic macrocomponents

Anions in leachate plumes are mainly important due to their capability of forming complexes and taking part in dissolution/precipitation processes. The formation of complexes may increase the mobility of cations and heavy metals. In addition, many reactions are influenced by pH, which to a large extent is governed by the carbonic acid components, in particular HCO_3^- . The S compounds, involved in the SO_4^{2-} reduction process, are of certain interest, but the prevalence of SO_4^{2-} reduction in leachate plumes is not very well understood.

The attenuation of cations is, besides by dilution, primarily governed by cation exchange processes. Calcium and Mg are also influenced by complexation and dissolution/precipitation processes. The attenuation of NH_4 and K due to cation exchange processes is significant, while Na will only be slightly retarded. Calcium and in some cases also Mg, typically dominating the cation exchange complex, will often be expelled and move at the front of the leachate plume.

Ammonium seems, at least based on the detailed investigation of the Grindsted Landfill (DK) leachate plume, to be significantly attenuated in the anaerobic part of the plume. The NH_4 plume is of limited extent followed by zones of increased concentrations of NO_3^- and N_2O , but the attenuation mechanisms are not understood. This issue deserves further research.

Dissolved Fe and Mn in the leachate will be subject to precipitation as sulfides or carbonates, ion exchange, oxidation and dilution. These processes tend to lower the aqueous concentrations of Fe and Mn along the flow lines, but reduction of sediment-associated Fe and Mn oxides may increase their concentrations further out in the plume, often exceeding the saturation indices with respect to carbonates. Organic complexation of Fe and Mn seems only of modest importance. Further down-gradient from the landfill at higher redox potentials, Fe and Mn may again precipitate as oxides.

8. Heavy metals

Heavy metals, or trace elements, do not constitute a frequent groundwater pollution problem at landfills,

partly because landfill leachates usually contain only modest concentrations of heavy metals (see Section 2: Landfill leachate) and partly because the heavy metals are subject to strong attenuation by sorption and precipitation in the plume. A survey in Germany (Arneeth et al., 1989) including 92 abandoned waste disposal sites, revealed that for Cd 78% and for Pb 85% of down-gradient groundwater samples were below detection limits (Cd: 1 $\mu\text{g/l}$, Pb: 10 $\mu\text{g/l}$) and only 3% of the samples exceeded the drinking water standards (Cd: 5 $\mu\text{g/l}$, Pb: 50 $\mu\text{g/l}$).

Heavy metals in leachate plumes will be attenuated primarily by sorption and precipitation in addition to dilution. Table 8.1 summarizes the processes involved in heavy metal attenuation in leachate plumes.

8.1. Heavy metal species in leachate plumes

Heavy metal concentrations in leachate plumes usually refer to total dissolved metal, determined e.g. on an acidified sample after removal of solids (e.g. $>0.45 \mu\text{m}$). However, various metal species such as colloidal metals and organic and inorganic metal complexes are expected in leachate plumes. Determining the speciation of heavy metals in complex solutions, such as leachate-polluted groundwater, by experimental methods is very difficult. As an alternative, metal species in leachate-polluted groundwater have been estimated by computer speciation programs. However, colloidal fractions are not included in such speciation programs and often also the organic complexes are neglected or handled very rudimentarily.

Colloids are present in leachate-polluted groundwater (Jensen et al., 1999b) in terms of organic and inorganic particles in the size range of 1 nm (0.001 μm) to the particle cut-off of the filters used in separating the sample into suspended matter and a dissolved fraction. This cut-off can vary, but often a cut-off of 0.45 μm is used. The colloidal content of two samples from the Vejen Landfill (DK) plume was 290 and 210 mg/l as compared to contents of dissolved solids ($<0.001 \mu\text{m}$) of 1910 and 800 mg/l, respectively. The heavy metal content of the leachate-polluted groundwater samples was too low for determining colloidal species. But Jensen et al. (1999b) spiked the leachate-polluted groundwater samples with heavy metals at environmentally relevant concentrations and, after calibration, separated the groundwater samples into size fractions in order to obtain information about the affinity of leachate plume colloids for heavy metals (Cd, Ni, Zn, Cu, and Pb). A substantial, but highly varying part of the heavy metals was associated with the colloids (Cd: 38–45%, Ni: 27–56%, Zn: 24–45%, Cu: 86–95%, Pb: 96–99%). Colloidal bound Cd, Ni, and Zn were primarily found in the smallest colloidal fraction (1–10 nm), whereas Cu and Pb to a large extent also were associated with larger colloids ($>10 \text{ nm}$). Of the

Table 8.1

Summary of processes involved in attenuation of heavy metals in leachate plumes (+ +: very important, +: important, (+): usually of minor importance, -: not important)

Process	Cadmium Cd	Chromium Cr	Copper Cu	Lead Pb	Nickel Ni	Zinc Zn
Dilution	+	+	+	+	+	+
Complexation ^a	+	+	++	++	+	+
Redox processes	-	- ^b	-	-	-	-
Sorption	+	+	+	+	+	+
Precipitation						
Sulphides	+	-	+	+	+	+
Carbonates	(+)	-	-	+	-	(+)
Other	+	++	+	+	-	-

^a Complexation is not an attenuation process, since complexation results in increased solubility and mobility.

^b Cr as Cr (III). Cr (VI) may appear in chemical waste, but presumably is rapidly reduced to Cr (III) under the anaerobic conditions in the landfill (Richard and Bourg, 1991).

smallest colloidal fraction (1–10 nm), organic colloids dominated with respect to Cd, Ni, Cu and Pb (< 10 nm: Cd 94–99%, Ni 92–99%, Cu 99%, Pb 87–96%), whereas inorganic colloids seemed most important for Zn, since organic colloids accounted for only 23–26%.

Holm et al. (1995b) speciated Cd in landfill-leachate polluted groundwater by dialysis, ion exchange, and computer methods, and found that Cd was present almost exclusively as organic complexes (99%), of which 70% were categorized as high molecular weight complexes and about 25% as stable complexes. Jensen et al. (1999b) determined organic complexes of the heavy metals Cd, Ni, Zn, Cu, and Pb in landfill-leachate polluted groundwater by an anion-resin method and found that organic complexes made up a significant part of the total content of heavy metals: Cd 85%, Ni 27–62%, Zn 16–36%, Cu 59–95%, and Pb 71–91%.

Since various metal species (whether bound to small colloidal particles or by dissolved organic or inorganic complexes) seem so prevalent in leachate-polluted groundwater, the free metal ion is expected to make up only a small fraction of the measured metal concentrations in leachate plumes. This is substantiated further by the results of the speciation calculations shown in Table 8.2 for a groundwater sample strongly polluted by leachate and for one weakly polluted by leachate. The free ionic fractions of Cu and Pb are very small, of the order of 1–2%, and for Cd, Ni and Zn of the order of 7–17%. The speciation calculations do not include inorganic colloids, but organic colloids contribute if included in the DOC measurements. The calculations were made by means of the WHAM-model (Tipping, 1994) assuming that DOC consisted of 90% fulvic acid and 10% humic acid as found by Christensen et al. (1998a). The WHAM model was chosen as this model previously has proven successful in describing heavy metal complexation by DOC in leachate polluted groundwater (Christensen et

al., 1998b, 1999; Christensen and Christensen, 1999, 2000). Except for an adjustment of the Zn/DOC (Christensen and Christensen, 1999) and the Cu/DOC (Christensen et al., 1999) complexation constant, the default database of the WHAM model was used.

Combination of the above-mentioned experimental results and calculations with the purpose of identifying in detail the various metal species in leachate plumes is not possible, because in some investigations small colloids have been included in the dissolved fraction, depending on how samples were filtered and separated. However, Jensen et al. (1999b) performed rigorous separation of two samples of leachate-polluted groundwater from the Vejen Landfill (DK) plume and performed speciation calculations on the truly dissolved fraction. The results are shown in Fig. 8.1. For Cd, Cu and Pb the free metal ion makes up less than 0.1% of the total metal concentration as measured on a sample filtered through a 0.4 µm filter. A substantial part of Cd, Ni, Cu and Pb seems to be related to organic matter that actually is small sized colloidal matter.

The presence of metal species in leachate plumes complicates the discussion of attenuation mechanisms in aquifers, because the different metal species may behave differently and even redistribute as the plume migrates down the aquifer, and because most of the available information on attenuation mechanisms only concern free divalent metal ions. There is no doubt that the significant heavy metal species in plumes will influence the attenuation of heavy metals by increasing metal solubility and mobility.

8.2. Sorption

The term sorption here covers all surface related reactions such as adsorption, absorption, surface complexation, surface precipitation and ion exchange. For reviews on sorption mechanisms, see e.g. Kramer and

Table 8.2

Calculated metal species in two groundwater samples with significant and marginal contents of leachate, respectively. The calculations were made at pH 6.8 by the WHAM-model as described in the text

Strongly leachate polluted groundwater	% Complexed with						
	CO ₃ ²⁻ 1300 mg/l	SO ₄ ²⁻ 50 mg/l	Cl ⁻ 700 mg/l	OH ⁻	NH ₄ ⁺ 190 mg N/l	DOC 300 mg/l	Free
Metal	% ^a	%	%	%	% ^b	%	%
Cd (5 µg/l)	17.5	0.5	16.6	0.0	0.3	48.6	16.5
Cu (20 µg/l)	3.7	0.0	0.0	0.0	0.0	96.3	0.0 ^c
Pb (20 µg/l)	2.2	0.0	0.0	0.0	0.0	97.7	0.1
Ni (20 µg/l)	52.7	0.1	0.1	0.0	0.2	40.3	6.6
Zn (500 µg/l)	57.0	0.4	0.3	0.0	0.1	27.2	15.0

Weakly leachate polluted groundwater	% Complexed with						
	CO ₃ ²⁻ 500 mg/l	SO ₄ ²⁻ 25 mg/l	Cl ⁻ 150 mg/l	OH ⁻	NH ₄ ⁺ 30 mg N/l	DOC 30 mg/l	Free
Metal	% ^a	%	%	%	% ^b	%	%
Cd (5 µg/l)	43.5	0.4	17.6	0.0	1.1	24.9	12.5
Cu (20 µg/l)	14.0	0.0	0.0	0.0	0.1	85.9	0.0 ^c
Pb (20 µg/l)	8.3	0.0	0.0	0.0	0.0	91.6	0.1
Ni (20 µg/l)	82.5	0.1	0.1	0.0	0.3	13.9	3.1
Zn (500 µg/l)	84.6	0.2	0.2	0.0	0.3	8.1	6.6

^a The concentration includes the species H₂CO₃/HCO₃⁻/CO₃²⁻. At pH 6.8 the dominant form is HCO₃⁻.

^b The concentration includes the species NH₄⁺ and NH₃. At pH 6.8, the dominant form is NH₄⁺.

^c The actually content of the free copper ion is 0.03%.

Allen (1988) and Sposito (1984). Divalent metal cations have a high affinity for sorption onto negatively charged sites associated with clay minerals, organic matter, oxides of Fe, Mn, Al and Si, and calcite (CaCO₃). The equilibrium distribution between sorbed metal and metal in solution is often expressed by the distribution coefficient, K_d , which is directly related to the average migration velocity of the metal (V_m) relative to the water flow velocity (V_w) by the approximate equation: $V_m/V_w = (5 K_d)^{-1}$ (Christensen et al., 1996b). If precipitation has also taken place in the experiments conducted for estimating K_d , application of the relative transport equation is not warranted.

K_d -values exist for many heavy metals in soils (e.g. Anderson and Christensen, 1988), but very few reports exist for aquifer materials (Christensen et al., 1996b, 2000a). Even fewer reports are found on sorption of heavy metals onto aquifer materials in the presence of a leachate matrix. Christensen et al. (1996a) measured in two cases, at pH-values around 6.6, linear sorption isotherms for Cd, Ni and Zn in the presence of water sampled 7 m downgradient from the Vejen Landfill (DK) as shown in Fig. 8.2. The K_d -values were fairly high, in spite of the presence of high ionic strength (I: 0.01–0.04 M) and high concentrations of DOC (139–230 mg C/l): Cd 60–175 l/kg, Ni 18–60 l/kg and Zn about 450 l/kg, suggesting relative metal migration velocities of the order of less than 1% of the water flow velocity.

K_d -values increase (and relative migration velocities decrease) significantly with pH of the aquifer-groundwater-leachate system as does complexation by DOC and carbonic acid species. This is illustrated in Fig. 8.3, where estimates of relative migration velocities of Cd, Ni, Zn and Cu are presented for pH ranging from pH 5 to 8 (likely interval for leachate plumes). Equations of relative migration velocities for free ionic metal species based on K_d -values determined for 17 sandy aquifer materials (from Christensen et al., 1996b, 2000a) were combined with estimates obtained by the WHAM-model of the fraction of free ionic species ($F_{\text{free ion}}$) in a strongly polluted (I=0.04 M, DOC=300 mg C/l) and a weakly polluted (I=0.01 M, DOC=50 mg C/l) groundwater sample into estimates of relative metal migration in leachate plumes. These estimations assume that only the free metal ion contributes to sorption onto the aquifer material: $[(V_m/V_w)_{\text{ionic}} = (V_m/V_w)_{\text{leachate}} (F_{\text{free ion}})]$. Fig. 8.3 suggests that complexation increases metal mobility at all pH-values (as the fraction of free metal ion is less than unity), but is greatest at high pH-values. For Cd, Ni and Zn, the overall migration velocity still decreases with increasing pH, and the major consequences of the complexation supposedly are found at low pH-values where metal migration velocities in the presence of leachate could be as high as 5–20% of the groundwater flow velocity. For Cu, the consequences are reversed. Complexation of Cu increases very

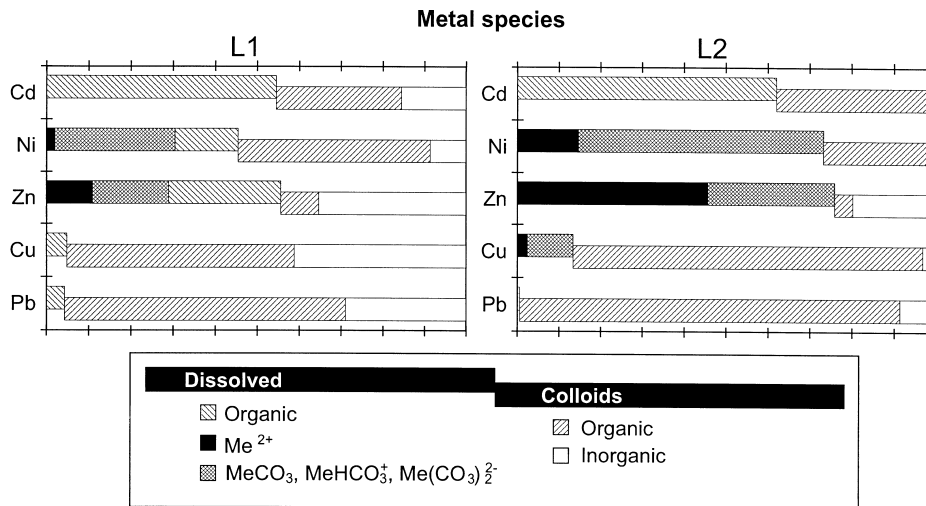


Fig. 8.1. Speciation of Cd, Ni, Zn, Cu and Pb spiked into two samples from the Vejen Landfill (DK) leachate plume showing free ionic metal, carbonate complexes and organic complexes in the truly dissolved fraction ($< 0.001 \mu\text{m}$) and organic and inorganic bound metal in the colloidal fraction ($0.001\text{--}0.400 \mu\text{m}$). Prepared from data presented by Jensen et al. (1999b).

dramatically with pH, while the migration velocity of the free ion decreases with a slope much less, leading to the highest overall migration velocities for Cu at high pH-values. At pH 7.5 in the presence of leachate in a sandy aquifer, Cu may migrate with a velocity of the order of 20–40% of the groundwater flow velocity. These simulations suggest that the effect of complexation, in particular with DOC, on metal migration in leachate plumes, may vary with the metal and depend upon pH of the plume.

8.3. Precipitation

The solubility of the heavy metals Cd, Ni, Zn, Cu and Pb in leachate plumes may be governed by sulfides or carbonates. Phosphates and hydroxides may also limit metal solubility. See also Table 8.1. It is difficult to evaluate the relative importance of possible precipitates governing the solubility of heavy metals in very complex solutions such as landfill leachates, but sulfides and carbonates are presumably the most important precipitates. However, very little has been done on leachate plumes in this regard, so precipitation of metals primarily is addressed in general terms.

Precipitation reactions may be relatively slow, requiring months to establish equilibrium. However, in the context of groundwater this is usually not critical although the kinetics of the reaction may lead to stretching of contaminant plumes. Prediction of solute equilibrium concentrations in terms of free metal ions is very uncertain because of possible supersaturation and uncertainty about the composition of the controlling

precipitate and its solubility products. However, in the SO_4^{2-} reducing zone, prediction of heavy metal concentrations at levels below the analytical detection limits is probably not necessary since even small concentrations of sulfides will precipitate all heavy metals. One exception is Cr, which does not form insoluble sulfides. Lindsay (1979) reported the following solubility products: $\text{ZnS}:10^{-22.50}$, $\text{CdS}:10^{-27.07}$, $\text{PbS}:10^{-27.51}$ and $\text{CuS} 10^{-36.10}$. Sillén and Martell (1964) refer to a solubility product of $10^{-20.7}$ for NiS. Reduced Fe will also precipitate as a sulfide and heavy metals may be occluded in this process (cf. Bisdom et al., 1983).

Although carbonates are much more soluble than sulfides, they may also control the solubility of Cd, Zn, Cu and Pb, but not Ni, outside the SO_4^{2-} reducing zone. In the literature (Sillén and Martell, 1964), CdCO_3 (octavite) solubility products vary from $10^{-13.74}$ to $1^{-11.28}$. More recent research suggests a CdCO_3 solubility product of $10^{-12.6}$ (Holm et al., 1996). Sillén and Martell (1964) summarized the solubility products at zero ionic strength (K_{s0}): $\text{NiCO}_3:10^{-6.84}$, $\text{CuCO}_3:10^{-9.86}$, $\text{ZnCO}_3:10^{-10.68}$ and $\text{PbCO}_3:10^{-13.14}$. In leachate with a pH equal to 7 and a typical total inorganic C concentration of 1000 mg/l this yields (assuming activity coefficients of one) the following solubilities (in $\mu\text{g/l}$): Ni^{2+} 270,000, Cu^{2+} 270, Zn^{2+} 43, Cd^{2+} 3.5 (using $K_{s0} = 10^{-12}$ for CdCO_3), and Pb^{2+} 0.5.

Chromium is expected to be present in the reduced environments of leachate plumes only as Cr(III), which forms relatively insoluble hydroxides resulting in solute concentrations around 10 $\mu\text{g/l}$ at pH equal to 7 (calculated from Richard and Bourg, 1991).

8.4. Experimental evidence

In a leachate plume the behavior of heavy metals is simultaneously controlled by sorption, possibly precipitation, and complexation. Proper evaluations of metal attenuation processes must therefore account for this complex system and actual metal concentrations.

Several reported investigations on metal migration in leachate loaded soils have employed highly elevated

concentrations of metals for spiking leachate (Griffin and Shimp, 1976; Griffin et al., 1976; Frost and Griffin, 1977; Alesii et al., 1980; Fuller et al. 1980; Loch et al., 1981; Campbell et al., 1983; Boyle and Fuller, 1987). However, in most cases substantial attenuation was observed yielding apparent migration velocities of 10–80% of the water transport velocity.

Experiments with actual (unspiked) metal leachate concentrations have shown very restricted migration of heavy metals: Kjeldsen and Christensen (1984) and

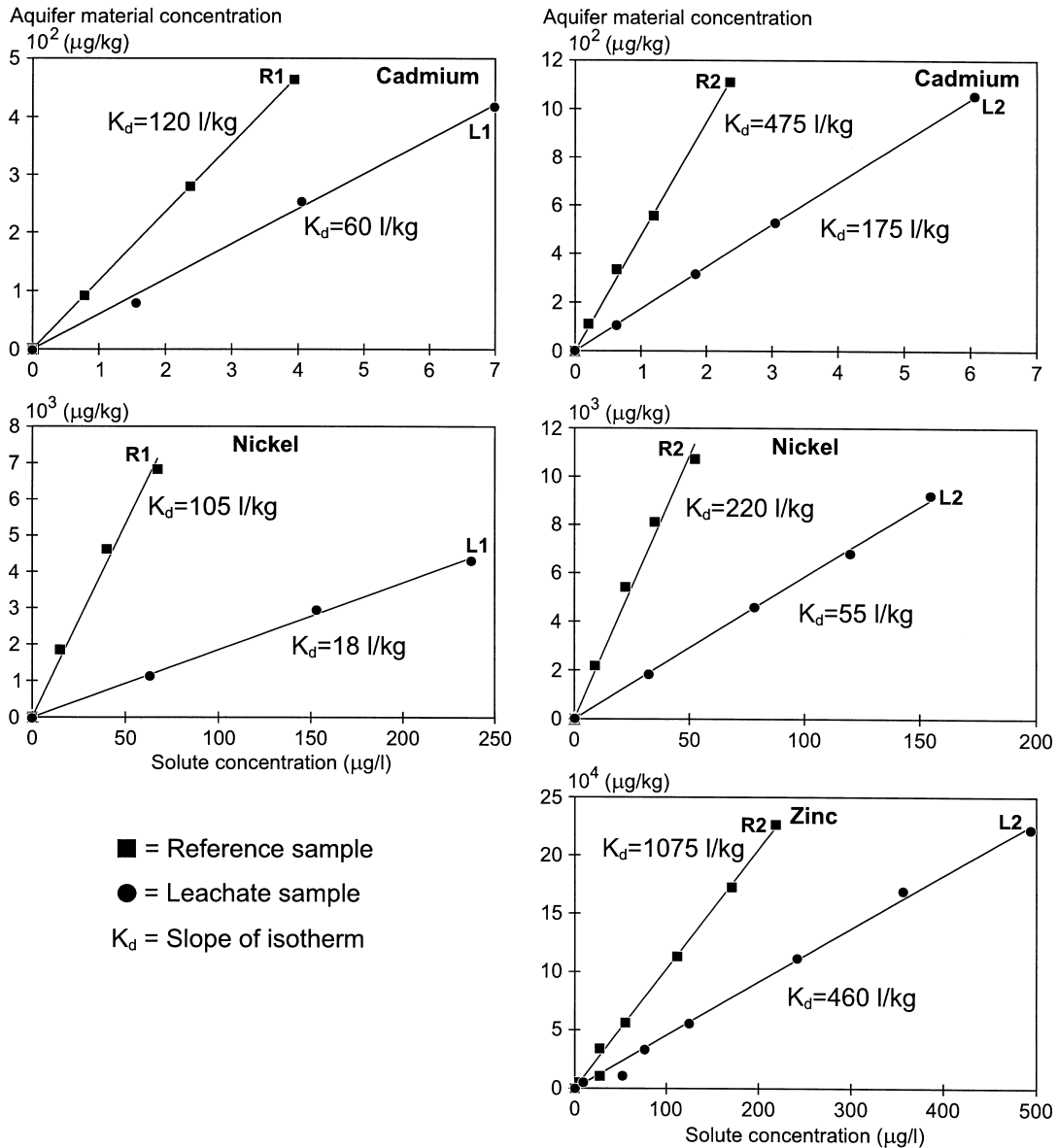


Fig. 8.2. Linear sorption isotherms and derived K_d -values for Cd, Ni and Zn in the presence of leachate-polluted groundwater (L) and a reference solution (R) mimicking the leachate-polluted groundwater except that no DOC was present. Prepared from Christensen et al. (1996a).

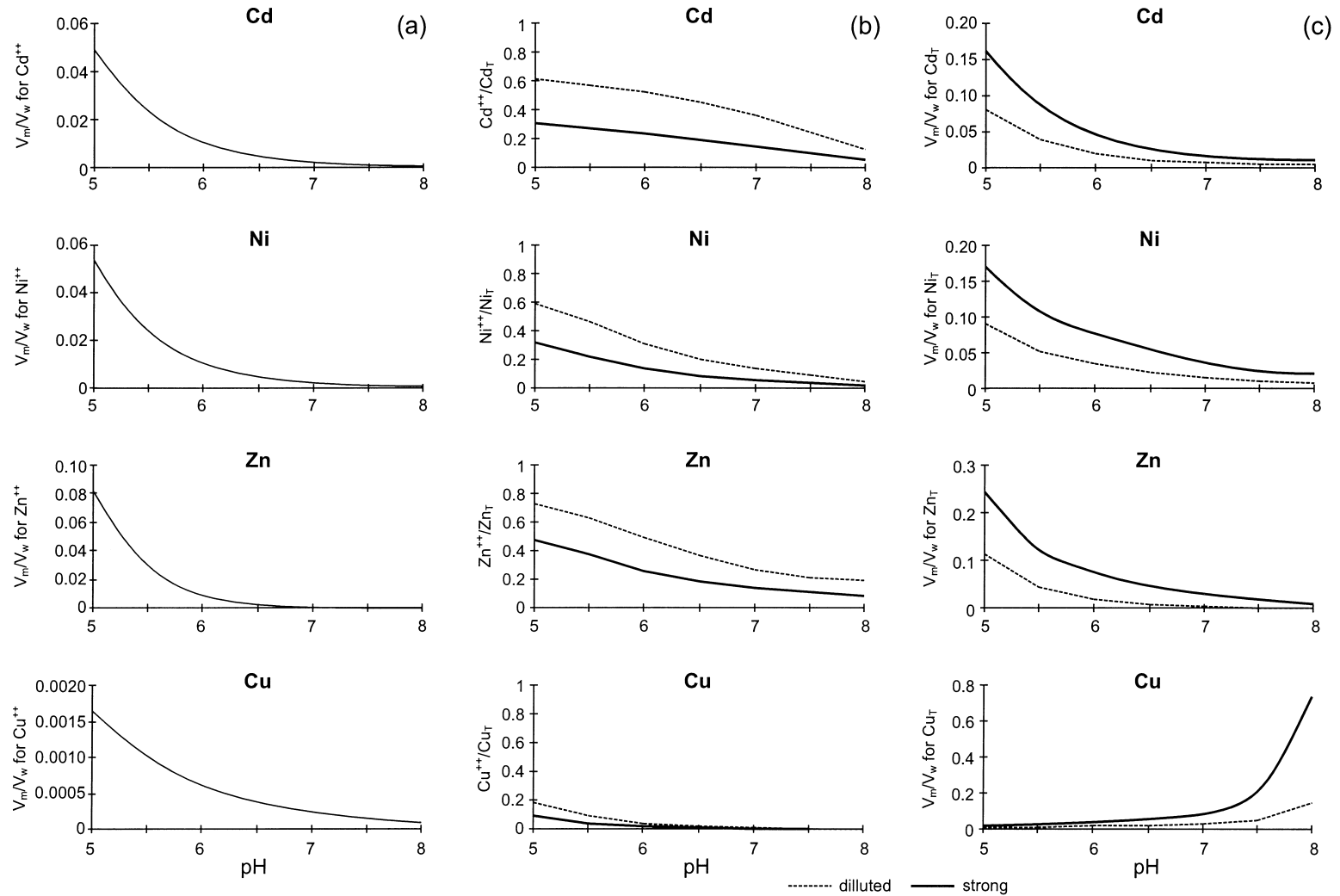


Fig. 8.3. Relative migration velocities (c) of Cd, Ni, Zn and Cu in leachate polluted groundwater (S: Strong; D: Dilute) for a range of pH-values estimated from regression equations (a) for laboratory determined K_d -values for free metal ions (Christensen et al., 1996b, 2000a) and (b) the fraction of free ionic metal in the samples estimated by the WHAM-model.

Kjeldsen (1986) found apparent migration velocities, based on determined metal profiles in sediment columns after leachate exposure, of the order of 0.5–2% for Cd and 0.4–3% for Zn. It is important to stress that these numbers are apparent migration velocities and that, due to likely precipitation in the columns, they cannot be extrapolated to the field.

Although most of the metals were retained in the upper few centimeters of the sediment columns, Kjeldsen and Christensen (1984) and Kjeldsen (1986) did see Cd and Zn in the column effluent, indicating that several species were present and subject to different degrees of attenuation. The significance of organic complexes in terms of increasing metal mobility has been demonstrated by Christensen (1989), Hoeks et al. (1979, 1984), and Loch et al. (1981) in laboratory columns. Christensen (1989) found that stable Cd complexes present in leachate were not attenuated in short soil columns. However, resin equilibration experiments reported by Christensen et al. (1996a) with leachate-polluted groundwater from the Vejen Landfill (DK) leachate plume did not indicate any significant amount of complexes that could not be redistributed. This suggests that the migration of stable complexes, as observed in column studies, has a very limited range or, alternatively, it maybe an artifact of column studies involving packed soils.

The most contaminated wells at the North Bay Landfill (CAN) showed low concentrations of all heavy metals: Cd 2–8 µg/l, Ni 10–80 µg/l, Zn 3–11 µg/l, Pb 16–67 µg/l, and Cr 33–85 µg/l (Barker et al., 1986). The complexation capacity of the organic matter in the samples, determined by Cu-titration, exceeded the actual concentration of metals by several orders of magnitude. Although a low input of heavy metals could be the cause of the low concentrations in the plume, attenuation by sorption and precipitation was considered significant.

In the Vejen Landfill leachate plume (DK) very low concentrations of heavy metals were observed: Cd <0.2 µg/l, Ni <5–7 µg/l, Zn <100–280 µg/l, Cu <10 µg/l, and Pb <0.5–1.5 µg/l (Andersen et al., 1991). Analysis of leachate revealed concentrations that were only slightly above what was found in the plume. All the above-mentioned concentrations in the Vejen Landfill plume were below drinking water standards.

In both the North Bay Landfill (CAN) and the Vejen Landfill (DK) leachate plumes, SO_4^{2-} reducing environments have been identified supposedly providing significant attenuation of heavy metals by sulfide precipitation. In the absence of sulfide precipitation, sorption will also be a significant attenuation mechanism although strong organic complexes may enhance the migration velocities. It appears that the strong attenuation of heavy metals in leachate plumes will restrict heavy metals to the most concentrated part of the plume near the landfill.

8.5. Conclusion: heavy metals

The behavior of heavy metals in a landfill leachate plume is simultaneously controlled by sorption, possibly precipitation, and complexation, and proper evaluations of metal attenuation must account for this complex system. Generally, heavy metals do not constitute a groundwater pollution problem at landfills because landfill leachates usually contain only modest heavy metal concentrations and the metals are subject to strong attenuation by sorption and precipitation. Sulfide producing conditions result in extremely low solubilities of heavy metals. The presence of colloidal as well as organically complexed metals does enhance solubilities and mobilities, but apparently not to the extent that the metals exhibit any appreciable migration in leachate plumes.

9. Xenobiotic organic compounds (XOCs)

Xenobiotic organic compounds (XOCs) are the organic chemicals identified as known, individual pollutants in the leachate. The number of known XOCs increases with time as better methods for analysis are developed. To date, more than 1000 organic chemicals have been identified in groundwater contaminated by landfills, most of which fall into the categories (see also Table 9.1):

- aromatic hydrocarbons;
- halogenated hydrocarbons;
- phenols;
- pesticides.

Other compounds such as anilines and sulfonated compounds are also found. Even though XOCs typically constitute less than a few per cent of the total dissolved C in leachate, the fate of XOCs in the affected aquifer is of major concern. This group of pollutants pose a potential health risk (Brown and Donnelly, 1988), and strict drinking water standards are enforced in many countries, with acceptable concentrations often as low as 0.1 µg/l for individual XOCs. These concentration criteria may be several orders of magnitude lower than concentrations observed in leachate (Table 2.3).

Attenuation of XOCs is (besides dilution) due to sorption and degradation. For some volatile compounds, volatilization may also occur. However, this is only important at shallow depths and in unsaturated zones beneath landfills, and as such will not be discussed here [see e.g. Robinson (1985, 1989) for a review of unsaturated zone attenuation of leachate XOCs]. In this section, the current knowledge on sorption and degradation is reviewed. Also included is a discussion of the toxicity towards biota caused by the presence of XOCs in the plume.

9.1. Sorption

Sorption of specific organic chemicals onto soils is well described in the literature (e.g., Karickhoff, 1984; Brusseau and Rao, 1989). Most information concerns non-polar compounds, while the sorption of polar compounds (e.g. organic acids and bases) is much less researched.

In general, sorption of non-polar compounds onto soil can be described as a partitioning into the solid organic C of the soil. The sorption process is considered to be kinetically controlled but in most practical cases concerning natural transport in leachate plumes, an equilibrium model is a fair approximation. Estimation of equilibrium distribution coefficients, K_d , is often done by empirical regression equations, paying attention to the organic C content of the soil and to the hydrophobicity of the specific organic compound expressed through its octanol/water partitioning coefficient (Karickhoff et al., 1979; Kenega and Goring, 1980; Brown and Flagg, 1981; Schwarzenbach and Westall, 1981; Schellenberg et al., 1984). These regression equations are well established for soil and sediments with organic C contents in excess of 0.1% C by weight. Many aquifer materials, however, have organic C contents below the limit of 0.1%. In such organic-poor sediments, a significant fraction of the active sorption sites (locations in the matrix where organic molecules can adhere) may be associated with oxide/hydroxide surfaces, clay minerals, or other poorly defined minerals. Thus, the traditional regression equations for estimation of sorption in aquifers yield very uncertain predictions of sorption coefficients (Boucher and Lee, 1972; Curtis et al., 1986; Abdul et al., 1987; Lee et al., 1988; Brusseau and Reid, 1991; Brusseau et al., 1991; Larsen et al., 1992a,b). Based on the data presented by Larsen et al. (1992b) it might be suggested that, if the estimation equations were used for aquifer material with very low C contents, a default C content of 0.05% should be used. This would, at least statistically, give better estimates than using the real lower C content which, in any event, would be difficult to measure accurately. At the moment no alternative estimation techniques for more precisely estimating sorption in aquifer materials with low organic C content have been developed. In the case precise information on the sorption in aquifers is needed, direct measurements must be performed. Lately, the reversibility of the sorption process has been investigated. In many cases the desorption process cannot be described by the same distribution coefficient used for describing the sorption process. Release of XOCs previously sorbed to soil and aquifer materials may be much slower than rates estimated from a sorption experiment (Luthy et al., 1997; Huang et al., 1998). However, the significance of these issues in landfill leachate plumes are not yet understood.

Sorption of XOCs in landfill leachate affected soils and aquifers have only been addressed in a few cases. Larsen et al. (1992a) quantified distribution coefficients for 12 non-polar XOCs [ranging in $\log K_{OW}$ from 2.1 (benzene) to 4.1 (biphenyl)] for three aquifer materials and found K_d in the range 0.005–1 l/kg, suggesting that retardation of these XOCs would be very limited in a sandy aquifer. This is in accordance with observations by Rügge et al. (1999a), who measured, over a 2 a period, the transport of TeCM, 1,1,1-TCA, PCE, benzene, toluene, *o*-xylene and naphthalene injected into the Grindsted Landfill leachate plume. Naphthalene traveled with a relative velocity of 90% and *o*-xylene with a velocity of 93%. Kjeldsen et al. (1990) used laboratory columns to investigate the sorption of chlorophenols and other XOCs in subsoil under landfills. In both soils employed, higher substituted phenols (pentachlorophenol) with high octanol/water partitioning coefficients were less retarded than lower substituted phenols (trichlorophenol) with lower octanol/water partitioning coefficients. This was partly due to differences in the acidity constants of the chlorophenols. The estimation model for chlorophenols as developed by Schellenberg et al. (1984), taking into account the octanol/water partitioning coefficients, acidity constants, soil organic matter, and soil pH, could not precisely simulate the observed breakthrough curves. This indicates that other parameters were of importance, e.g. the effect of high ionic strength as reported by Westall et al. (1985). In some cases, the dynamics of pH, introduced by the high alkalinity of landfill leachate, could contribute to the difficulty in simulating phenol retardation in leachate plumes.

Since XOCs partition into solid organic C, it has been hypothesized that they also partition into dissolved organic matter as present in landfill leachate. This was investigated by Larsen et al. (1992c) in a study involving several leachate and aquifer materials in flow and batch laboratory experiments. The interaction between aquifer material, leachate and XOCs was very complex. In some cases, the presence of leachate increased the sorption of XOCs onto the aquifer material; in other cases, the effect was a decrease. K_d -values [ranging in $\log K_{OW}$ from 2.1 (benzene) to 4.1 (biphenyl)] for three aquifer materials measured in leachate and in groundwater are compared in Fig. 9.1. It was concluded that with respect to estimating the relative transport velocity of the specific compounds, neglecting the presence of leachate would yield a bias of not more than $\pm 20\%$. Larsen et al. (1992c) did not find this detrimental compared with all the other uncertainties involved in estimating transport velocities of XOCs in pollution plumes.

In brief, the importance of sorption as an attenuation mechanism for XOCs in the plumes can be evaluated if a reliable K_d can be estimated. However, most aquifers are poor in organic matter, and sorption is relatively limited. For BTEX and chlorinated aliphatic com-

pounds migration velocities in sandy aquifers will often be less than 20% slower than the transport velocity of the groundwater (see e.g. Larsen et al., 1992a). In plumes where several pore volumes of leachate-contaminated water have migrated through the down-gradient aquifer, sorption may be insignificant in terms of attenuating the XOCs continuing to leach from the landfill. However, sorption should always be evaluated in terms of XOCs of interest, type of aquifer, groundwater flow velocities and time frames involved.

9.2. Degradation overview

Degradation of XOCs in aquifers is reviewed in Ghiorse and Wilson (1988), Beelen (1990), Grbic-Galic (1990a,b), Dobbins et al. (1992), Krumholz et al. (1996) and Lee et al. (1998). However, leachate plumes differ dramatically from other plumes in that XOCs typically constitute only a few per cent of the organic C present.

Degradation results obtained from oil- or gasoline-contaminated aquifers cannot be directly extrapolated to leachate plumes as substrate mixtures, redox conditions and the presence of inhibitors may differ significantly. In e.g. a gasoline-contaminated aquifer, the gasoline itself is the major source of energy (and C) for the degradation reactions, and the consumption of electron-acceptors is a good indicator of the amount of organics degraded. In leachate plumes, the poorly defined DOC fraction dominates over XOCs on a mass basis, and degradation of individual XOCs may not lead to measurable changes in the aquifer geochemistry. The XOCs migrate through a series of redox environments created by reactions of DOC and inorganic macro-components, and other autotrophic and geochemical processes. The redox environments do not exist because the XOCs are degrading, and as such may not necessarily support degradation of the XOCs.

The term degradation has been used liberally in the literature. It has been defined as compound disappearance (compared with no disappearance in control experiments), by identification of end products (using e.g. radio-labeled molecules or isotopes), or by revealing degradation pathways, intermediate compounds, and active bacterial species. The different definitions and perceptions of what degradation is makes it very difficult to compare degradation results from different studies.

The degradability of XOCs in leachate-affected aquifers can be investigated by three different approaches: Microcosm studies (both laboratory and in-situ incubations), field injection experiments with minimal disturbance of the plume, and detailed monitoring of XOC distribution in plume transects, e.g. along a flowline.

In the following, methodology and results for these three approaches to degradation are discussed and the overall patterns observed are summarized. The current results of degradation of XOCs from the experimental

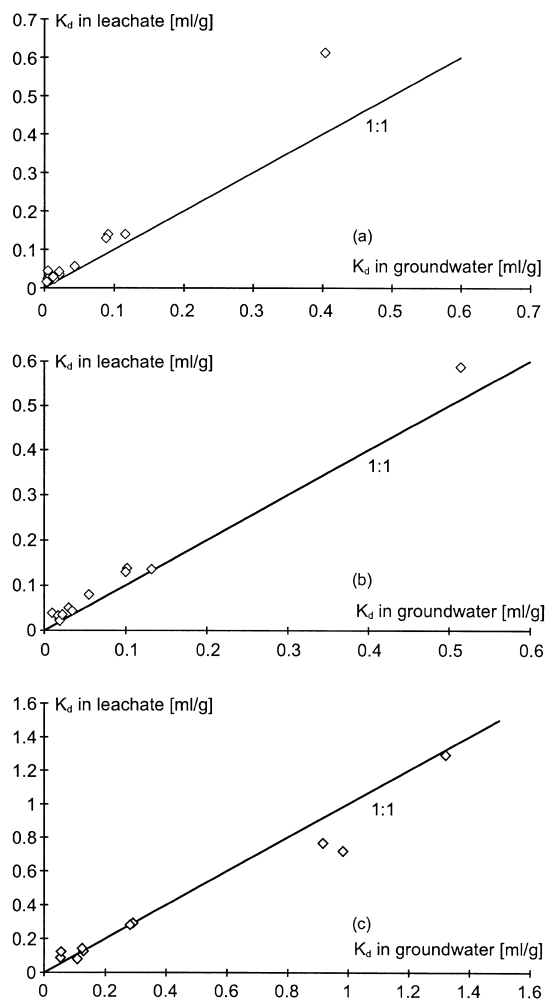


Fig. 9.1. Distribution coefficients, K_d for sorption of 12 organic chemicals (ranging in log K_{ow} from 2.1 to 4.1) onto 3 sandy aquifer materials (a, b, c) measured in groundwater and in landfill leachate. The aquifer materials had very low contents of organic C: 0.012–0.029% (Larsen et al., 1992c, with permission).

studies (Section 9.3 and 9.4) in leachate-affected aquifers have been summarized in Table 9.1. Since redox environments are so dominant for the occurrence of electron-acceptors and donors, attempts have been made to list the degradation results in the proper redox environment. In some of the reported anaerobic experiments, no attempt was made to describe the redox environment during incubation, or a detailed analysis failed to reveal a dominant redox reaction. These results are categorized as “unspecified anaerobic”.

9.3. Microcosm studies

Microcosm studies typically involve isolating a volume of aquifer material and groundwater, XOC

amendment, and subsequent measurement of XOC fate in the reactor. Both laboratory microcosms (Wilson et al., 1986; Nielsen et al., 1995a,b; Johnston et al., 1996) and in-situ microcosms (Acton et al., 1983; Acton and Barker, 1992; Nielsen et al., 1995a,b, 1996a,b) have provided useful insight into the degradation of XOCs in leachate plumes. An example of the fate of XOC in methanogenic microcosms is shown in Fig. 9.2.

The redox environment in a microcosm study may be characterized in a number of ways. Kuhn and Suffita (1989b) considered CH₄ production during incubations

as evidence of methanogenesis. Smolinski and Suffita (1987) used molybdate as an inhibitor of SO₄²⁻ reduction. Smolinski and Suffita (1987) and Johnston et al. (1994, 1996) used bromoethane sulfonic acid (BESA) as an inhibitor of methanogenesis to provide evidence for SO₄²⁻ reduction and to show that CH₄ production was biotic. Klecka et al. (1990) used ³⁵S-labeled SO₄²⁻ and measured production of ³⁵S-S. Acton and Barker (1992) used acetylene to inhibit reduction of N₂O to N₂ as evidence of NO₃⁻ reduction, whereas Klecka et al. (1990) measured the formation of N₂O without an inhibitor.

Table 9.1

Degradation potentials of XOCs in landfill-leachate contaminated aquifers observed in degradation experiments under various redox conditions (updated from Christensen et al. 1994).

Compound	Anaerobic						Aerobic					
	Unspecified		Methanogenic		Sulfate reducing		Iron reducing		Nitrate reducing			
	N	D	N	D	N	D	N	D	N	D	N	D
Aromatic hydrocarbons												
Benzene	5,16,24	27	1,10,20		4		5,20,24		1,20			4,16,17,18
Toluene	5,16	5,27,24	10,20	1,10	4	1	20	2,5,24	1,20	20		4,8,16,17,18
Ethylbenzene	5	1,27	10	1	4	1	5		1			4
o-Xylene	5,16	1,27,24	10,20	1	4	1	5,20	5,24	1,20			4,16,17,18
m-Xylene	5		10	1	4	1	5	5	1			4
p-Xylene	5				4		5	5				4
1,2,4-Trimethylbenzene				1	1	1			1			
Naphtalene	5,16,24		20				5,20,24		20			16,17,18
Biphenyl			20				20		20			17,18
Cumene									1			
Halogenated hydrocarbons												
Chlorobenzene					1							
1,2-Dichlorobenzene			20				20		20			17,18
1,4-Dichlorobenzene			20				20		20			17,18
Trichloromethane									8		8	
Tetrachloromethane		5,16,24		20			20	5,20,24		20		16,18
Trichloroethene	5,16	5,27,24		10,20			5	20, 24		20		16,18
Tetrachloroethene	5,16	5,24	20	3,20		3	5	20, 24		20		16,18
1,1-Dichloroethene		27										
1,2-Dichloroethene		27										
1,2-Dibromoethane		27										
1,1,1-Trichloroethane		5,16,24		12,20		12	20	5, 24	12,20			12,16,18
Phenols												
Phenol		10,22	19	6		6	19	19	19			12,18
o-Cresol			19,26		26		19		19			18
m-Cresol			21	26		21,26				21		
p-Cresol				26		26						
2-Chlorophenol		11		6	6							
3-Chlorophenol				6	6							
4-Chlorophenol				6	6							
2,4-Dichlorophenol			19	6,19	6		19		19			18
2,5-Dichlorophenol				6	6							
2,6-Dichlorophenol			19	19	6		19		19		18	18
3,4-Dichlorophenol			6		6							
2-Methyl-4-chlorophenol		11										
2,4,5-Trichlorophenol		11	6		6							
Pentachlorophenol		11										
2-Nitrophenol		11		19				19		19	18	18

(continued on next page)

Table 9.1 (continued)

Compound	Anaerobic								Aerobic			
	Unspecified		Methanogenic		Sulfate reducing		Iron reducing		Nitrate reducing		N	D
	N	D	N	D	N	D	N	D	N	D		
4-Nitrophenol		11		19				19	19			18
2,4-Dinitrophenol		11										
4,6-Dichlorocresol			19				19		19		18	18
Pesticides												
2-Hydroxybiphenyl			15			15			15		15	
2,4,5-Trichlorophenoxyacetate				7		7						
Mecoprop, MCP	25						25					9
Atrazine	25					25						
Miscellaneous												
Aniline	23		14			14	23					
o,m,p-Toluidine			14		14	14						
o,m,p-Aminobenzoate				14		14						
Benzamide				14		14						
Methylbenzamide			14			14						
Dimethylbenzamide			14		14							
p-Toluamide				14		14						
Pyridine				13		13						
Furan				13		13						
Thiophene			13		13							
Nitrobenzene		23		20			20	20, 23	20	20	20	

Note: The table includes investigated compounds as well as the most frequently observed XOCs in leachate (compare with Table 2.3); N: Not degraded; D: Degraded. The numbers in the table refer to the references.

References: 1. Acton and Barker (1992); 2. Albrechtsen et al. (1994); 3. Beeman (1990); 4. Berwanger and Barker (1988); 5. Bjerg et al. (1999); 6. Gibson and Suffita (1986); 7. Gibson and Suffita (1990); 8. Harrison and Barker (1987); 9. Heron and Christensen (1992); 10. Johnston et al. (1996); 11. Kjeldsen et al. (1990); 12. Klecka et al. (1990); 13. Kuhn and Suffita (1989a); 14. Kuhn and Suffita (1989b); 15. Liu et al. (1991); 16. Nielsen et al. (1992); 17. Nielsen and Christensen (1994); 18. Nielsen et al. (1996a); 19. Nielsen et al. (1995a); 20. Nielsen et al. (1995b); 21. Ramanand and Suffita (1991); 22. Rees and King (1981); 23. Rügge et al. (1998); 24. Rügge et al. (1999a); 25. Rügge et al. (1999b); 26. Smolinski and Suffita (1987); 27. Wilson et al. (1986).

Recently, degradation in Fe reducing zones has received increasing attention. Nielsen et al. (1995a) used a detailed quantification of electron-acceptors, electron-donors, and inorganic end products to categorize anaerobic environments as Fe reducing, SO_4^{2-} reducing and methanogenic. Both analysis of dissolved species and solid minerals may be necessary for assessment of on-going redox reactions in microcosms, since sometimes the major reactive pools are insoluble (as evidenced in Albrechtsen et al., 1995). Also, it was shown that the redox conditions may very well change during the course of an experiment, as a result of temporary disturbances during sampling, handling and microcosm setup. These observations suggest that the result of studies, where the on-going redox reactions may not have been positively identified, should be interpreted very carefully.

Several factors may complicate the interpretation of microcosm studies. These include:

- Kinetic as well as equilibrium sorption onto aquifer solids may interfere with the interpretation of degradation and determination of degradation

rates. Abiotic control experiments should be performed to make it possible to account for sorption (see Bjerg et al., 1996).

- The XOC concentrations studied vary from dilute (1–100 $\mu\text{g/l}$) to concentrated, potentially toxic levels (mg/l range)
- Compound interactions may be important, e.g. co-metabolism (accidental degradation of one compound in the presence of a primary substrate), diauxy (preference of one substrate over another) and inhibition (the presence of one compound inhibits the degradation of another)
- Repeated sampling may cause significant changes in headspace volume and solid to solution ratios complicating the interpretation of results, for example, obtained as concentrations in solution
- Some studies have been performed with amendment of nutrients, some without, which may lead to dramatic differences in the observed degradation rates (Johnston et al., 1996)
- Degradation studies have been performed at different temperatures

- The incubation time may or may not exceed lag phases, i.e. the period of adaptation to a disturbed environment prior to measurable degradation. Lag phases exceeding 200 days may complicate interpretation (Johnston et al., 1994; Nielsen et al., 1995a, Bjerg et al., 1999)
- Some microcosms have been performed without aquifer material, excluding the solid-water interactions typical of an aquifer plume. This could rule out Fe and Mn reduction, leading to misinterpreted results
- The terminal electron-acceptor is hard to identify during an incubation study, since concentration changes in redox sensitive species may be relatively minor (see discussion above)

Despite these limitations, an attempt has been made grouping the literature results on XOC degradation in leachate plumes into Table 9.1.

9.4. Field injection experiments

In order to study the degradation of XOCs in undisturbed plume environments, dilute plumes may be injected into an aquifer followed by detailed monitoring downgradient (Acton and Barker, 1992; Rügge et al., 1999a,b). A stock solution of the XOCs in question is injected into the aquifer, and a cloud of XOCs is formed. A detailed network of sampling points is used to follow the cloud, including conservative tracers such as Br^- .

Rügge et al. (1999a,b) and Albrechtsen et al. (1999) reported on a large natural gradient injection experiment in the Grindsted landfill (DK) leachate plume. Over a period of 200 days a cloud of 18 XOCs at trace concentrations and a conservative tracer (Br) were injected in the strongly reducing zone 15 m downgradient from the landfill. Breakthrough curves as well as snapshots were performed during nearly 3 a involving

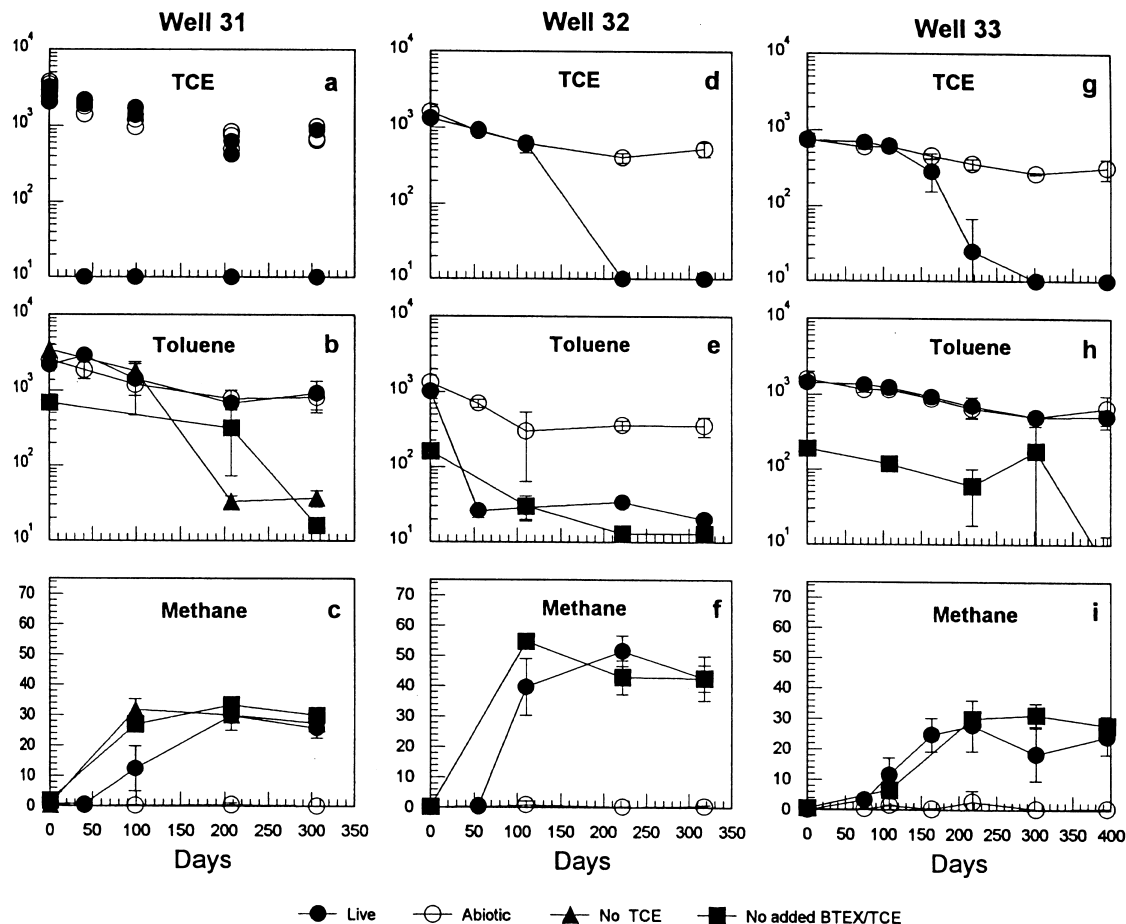


Fig. 9.2. Microcosm studies on TCE and toluene degradation and CH_4 production using materials from three wells in the reduced zone of Wilders Grove Landfill (USA) plume. Data and error bars represent average values of three replicates and 1 standard deviation (from Johnston et al., 1996, with permission).

more than 1000 sampling points. Breakthrough curves for Br^- and 3 XOCs are shown in Fig. 9.3 (Rügge, 1999a). It is seen, that e.g. toluene hardly reaches the 35 m fence, and hence was degraded in the plume between the injection point and this fence. Other compounds, such as naphthalene, show little sign of attenuation. This may be evaluated in greater detail by

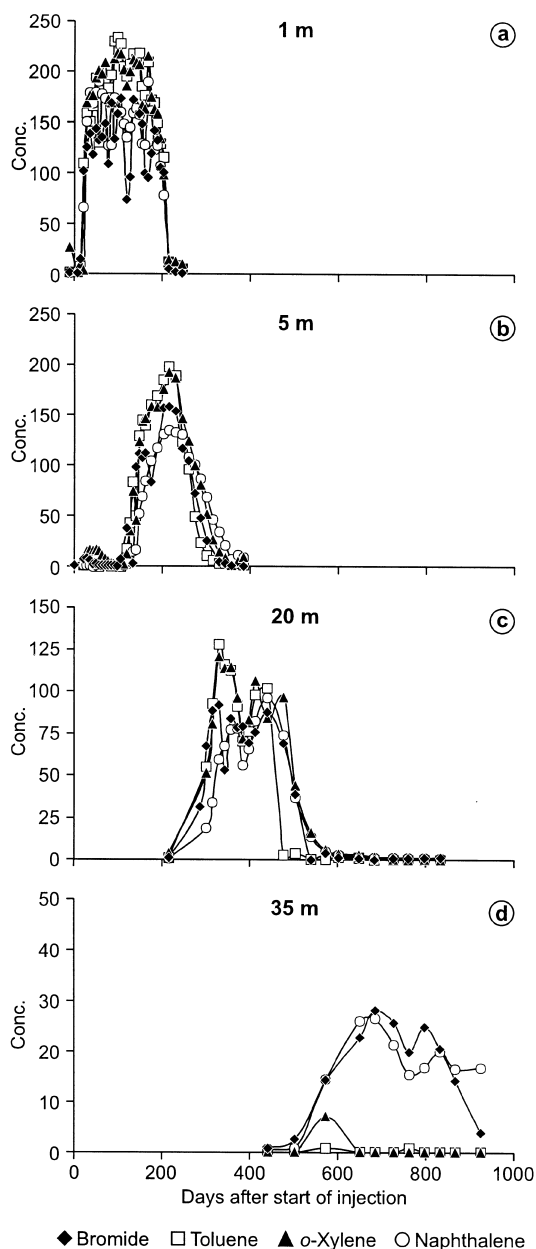


Fig. 9.3. Breakthrough curves at different distances from the release point during a natural gradient field injection experiment. Bromide concentrations are in mg/l, XOC concentrations are in $\mu\text{g/l}$ (from Rügge et al., 1999a, with permission).

spatial snapshots of the cloud (Fig. 9.4), and integration of the mass of XOC in the cloud (Fig. 9.5). Each of these masses represents values integrated over approximately 700 sampling points. Decreases in the mass over time (between snapshots) can be interpreted as degradation, but minor mass losses could also be due to non-reversible or slow-kinetic desorption from the aquifer solids. Nitroaromatic compounds showed rapid degradation (half-lives less than 1 day, Rügge et al., 1998). First order transformation rates were $0.028\text{--}0.039\text{ d}^{-1}$ for toluene and $0.0014\text{--}0.0028\text{ d}^{-1}$ for *o*-xylene. The rates for the chlorinated aliphatic compounds were: $>0.7\text{ d}^{-1}$ for tetrachloromethane, $0.0044\text{--}0.0054\text{ d}^{-1}$ for 1,1,1-TCA, $0.0012\text{--}0.0038\text{ d}^{-1}$ for tetrachloroethylene and $0.0003\text{--}0.001\text{ d}^{-1}$ for trichloroethylene. Naphthalene, benzene, atrazine and Mecoprop were not degraded during the 3 a long experiment (Rügge et al., 1999a,b).

One potential weakness of multi-XOC injection experiments is the risk of reaching toxic level of XOCs ($10\text{--}20$ XOCs each at $100\text{--}200\text{ }\mu\text{g/l}$). This could lead to artificially long lag-phases and to erroneous negative degradation results. However, multiple-compound interactions are also important for the fate of XOCs, and no better approach has been suggested for testing the fate of such compound mixtures in leachate affected aquifers.

9.5. Detailed monitoring in plumes

The fate of XOCs has been studied in great detail only at a few landfill plumes, due to the labor- and cost-intensive sampling and analysis needed. An example is given in Fig. 9.6. In most other reports, the data is scarce and do not allow for evaluation of the contributions by dilution, sorption, and degradation to the attenuation of the XOCs.

DeWalle and Chian (1981) measured concentrations of VOC in the Army Creek Landfill (USA) leachate plume and found a logarithmic decrease with distance from the landfill for the first 1000 m of the plume. Reinhard et al. (1984) measured XOCs in two Canadian leachate plumes (Woolwich and North Bay) and corrected for dilution using Cl^- as a conservative tracer. Dichlorobenzene did not seem to degrade, while xylenes were removed selectively, presumably by biotransformation. Barker et al. (1986) concluded that *o*-xylene was degrading in the North Bay Landfill (CAN) leachate plume, and that ethylbenzene was not.

Eganhouse et al. (1999) measured volatile organic compounds in a 225 m long section of the Norman Landfill (USA) leachate plume. By comparing relative concentrations it was concluded that several compounds were attenuated by degradation. Johnston et al. (1994, 1996) monitored XOC concentrations in a series of wells in the plume beneath the Wilder's Grove Landfill (USA). They concluded that spatial and temporal var-

iations in XOC concentrations prevented conclusions on biodegradation based on the monitoring alone. However, this study was restricted to a short aquifer section compared to the entire plume and, therefore, is not

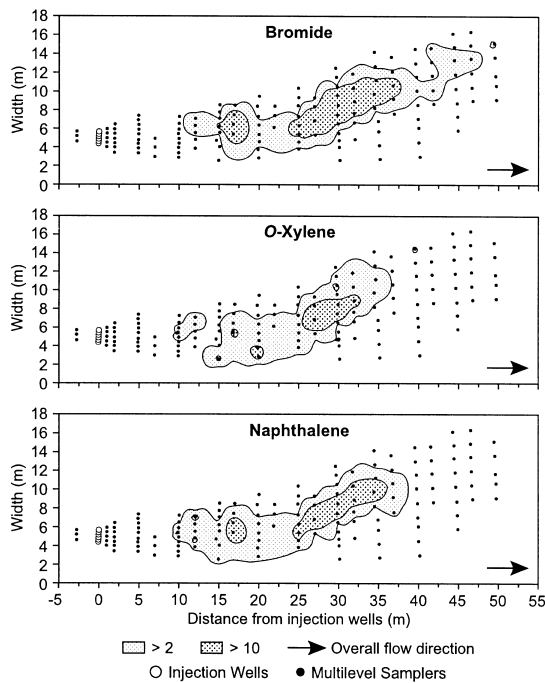


Fig. 9.4. Snapshot of clouds of selected XOCs during a natural gradient field injection experiment. The clouds had migrated in the aquifer for 503 days. Each dot represents a multi-level sampler, and values represent the depth integrated mass per unit area (Br^- in g/m^2 , XOCs in mg/m^2) (from Rügge et al., 1999a, with permission).

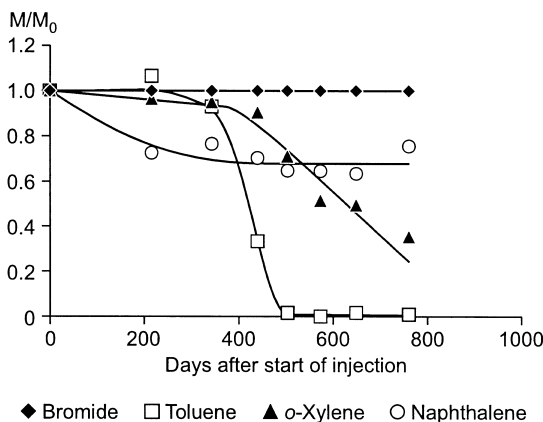


Fig. 9.5. Mass of Br^- and selected XOCs normalized to the injected mass of each compound and of the tracer during a natural gradient field injection experiment. The observed degradation took place under Fe reducing and SO_4^{2-} reducing conditions (from Rügge et al., 1999a, with permission).

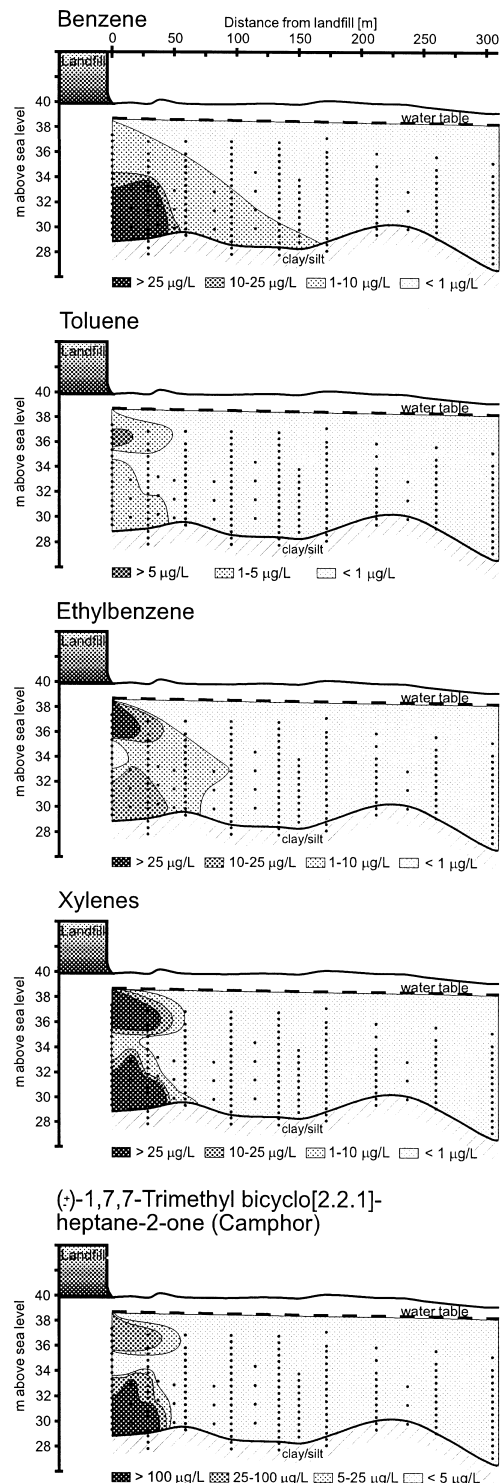


Fig. 9.6. Isoconcentration plots of XOCs in the Grindsted Landfill (DK) plume (from Rügge et al., 1995, with permission).

directly comparable to studies involving entire plume transects.

Lyngkilde and Christensen (1992b) corrected the XOC concentrations for dilution (Fig. 9.7) and found

indications for degradation of many XOCs in the anaerobic part of the leachate plume at the Vejen Landfill (DK). This allowed for demonstration of substantial natural attenuation, since the corrected XOC concentrations

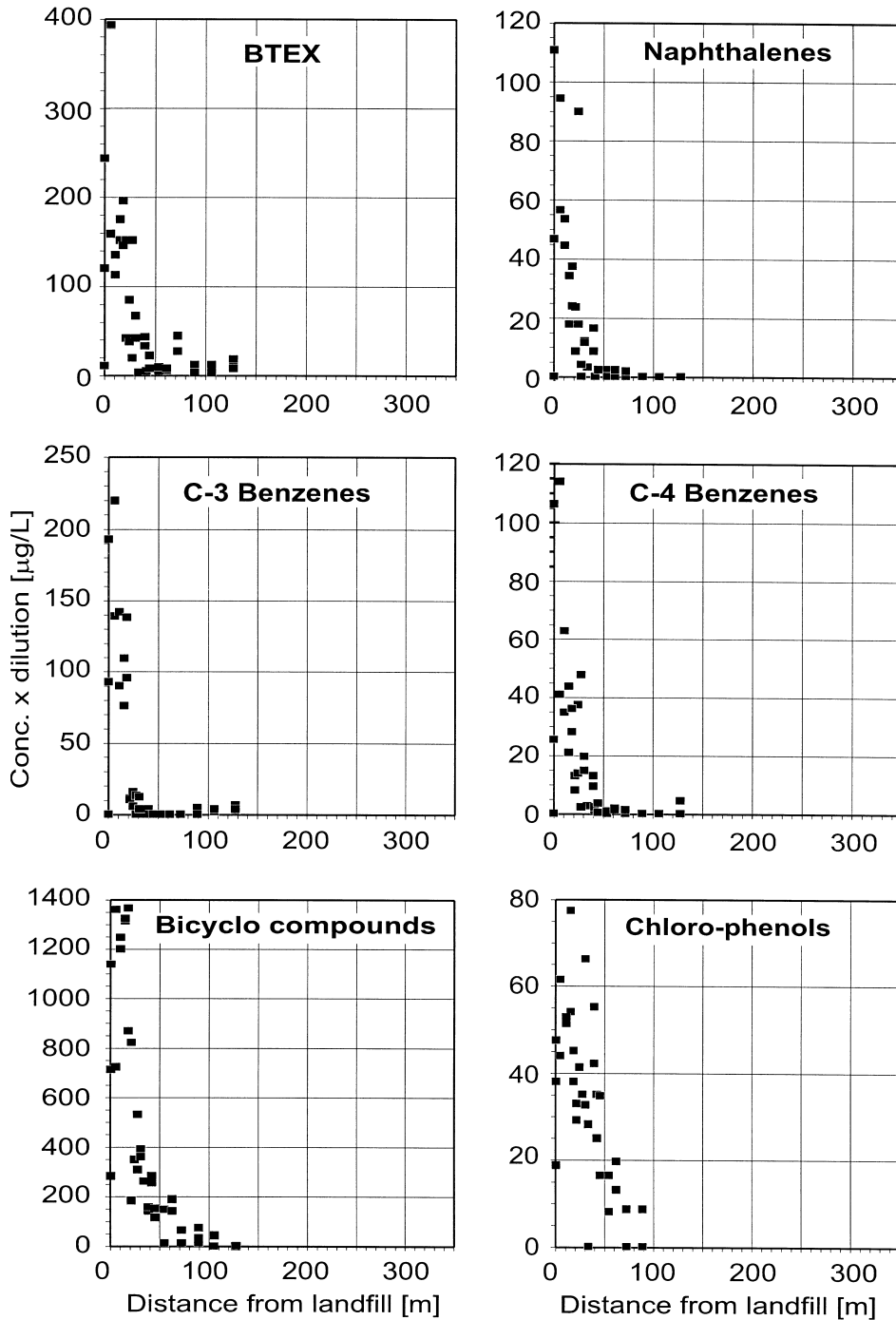


Fig. 9.7. Aqueous concentrations of selected XOCs in the plume downgradient of the Vejen Landfill (DK), corrected for dilution using Cl^- as conservative tracer (from Lyngkilde and Christensen, 1992a, with permission).

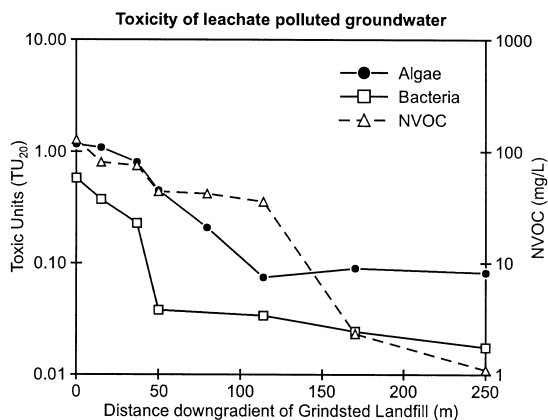


Fig. 9.8. Toxicity of leachate polluted groundwater from the Grindsted landfill (DK) plume. Samples were pre-concentrated by SPE (XAD-2) and tested in algal and bacterial tests. TU₂₀ expresses the number of times a sample needs to be diluted to give 20% effect. NVOC is also included for the corresponding water samples prior to SPE (from Baun et al., 2000, with permission).

decreased with distance. The majority of the compounds were apparently degraded in the Fe reducing zone. These findings have led to several detailed studies in the anaerobic zones of leachate plumes, with increased focus on the Fe- and Mn reducing environments (Nielsen et al., 1995a,b; Rügge et al., 1995, 1999a,b; Bjerg et al., 1999). These recent results have been summarized and included in Table 9.1.

Ravi et al. (1998) determined rate constants for the natural degradation of benzene and dichloroethane in the KL Landfill (USA) plume. Benzene concentrations were 200–1500 µg/l and dichloroethane were 100–600 µg/l close to the landfill. Benzene showed no degradation within the first 600 m of the plume, but repeated monitoring in wells located further downgradient showed persistent degradation of benzene at a rate of 0.001 d⁻¹. 1,1-DCA showed a similar degradation constant, while the degradation constant for 1,2-DCA was slightly lower, about 0.0007 d⁻¹. The XOCs had migrated as far as approximately 1500 m down to the shores of a small groundwater-fed lake. The plume was strongly anaerobic showing methanogenesis, SO₄²⁻ reduction and Fe-reduction.

Generally, detailed monitoring in plumes and correction for dilution (using e.g. Cl⁻) has resulted in conclusions on substantial degradation, especially under anaerobic conditions. Evaluation of sorption has been done for some studies (Rügge et al., 1995), and generally sorption was concluded not to be very important for many compounds. However, this has only been shown for older plumes in sandy aquifers, supposedly under steady-state conditions.

9.6. Overall degradation patterns

There is reasonable agreement between degradation results obtained using the different methods. However, some variation is also observed, and it is difficult to clearly separate variation in compound degradability from differences in environmental conditions and experimental methods

The *chlorinated aliphatic hydrocarbons* generally degrade by reductive dechlorination under anaerobic conditions (Vogel et al., 1987). The understanding of this process has increased during the last few years, and it is now generally accepted that the chlorinated compounds can act as electron acceptors. This also means that the reductive dechlorination process requires an electron donor such as naturally occurring C, petroleum hydrocarbons or organic C in landfill leachate. Degradation under aerobic conditions of higher chlorinated aliphatic compounds such as PCE and TCE has not been demonstrated, but degradation products as DCE (primarily *cis*-DCE) can be oxidized to CO₂. Recent studies indicate that oxidation of *cis*-DCE and vinyl chloride (VC) to CO₂ may be possible also under Mn and Fe reducing conditions (Bradley and Chapelle, 1996, 1997, 1998). Information obtained from different plumes, in general, is in accordance with observations from landfill leachate plumes, where the expectation is that PCE and TCE will be degraded by reductive dechlorination. This is supported by observations of lower chlorinated compounds and TCE, where PCE was the parent compound, DCE and VC in leachate plumes and by degradation experiments. The transformation of chlorinated ethenes has been observed under various redox conditions ranging from methanogenic to NO₃⁻ reducing conditions (Nielsen et al., 1995a; Johnston et al., 1996; Chapelle and Bradley, 1998; Rügge et al., 1999a). Tetrachloromethane will rapidly degrade in landfill plumes by sediment-associated Fe and organic C (Pecher et al., 1997; Rügge et al., 1999a). The transformation of 1,1,1-TCA in anaerobic environments is rapid and seems to be affected by both abiotic and biotic degradation processes (Nielsen et al., 1995b; Bjerg et al., 1999). Recent studies of full scale landfill plumes have shown a significant degradation of TCE (Chapelle and Bradley, 1998) and 1,1-DCA (Ravi et al., 1998). However, in the case of 1,1-DCA complete dechlorination to ethane was not shown. In summary, the current information suggests that landfill plumes host redox environments, microorganisms and/or geochemical processes that effectively can attenuate chlorinated solvents.

The *aromatic hydrocarbons* generally degrade readily under aerobic conditions, but very sparingly under anaerobic conditions. However, recent observations in a number of natural attenuation studies suggest a significant potential for anaerobic degradation, especially

for BTEX. The first order degradation rates observed under unspecified anaerobic conditions (Rifai et al., 1995) are typically 1 or 2 orders of magnitude lower than rates reported for aerobic conditions (Nielsen et al., 1996a). The observations in landfill leachate plumes have indicated degradation of mainly toluene and xylenes (Barker et al., 1986, Lyngkilde and Christensen, 1992b; Rügge et al., 1995), but positive results regarding benzene are few. Recently, Ravi et al. (1998) proved that benzene degradation took place in the very long plume at West KL Landfill (USA). The degradability of toluene and xylenes observed in plumes has been supported by experimental evidence from field and laboratory experiments (Acton and Barker, 1992; Nielsen et al., 1995a; Johnston et al., 1996; Bjerg et al., 1999; Rügge et al., 1999a), while recalcitrance of benzene has been shown in experiments by the same authors. This adds to the belief that benzene is less readily degradable than most of the other BTEXs under strongly anaerobic conditions.

The *phenolic compounds* generally degrade readily under aerobic conditions (Table 9.1). Information for anaerobic conditions is mixed, and no distinct pattern is evident. Recent studies indicate persistence of phenol, *o*-cresol, 2,4-dichlorophenol and 2,6-dichlorophenol under Fe reducing and NO₃⁻ reducing conditions (Nielsen et al., 1995a). Grbic-Galic (1990b) reviewed the methanogenic transformation of phenolic and aromatic compounds in aquifers in more general terms, and found transformation of several phenols.

The *pesticides* are another important group of pollutants in leachate. Mecoprop is frequently observed in leachate (Table 2.3), and at the Vejen Landfill (DK) Mecoprop was observed in the plume 130 m downgradient of the landfill at a concentration of 95 µg/l (Lyngkilde and Christensen, 1992b). Rügge et al. (1999b) found in the injection experiment in the Grindsted Landfill (DK) plume that Atrazine and Mecoprop were recalcitrant under strongly anaerobic conditions. However, only very little is known about pesticide degradation potentials in leachate plumes, and studies on pesticide degradation in different anaerobic environments are few.

9.7. XOC-associated toxicity

Although potential risks associated with contamination of groundwater aquifers with XOCs originating from landfill leachate have been pointed out by several authors (e.g. Cameron and Koch, 1980; Brown and Donnelly, 1988; Kross and Cherryholmes, 1993), the toxicity of XOCs in leachate polluted groundwater has received very little attention.

In a study by Baun et al. (1999), groundwater samples collected downgradient of Grindsted and Vejen Landfills (DK) were tested in a series of biotests. High toxic-

ity towards algae, daphnids, and bacteria was observed in tests of samples collected close to both landfills. A decrease in toxicity was observed with increasing distances from the landfills. Due to the complex composition of the samples with respect to inorganic constituents, the major part of the toxicity most probably reflected the high content of alkalinity and NH₄ and, thus, was not related to the presence of XOCs (Baun et al., 1999). Solid phase extraction (SPE), by which non-volatile XOCs were concentrated on a SPE resin, eliminated the matrix problem and allowed testing of samples with low concentrations of XOCs. The combination of SPE and biotests has previously been applied to other complex environmental samples like industrially polluted rivers and pesticide contaminated surface water (Galassi et al., 1992; Hendriks et al., 1994; Baun and Nyholm, 1996).

In another study (Baun et al., 2000), 27 groundwater samples were collected in the leachate plume downgradient from Grindsted Landfill (DK). The non-volatile XOCs were extracted by means of SPE, and the SPE-eluates were tested in a series of biotests. Toxicity decreased as a function of distance from the landfill, and the decrease in toxicity could not be explained by dilution. At distances greater than 114 m downgradient, the toxicity towards luminescent bacteria and freshwater algae was comparable to that of unpolluted reference samples (Fig. 9.9). Previous investigations of the Grindsted Landfill (DK) plume have shown that the majority of XOCs could not be detected at distances exceeding 60 m from the landfill (Rügge et al., 1995).

Baun et al. (2000) did not detect genotoxicity in leachate polluted groundwater samples which were pre-concentrated more than 120 times. In a study of the genotoxicity of various aqueous environmental samples, Helma et al. (1996) used a SPE pre-concentration technique on leachate and leachate polluted groundwater. The samples were pre-concentrated 4000–10 000 times, and only marginally positive and negative results were obtained. On the other hand leachates from municipal and mixed municipal and industrial landfills were the most potent genotoxic environmental samples tested.

The few studies performed to assess the toxicity of landfill leachate polluted groundwater indicate that biotests can be useful tools for toxicity characterization of XOCs in landfill leachate plumes, providing information which cannot be deduced solely from chemical analysis. For optimal performance, the application of a biotest battery should, however, be combined with chemical-analytical characterization of sample composition with respect to both XOCs and inorganic constituents. It is noteworthy that the toxicity of inorganic species such as NH₄ (present at concentrations in the mg/l range) often dominates the toxicity of trace amounts of XOCs (present at concentrations in the µg/l range).

9.8. Conclusions: XOCs

In aquifers characterized by low organic C content, most of the XOCs found in leachate plumes are only weakly attenuated by sorption. This applies to the aromatic hydrocarbons, chlorinated hydrocarbons, and the polar compounds. Very few detailed sorption studies involving landfill leachate have been reported. Preliminary evidence suggests that the presence of leachate, in particular in terms of dissolved organic C, does not affect the sorption of XOCs significantly and as such the traditional methods for estimating retardation are valid.

Recently, information on XOC degradation in different landfill plume redox environments has been expanded. As more results become available, more XOCs are found degradable in the intermediate redox zones dominated by SO_4^{2-} , Fe and NO_3^- reduction. Transformation of chlorinated aliphatics seems to occur not only under methanogenic conditions, but also in less reducing zones. Aromatic hydrocarbons degrade readily in aerobic environments, but only slowly in reducing environments. Benzene may, in particular, be recalcitrant under strongly reducing conditions. As the understanding of how to perform degradation studies has improved significantly during the 1990s, more detailed information on complex degradation patterns and compound interactions have been revealed. Overall, several compounds have been shown to disappear in plumes, but direct evidence of microbial degradation has only been established for some of these XOCs.

10. Conclusion

Leachate from landfills contains a wide range of contaminants: dissolved organic matter, inorganic cations and anions, heavy metals, and xenobiotic organic compounds. Where leachate enters the groundwater, significant changes in water quality are observed and complicated biogeochemical patterns develop in the leachate pollution plume.

The general shape of the leachate plume is governed by the flow field of the aquifer, the leachate mound often observed below landfills, the increased density of the leachate and the dispersion. However, the highly varying leaching pattern at landfills may locally affect the size, location and composition of the plumes. In most cases the plumes are relatively small: a few hundred meters wide and less than a thousand meters long. In a few cases, the plumes have stretched more than 1000 m. The dilution of the leachate contaminants is substantial, primarily due to local heterogeneities in the hydrogeology. Most of the information on leachate plumes originates from plumes in sandy aquifers.

The reduced leachate creates a sequence of redox zones in the groundwater, with methanogenic conditions

close to the landfill and oxidized conditions in the outskirts of the plume. Local conditions govern which redox zones are the most important, but all reported plume studies indicate the presence of various redox zones. The anaerobic zones are driven by microbial utilization of dissolved organic matter in the leachate in combination with reduction of oxidized species in the aquifer. Fe reducing conditions seem to be significant at many landfills, providing substantial buffering with respect to redox by reducing Fe oxides on the aquifer sediment and precipitating reduced Fe species.

Dissolved organic matter in leachate plumes seems to be dominated by fulvic-like compounds of moderate molecular size. Sorption of these compounds is moderate in aquifers, but they seem to degrade over time according to field observations. Degradation rates have so far not been measurable in laboratory experiments, but preliminary estimates based on field observations suggest half-lives in the order of 1–3 a.

The cations and anions (excluding Cl^- that is a conservative compound) are subject to ion exchange, reduction/oxidation (SO_4^{2-} , NO_3^- , Fe, Mn, NH_4), complexation and precipitation, and exhibit very intricate patterns in the leachate plume. Although it is difficult to generalize, NH_4 and K seem to be the most retarded macro-ions while Ca and Na usually are found furthest away from the landfill. Ammonium may constitute a significant long term pollutant in leachate plumes, because NH_4 concentrations in leachate stay high for extended time, and because the apparent attenuation, probably involving anaerobic oxidation, is not yet understood.

Heavy metals are not considered a major groundwater pollution problem in landfill leachate plumes, because concentrations usually are low in the leachate, and because heavy metals are strongly attenuated by sorption and precipitation. The presence of SO_4^{2-} reducing zones may provide a precipitation trap for heavy metals. Although the dissolved organic matter in the plume does complex heavy metals, in particular Pb and Cu, this is usually not sufficient to make heavy metals mobile in leachate plumes.

Xenobiotic organic compounds in leachate are not very extensively attenuated by sorption onto aquifer material, but recent reports show that many organic compounds are degradable in the strongly anaerobic environments in leachate plumes. Field studies on actual plumes tend to suggest more abundant degradation of organic compounds than documented by controlled experiments in the laboratory and in field systems. This may to some extent be due to the very low degradation rates involved. The information on the degradability of xenobiotic organic compounds in strongly reducing redox environments is still fairly scarce, and for many compounds found in leachate, no information is available. The Fe reducing zone seems to play an emerging but significant role in this context. Due to their low

water quality criteria, xenobiotic organic compounds may constitute a very significant group of leachate contaminants, although they constitute only a few per cent of the total DOC. However, their fate and correlation with the other biogeochemical reactions in the plume is not yet fully understood.

This review of the biogeochemistry of landfill leachate plumes reveals that natural attenuation is substantial for many contaminants, but much remains to be learned if we are to develop a coherent general understanding of the governing factors as needed for proper risk assessment, design of safety zones and remedial measures. This may also explain why monitored natural attenuation still has not been applied very often as a remediation approach for leachate plumes (Christensen et al., 2000b).

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