

Redox zones of a landfill leachate pollution plume (Vejen, Denmark)

John Lyngkilde and Thomas H. Christensen

*Department of Environmental Engineering, Groundwater Research Centre, Technical
University of Denmark, Building 115, DK-2800 Lyngby, Denmark*

(Received September 3, 1991; accepted for publication December 2, 1991)

ABSTRACT

Lyngkilde, J. and Christensen, T.H., 1992. Redox zones of a landfill leachate pollution plume (Vejen, Denmark). *J. Contam. Hydrol.*, 10: 273–289.

Downgradient from an old municipal landfill allowing leachate, rich in dissolved organic carbon, to enter a shallow sandy aerobic aquifer, a sequence of redox zones is identified from groundwater chemical analysis. Below the landfill, methanogenic conditions prevail, followed by sulfidogenic, ferrogenic, nitrate-reducing and aerobic environments over a distance of 370 m. This redox zone sequence is consistent with thermodynamical principles and is closely matched by the leachate plume determined by the chloride plume distribution. The redox zone sequence is believed to be key in controlling the fate of reactive pollutants leached from the landfill.

INTRODUCTION

Numerous reports exist in the literature on groundwater contamination caused by landfills with insufficient leachate collection systems and by old waste dumps with no measures to prevent leachate from entering the groundwater (e.g., Baxter, 1985; Albaiges et al., 1986; Barker et al., 1986, 1988).

Leachate from landfills containing organic matter has a content of dissolved organic carbon (DOC) in the range of thousands of mg L^{-1} C (Ehrig, 1983). The DOC, including for example fatty acids, and humic- and fulvic-like compounds, may act as a substrate for microbial processes in the aquifer potentially inducing major changes in the governing redox environment. Close to the landfill, the aquifer supposedly will become methanogenic, similar to the methanogenic conditions that exist in most landfills. Depending on the interaction between migrating leachate rich in organic carbon, the

Correspondence to: T.H. Christensen, Department of Environmental Engineering, Groundwater Research Centre, Technical University of Denmark, Building 115, DK-2800 Lyngby, Denmark.

kinetics of the actual redox processes and the availability of the electron acceptors, a sequence of redox zones may, from a thermodynamic point of view, develop downgradient from the landfill ranging from methanogenic, sulfidogenic (sulfate reduction), ferrogenic (Fe(III) reduction), manganogenic (Mn(IV) reduction), nitrate-reducing to aerobic conditions in the most diluted part of the plume farthest away from the landfill. This hypothesized sequence assumes that the oxidized species are present in the aquifer in significant quantities: free oxygen, nitrate and sulfate in the groundwater and oxidized Fe and Mn compounds in solids associated with the aquifer sediment. If some of these electron acceptors are missing, the corresponding redox zones, of course, are also missing.

The presence in landfill leachate plumes of zones with redox conditions deviating from the dominating redox potential in the aquifer has previously been proposed by Champ et al. (1979) but to our knowledge this has never been documented in any detail. This is unfortunate, since the behaviour of most reactive contaminants depends highly on the redox environment, and in the case of landfill leachate pollution plumes, where a sequence of redox zones is hypothesized, the redox environment present supposedly is the main key to understanding the fate of pollutants in the plume.

The purpose of this paper is to investigate the type and extent of redox zones present in a shallow, naturally well-oxidized aquifer polluted by an actual, old landfill containing among other waste materials degradable organic waste such as household refuse. A following paper deals with the fate of organic pollutants in this sequence of redox zones (Lyngkilde and Christensen, 1992).

VEJEN LANDFILL

The Vejen Landfill is located in the western part of Denmark (Fig. 1) in a glacial outwash plain from the Weichselian Period (late Quaternary). The landfill is partly located on the ground surface and partly dug into the ground. The upper aquifer is a 10–20-m-deep sandy deposit with small random clay and silt clasts. The water table is located 3–5 m below ground surface. The landfill is located ~5 km from the water divide and the groundwater pore flow velocity in the area is in the order of 150–200 m yr⁻¹. The area is intensively farmed and the annual precipitation is of the order of 700–900 mm. The upper part of the shallow aquifer is well oxidized, containing free oxygen, high nitrate concentrations and some sulfate (Pedersen et al., 1991). The bottom part of the shallow aquifer is anoxic and has no nitrate.

In the period 1962–1981 the landfill received ~0.45 Mt* of waste including

* 1 Mt = 1 megatonne = 10⁹ kg.

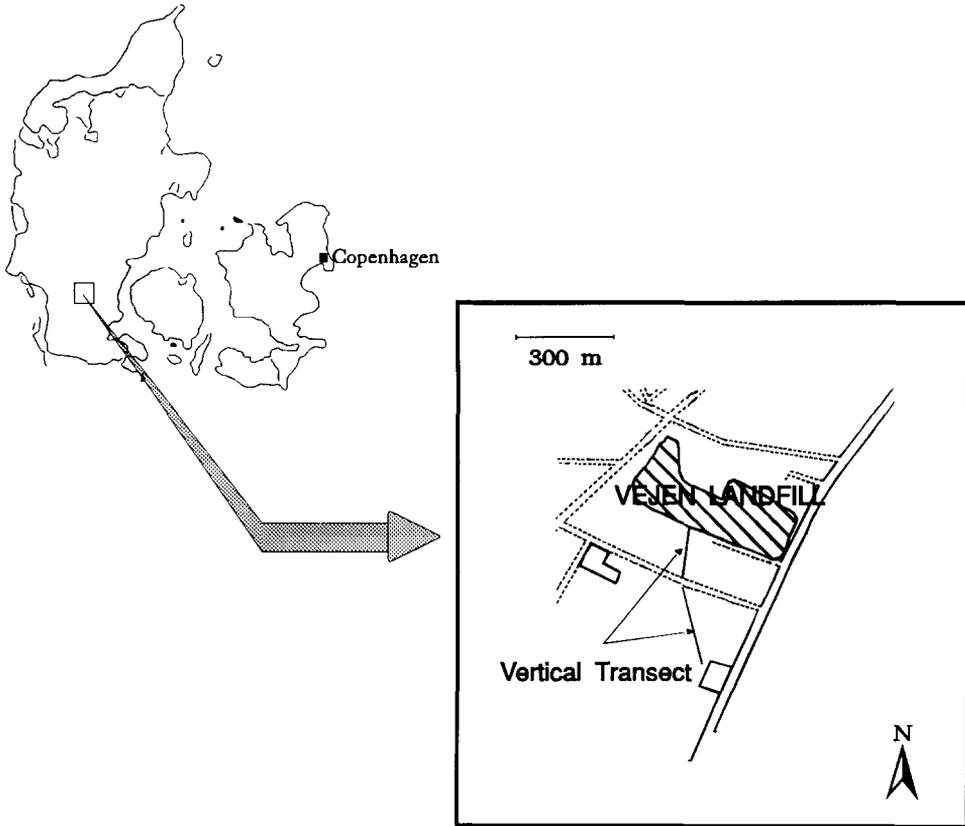


Fig. 1. Geographical location of Vejen Landfill, Denmark. The magnified section shows the location of the vertical transect downgradient of the landfill from where groundwater samples were collected.

municipal waste, demolition waste, industrial waste and chemical waste (Kjeldsen, 1991). The landfill has no engineered leachate collection system and a combination of various soil types forming the base of the landfill and the presence of drainage ditches forms a relatively complicated landfill hydrology. The longitudinal transect of the aquifer, which has been studied with respect to redox zones, begins in an area primarily containing household waste and minor amounts of demolition waste. At this area of the landfill its upstream length is ~ 100 m and the waste placed on the ground surface to a height of 6 m. This section of the landfill was in use in the period 1973–1977. The landfill is covered by a soil cover. Leachate sampled inside the landfill contains DOC of the order of $500 \text{ mg L}^{-1}\text{C}$, a BOD_5/COD (5-day biological oxygen demand/chemical oxygen demand) ratio of 0.08, a pH of 6.8 and levels of inorganic and organic contaminants resembling municipal landfill leachate in general (Kjeldsen, 1991).

TABLE 1

Criteria for redox parameters used for assigning redox status to groundwater samples (all values in mg L^{-1})

Parameter	Aerobic	Nitrate-reducing	Manganogenic	Ferrogenic	Sulfidogenic	Methanogenic
Oxygen	> 1.0	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0
Nitrate	-	-	< 0.2	< 0.2	< 0.2	< 0.2
Nitrite	< 0.1	-	< 0.1	< 0.1	< 0.1	< 0.1
Ammonium	< 1.0	-	-	-	-	-
Mn(II)	< 0.2	< 0.2	> 0.2	-	-	-
Fe(II)	< 1.5	< 1.5	< 1.5	> 1.5	-	-
Sulfate	-	-	-	-	-	< 40
Sulfide	< 0.1	< 0.1	< 0.1	< 0.1	> 0.2	-
Methane	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	> 1.0

- = no criterion is applied.

REDOX CRITERIA

Electrochemical determination of redox potentials is mechanically very simple, but according to experience often yields results difficult to interpret or in some cases even misleading (Germanov et al., 1959; Lindberg and Runnels, 1984). Identifying redox zones is assumed to be a key to understand leachate pollutant fate in the plume. These realizations and the fact that determination of an exact redox potential is not needed but rather an identification of the dominating redox processes as expressed by the electron acceptor being reduced by the DOC, lead to the choice of assigning redox status of the aquifer based on analysis of groundwater samples for redox-sensitive compounds.

Introductory drilling and groundwater characterization in the leachate polluted aquifer provided experience with sampling, analysis of redox-sensitive parameters and data on the leachate affected groundwater quality. This led to the development of criteria for assigning redox status based on concentrations of oxygen, nitrate, nitrite, ammonium, manganese, iron, sulfate, sulfide and methane as shown in Table 1.

Aerobic conditions are identified by free oxygen (O_2) concentrations in excess of 1.0 mg L^{-1} and very low concentrations of all reduced species. The value of 1.0 mg L^{-1} is defined in order to minimize the presence of nitrate-reducing microenvironments in the aerobic aquifer. Pedersen et al. (1991) showed that in the same aquifer nitrate reduction could be observed even when free oxygen was determined in sampled groundwater. The criterion concentration for Fe in the aerobic environment is paying attention to the experience that although all samples are filtered through a $0.15\text{-}\mu\text{m}$ filter (refer

to Materials and Methods) the possibility exists that very small particles of oxidized iron may pass the filter leading to a detectable concentration of Fe upon acidification of the filtered sample. Methane produced in the methanogenic zone may spread to other zones by the water flow if not oxidized. The rates of methane oxidation by sulfate and nitrate are not well determined in aquifers but are expected to be slow. Therefore, a low concentration of methane does not exclude more oxidized redox conditions. Methane may also originate from strongly anaerobic silt and clay clasts in the sandy aquifer.

In the nitrate-reducing zone, the concentration levels must be low for oxygen as well as for the more reduced species, but no criteria are associated with the nitrogen compounds. Nitrate concentrations could be high in the nitrate-reducing zone, if the organic carbon is the limiting factor, or low if nitrate is the limiting factor.

The manganese- and ferrogenic zones are defined by the presence of substantial concentrations of dissolved Mn and/or Fe. In their oxidized state, Mn and Fe are practically insoluble at the actual pH levels (5–7) and dissolved concentrations are considered to represent reduced species: Fe^{2+} and Mn^{2+} . Correlating this method of quantifying total amounts of dissolved Fe by atomic absorption with respect to direct determination of reduced Fe by spectrophotometrical analysis using the Ferrozine[®] method gave excellent results (Postma et al., 1990).

The sulfidogenic zone contains some sulfide. However, the presence of reduced Fe and Mn may cause precipitation of metal sulfides and may lead to very low concentrations of sulfide. At the same time sulfate may still be high if the reduction process is limited by organic matter.

The methanogenic zones and the sulfidogenic zones may be very closely related, due to their similar redox potentials, and a strict distinction may be difficult. However, sulfate concentrations should not be too high and methane should be present in significant levels.

The applied criteria are consistent with thermodynamical principles, but concentration-based criteria are established since a meaningful calculation of the redox potential from the Nernst equation is not warranted in such a complex system as a leachate polluted aquifer. The actual criterion concentrations are operationally defined paying attention to the water chemistry of the compounds, and experiences on sampling and water sample analysis.

METHODS AND MATERIALS

Field sampling and analysis

All groundwater samples were taken from 1-in (2.54 cm) iron pipes rammed into the ground by a motor-driven hammer. The iron pipes were fitted with tips supplied with 10-cm-long iron screens and Teflon[®] check valves. Samples

were taken every 0.5 m during the ramming through a Teflon[®] tube lowered into the iron pipe by pressuring the pipe with nitrogen. The Teflon[®] tube was connected to a multiboard device (Fig. 2) to allow sampling of groundwater and direct analysis of oxygen, pH, redox potential, temperature and chemical conductivity in flow cells. Measurements of oxygen was performed using a WTW Oxi 196[®] instrument and a WTW EO 196-1,5[®] oxygen electrode. Measurements of redox potential were performed using a WTW pH 196[®] instrument and an Ingold Pt-4805[®] electrode. pH was measured using a WTW pH 196[®] instrument and a WTW SenTix 96[®] pH electrode. Chemical conductivity was quantified using a WTW Conductometer LF 191[®] instrument and a WTW LS 1/T-1,5[®] conductivity electrode. Sample filtering took place in one or two containers that could be pressurised with nitrogen. For volatile components like methane and sulfide, sampling took place in an unbroken water stream before filtering. All samples, except those for methane and sulfide analysis, were pressure-filtered through a Schleicher and Schnell OE65[®], Ref. No. 404 216, 0.15- μm membrane filter. Alkalinity was measured in the field by Gran titration (Macca and Bombi, 1989) with diluted sulphuric acid (0.02 M). All other analysis — except those performed in the flow cells — were performed in the laboratory.

Preservation of samples was done in the field after the sampling. Samples for NVOC (non-volatile organic carbon) and metal determination were preserved by adding 1 mL conc. sulphuric acid to 100 mL groundwater and 1 mL conc. nitric acid to 60 mL groundwater, respectively. Samples for ammonium were preserved by adding 50 μL conc. sulphuric acid to 10 mL groundwater, and those for nitrate and nitrite determination were preserved with 1 drop of a 0.22 M solution of mercury chloride to 10 mL groundwater. Samples for analysis of sulfate and chloride were not preserved, but kept cool at 0–10°C. If sulfide was present, it was driven out of the sample with nitrogen gas at the site immediately after the sample for sulfate analysis was taken. At pH > 7.5, the sulfide was driven out of the water sample by using carbon dioxide instead of nitrogen. For methane analysis, 6.5-mL water samples were transferred from the unbroken water stream before the pressurised filter containers to an evacuated Venoject[®] blood sample vial (13 mL) by use of a syringe. Three drops of conc. sulphuric acid were added to the Venoject[®] vials for preservation by use of a syringe. The samples for sulfide determination were preserved by adding 10 mL of a strong basic, antioxidating solution (Midgley and Torrance, 1978) to the 10-mL groundwater sample. All samples except those for methane determination were kept in polyethylene bottles.

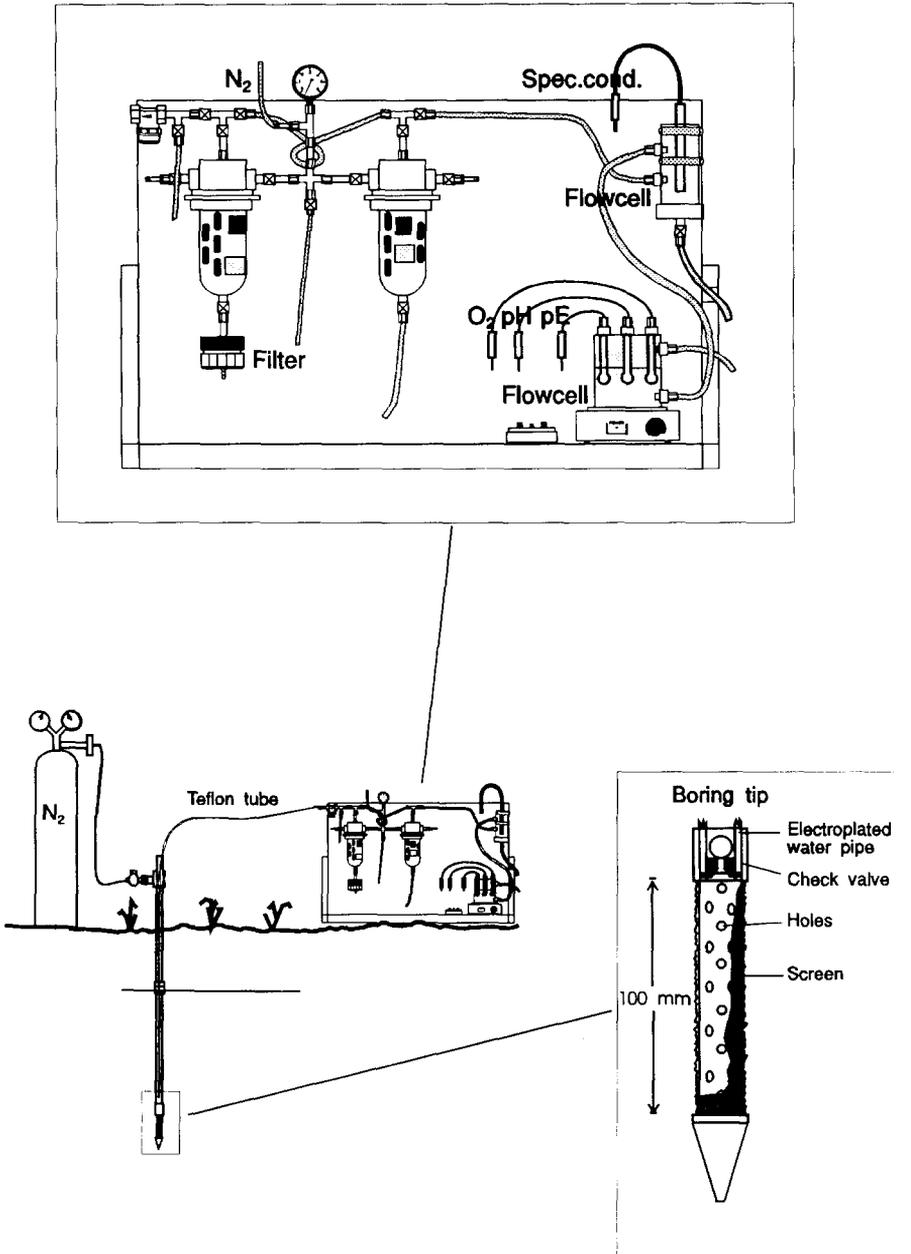


Fig. 2. Set-up used for collecting redox-sensitive groundwater samples. The iron tube provided with a filter-tip is rammed into the ground by a motor-driven paviour.

Laboratory analysis

Sulfide determination was done with a Radiometer F1212S[®] selective sulfide electrode. The detection limit was $100 \mu\text{g L}^{-1} \text{S}^{2-}$. It is important to carry out the quantification of sulfide in close to darkness to get consistent results. Changes in light conditions cause the electrical potential in the reaction chamber to deviate by as much as 40–50 mV, corresponding to a difference in sulfide concentration in the order of 2–3 decades. This means that small concentrations of sulfide can be vastly overestimated, especially in the field analysis where light conditions can vary significantly during the time of measurements. The need of such precautions of excluding interfering light is not mentioned by Midgley and Torrance (1978), and the mechanism of interference is not known to us, but is probably caused by formation of active radicals by interaction of light.

NVOC analysis was performed by standard procedures on a Dohrmann DC-80[®] TOC (total organic carbon) analyzer.

Metals were quantified on a Perkin-Elmer 370[®] atomic absorption spectrophotometer. Wavelengths for Fe, Mn and Ca are 247.9, 279.5 and 422.4 nm, respectively.

All nitrate, nitrite, ammonium, sulfate and chloride analysis were performed by a standard autoanalyzer routine (Technicon[®] Autoanalyzer II).

Methane was quantified by injecting 100–500 μL of the air-phase from the Venoject[®] vials on a Carlo-Erba Mega 5300[®] gas chromatograph equipped with a flame ionization detector, and a J&W column DB-5[®], 30 m \times 0.53-mm OD, 1.5- μm film thickness. Nitrogen was used as a carrier gas at 10 mL min^{-1} at 40°C. The oven temperature was isothermally kept at 40°C. The injector temperature was kept at 250°C, and the detector was kept at 275°C. The results were compared to external standards made by injecting known volumes of methane into vials containing 6.5 mL water and three drops of conc. sulphuric acid.

Monitoring strategy

Groundwater sampling was performed in two different types of borings: B- and P-borings.

A transect composed of 9 B-borings was placed along the main flow direction of the plume reaching 370 m out from the landfill. All B-borings were monitored only once, and they were left at their final depths below the plume. An average of 0.5 m between sampling points was used and the number of sampling points per boring was in the range of 13–31.

P-borings were sampling filters permanently located inside the plume. They were monitored several times. The P-borings were established to evaluate

redox consistency within the plume and fluctuations over time in redox assignment. All P-borings were placed within 130 m from the landfill.

Sampling of the transect (B-borings) was accomplished within 2 months and approximates a snapshot of the plume distribution in the aquifer. Because of the age of the landfill and the relatively short time of sample collection, stationarity of the pollution plume was assumed. The year before the sampling, however, the largest precipitation within 30 years occurred and in the field investigation period there was no precipitation at all. These conditions could influence the redox zones and the permanent P-borings were installed to allow for sampling over time to evaluate any changes.

RESULTS AND DISCUSSION

The results of the groundwater characterization is presented in terms of: (1) a vertical transect of chloride illustrating the pollution plume; (2) selected vertical profiles of several parameters illustrating the groundwater quality and its variation over depth; and (3) redox zones identified in the vertical transect. Finally, the variation over time is evaluated based on the data from the permanent filters located inside the pollution plume.

Chloride plume

Based on the analysis of the chloride content in groundwater samples, a vertical transect of the pollution plume was determined as shown in Fig. 3. The most significant intrusion of leachate into the groundwater is located within a 2–3-m-deep area 3 m below the groundwater table where chloride concentrations of the order of 500–1200 mg L⁻¹ are observed. Within the first 50 m downgradient of the landfill, the plume splits into two separated parts. At a distance of 100 m, dilution of the plume has become significant and again only one front is recognizable. In yet greater distance downgradient of the landfill (200–300 m) differences in concentration of chloride occurs over depth. However, the differences are small — less than a factor of 2 — and this makes it impossible to distinguish between a splitting of a homogeneous plume and the occurrence of local, elevated chloride concentrations. The geology of the aquifer is not known in detail but during drilling and collection of groundwater samples substantial variations have been encountered within short distances from the landfill.

Characterization of the polluted groundwater

The presence of the pollution plume influences the groundwater quality dramatically as shown for three selected profiles (Fig. 4) presenting data for

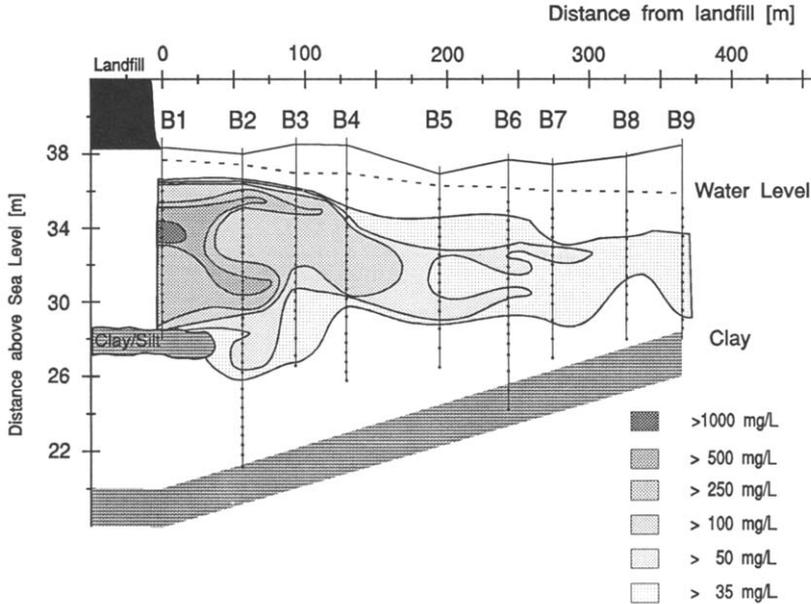
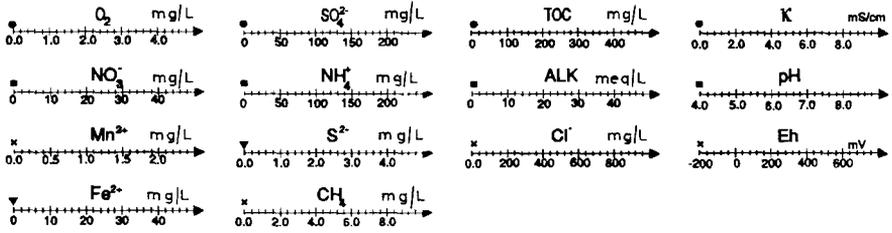


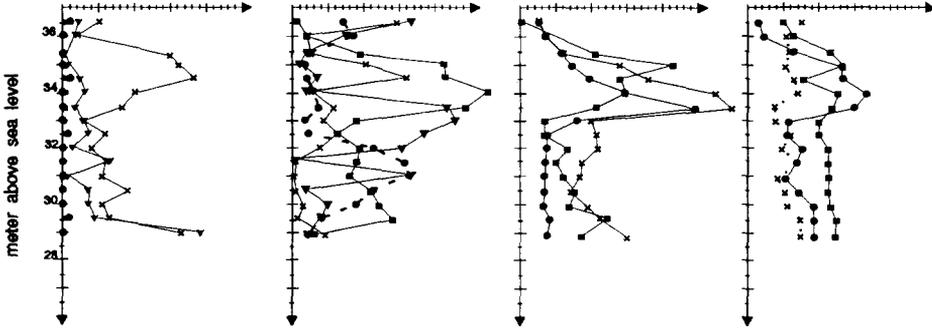
Fig. 3. Chloride contours in a vertical transect downgradient of Vejen Landfill, Denmark. The contours indicate the pollution plume migrating from the landfill into the groundwater. The *small dots* on the vertical borings represent sample points.

the redox-sensitive species and for pollution indicators over depth. Boring B1 is located 5 m from the physical boundary of the landfill and represents strongly polluted groundwater. In this zone strongly reduced species such as methane, sulfide and ammonium predominate with concentrations up to 6.3, 4.5 and 262 mg L⁻¹, respectively. In some of the permanent filters in this area concentrations of methane as high as 17.6 mg L⁻¹ have been observed which is close to the solubility of methane in water in equilibration with methane at 1 atm. (24 mg L⁻¹, $T = 290$ K; Windholz et al., 1983). Fe concentrations in B1 are low, probably because of precipitation of iron sulfide and iron carbonate, due to the high concentrations of sulfide and alkalinity. The groundwater near the landfill is well buffered with respect to pH and redox potential. In all other borings pH increases with depth, as in borings B3 and B9. The redox potential in other borings shows more individual variations. Boring B3 (95 m) represents moderately polluted groundwater diluted 3–10 times compared to the water quality of boring B1. Most of the strongly reduced species are at insignificant concentration levels and here Fe, Mn and SO₄²⁻ predominate at concentrations of 40, 1.2 and 80 mg L⁻¹, respectively. Boring B9 (365 m) represents only slightly polluted groundwater diluted

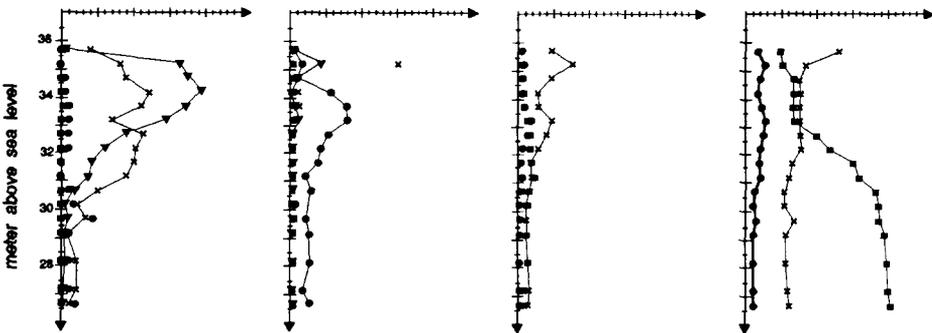
Fig. 4. Selected profiles (borings 1, 3, 9) for various groundwater parameters. All values are mg L⁻¹, except pH, Eh (mV), alkalinity (meq L⁻¹) and specific chemical conductivity (mS cm⁻¹).



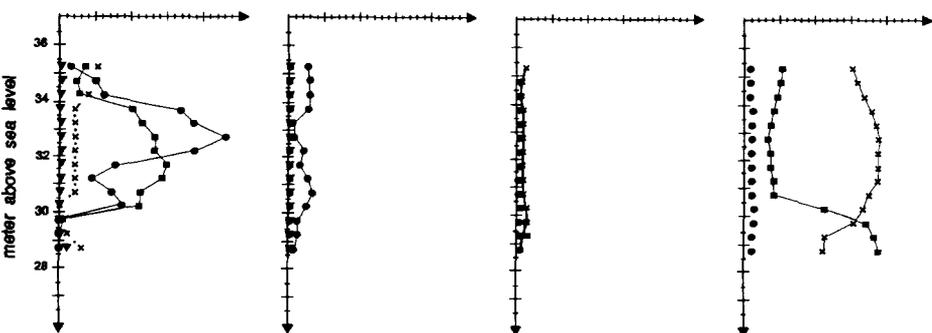
BORING 1



BORING 3



BORING 9



30–50 times compared to the groundwater in boring B1. At this distance from the landfill, oxygen and nitrate occur in the groundwater and sulfate and chloride exhibit only slightly elevated levels compared to background concentrations, as described by Bjerg and Christensen (1992).

Redox zones

According to the scheme in Table 1, each groundwater sample was assigned a redox status based on the concentrations of redox-sensitive parameters. The redox status is based solely on the chemical characteristics of the groundwater, tacitly assuming that the redox species are approaching chemical equilibrium. Only a few of the water samples (5%) do not comply with the criteria. Typically, these are samples with high contents of iron and sulfate, and methane concentrations within the range $1\text{--}5\text{ mg L}^{-1}$. These samples were evaluated in comparison with characteristics of adjacent samples and typically were characterized as ferrogenic, assuming that methane had been transported to the sampling point by the groundwater from an upgradient zone with methanogenic conditions.

The characteristics of the groundwater samples from the B-borings assigned the same redox status are summarized in Table 2 in terms of parameter range and average. The large range observed for most of the parameters within each redox status shows the wide span of groundwater samples belonging to the same group. However, average values reveal that redox status is closely correlated to the pollution level, showing high concentrations of chloride, alkalinity, NVOC, methane and ammonium in the methanogenic zone and levels approaching background values in the aerobic zone. Some of the discrepancies between redox zone and pollution level is found in the deep borings reaching deep below the plume. In some of these depths methane development and sulfate reduction occurs in the presence of very low levels of NVOC ($2\text{--}4\text{ mg L}^{-1}$) and these reactions are assumed to be natural processes. Concentrations of chloride at background levels in these locations indicate no influence from the landfill plume.

The assigned redox status of the groundwater is shown in the longitudinal transect (Fig. 5). A methanogenic zone is located within 50 m from the landfill and is surrounded by a discontinuous sulfidogenic zone. This sulfidogenic zone is split into two layers of which the upper one near the surface has a very sharp contour, just like the chloride map shown in Fig. 3.

By far the most extensive redox zone is the ferrogenic zone stretching at least 350 m downgradient from the landfill. The ferrogenic zone is supposedly formed by reduction and solubilization of iron oxyhydroxides naturally associated with the sediment, caused by the reducing organic matter of the leachate. The groundwater samples assigned a manganogenic redox status do

TABLE 2

Summary of groundwater characteristics (range, average and number of samples, *n*) according to defined redox zones

Parameter	Aerobic Range Avg. (<i>n</i> = 43)	Nitrate-reducing Range Avg. (<i>n</i> = 159)	Mangano-genic Range Avg. (<i>n</i> = 14)	Ferro-genic Range Avg. (<i>n</i> = 105)	Sulfido-genic Range Avg. (<i>n</i> = 31)	Methano-genic Range Avg. (<i>n</i> = 14)
Oxygen	1.0–7.0 3.01	0.0–0.9 0.15	0.0–0.5 0.13	0.0–0.9 0.07	0.0–0.3 0.06	0.0–0.2 0.05
Nitrate	0.84–29.47 11.973	0–27.70 1.634	0–0.80 0.125	0–0.48 0.042	0–0.29 0.086	0–0.47 0.154
Nitrite	0–0.48 0.032	0–0.20 0.014	0–0.14 0.017	0–0.03 0.002	0–0.02 0.002	0–0.13 0.015
Ammonium	0–0.35 0.021	0–0.95 0.084	0–1.01 0.208	0–81.30 1.094	0–139.40 24.693	0–262.20 77.486
Mn(II)	0–0.5 0.10	0–0.5 0.09	0.3–0.9 0.41	0–1.2 0.35	0–1.6 0.60	0.1–1.8 0.73
Fe(II)	0–5.6 0.64	0–7.1 0.61	0–1.4 0.83	1.5–39.0 8.88	0–76.0 21.00	0.5–38.0 7.54
Sulfate	2–301 42.3	6–95 35.3	6–70 34.6	6–155 57.5	0–156 51.7	1–38 14.5
Sulfide	0 0.00	0 0.00	0 0.00	0–0.2 0.00	0–33.0 3.98	0–4.5 1.05
Methane	0–0.14 0.033	0–1.60 0.064	0–0.51 0.078	0–4.48 0.391	0–5.87 0.550	1.03–6.30 2.524
Redox potential	+103 to +546 +385.0	–91 to +546 +155.1	+20 to +319 +123.0	–83 to +409 +113.0	–29 to +169 +85.3	–55 to +150 +63.1
NVOC	1.2–6.3 2.80	1.2–20.5 2.91	1.3–7.5 2.36	1.2–71.9 6.43	2.1–119.1 32.57	2.3–484.0 104.70
Alkalinity	0.0–1.6 0.28	0.0–5.3 1.81	0.3–5.2 2.48	0.0–10.1 1.92	0.3–23.9 6.46	0.7–42.9 12.08
Chloride	16–71 30.1	14–108 36.3	16–188 48.4	15–341 75.5	13–764 225.3	13–1,181 384.7
pH	4.6–7.2 5.27	4.7–8.2 7.00	4.9–8.0 7.18	4.9–7.9 6.38	5.0–7.6 6.27	5.0–7.3 6.51

All units are in mg L⁻¹, except alkalinity (meq L⁻¹), redox potential (mV) and pH (dimensionless). Nitrate, nitrite and ammonium units are mg L⁻¹ N. NVOC unit is mg L⁻¹ C.

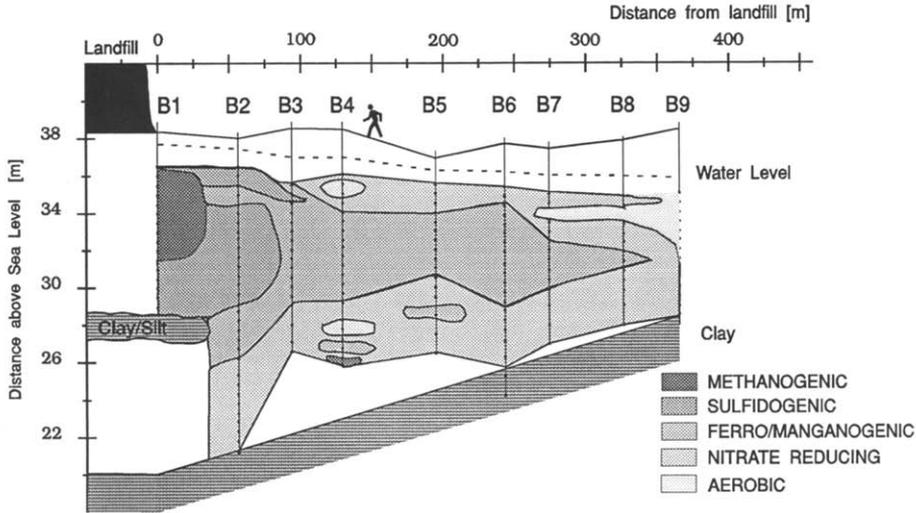


Fig. 5. Distribution of redox zones in the groundwater downgradient of Vejen Landfill, Denmark. The dots on the vertical borings represent individual sample points where groundwater samples have been collected and characterized.

not constitute a continuous zone, but are usually found as small independent areas, often characterized by low NVOC values. Theoretically, the manganogenic zones will appear in the boundaries between the ferrogenic and nitrate-reducing zones. One probable reason for the absence of continuous manganogenic zones is a low initial content of oxidized Mn in the sediment and removal of the dissolved Mn(II) from the deoxygenated part of the aquifer. Typically the Mn content of the sediment is much lower than the Fe content. Alternatively, Mn can be totally missing in some locations and a manganogenic zone will never develop. Another explanation for missing manganogenic zones is that Fe(II) liberated from the upgradient ferrogenic zone enters the manganogenic zone, resulting in elevated Fe concentrations in the manganogenic zone and thereby causing a wrong assignment of redox status. These considerations support the choice of mapping the ferrogenic and manganogenic zone as one unified zone, but it should be emphasized that the redox characterization is based solely on chemical analysis of inorganic species in water samples.

A significant nitrate-reducing zone is found, convoluting the ferrogenic/manganogenic zone. The nitrate available for reduction is believed to originate from the agricultural fields. The fields in the area are intensively fertilized and nitrate concentrations of the order of $20\text{--}30\text{ mg L}^{-1}$ are common. The extensive nitrate-reducing zone in the bottom part of the aquifer is primarily located below the plume and is considered to be governed

by natural processes and the flow of anoxic groundwater passing below the silt-clay lens found under the landfill.

Variations over time

The results from the permanent P-borings obtained over a period of 9 months are generally in agreement with the results from the non-permanent B-borings showing that the identified redox zones within the first 130 m from the landfill are fairly stable in space and time. This means that occurrence and distribution of the redox zones are confirmed within 130 m from the landfill. One exception is total absence of sulfide in all permanent filters. Maximum concentrations of sulfide of $\sim 30 \text{ mg L}^{-1}$ were found in the B-borings. One concern was Zn and Fe released from the filters potentially precipitating any sulfide present in the groundwater. A closer examination of this and installation of metal-free Teflon[®] filters excluded the possibility that absence of

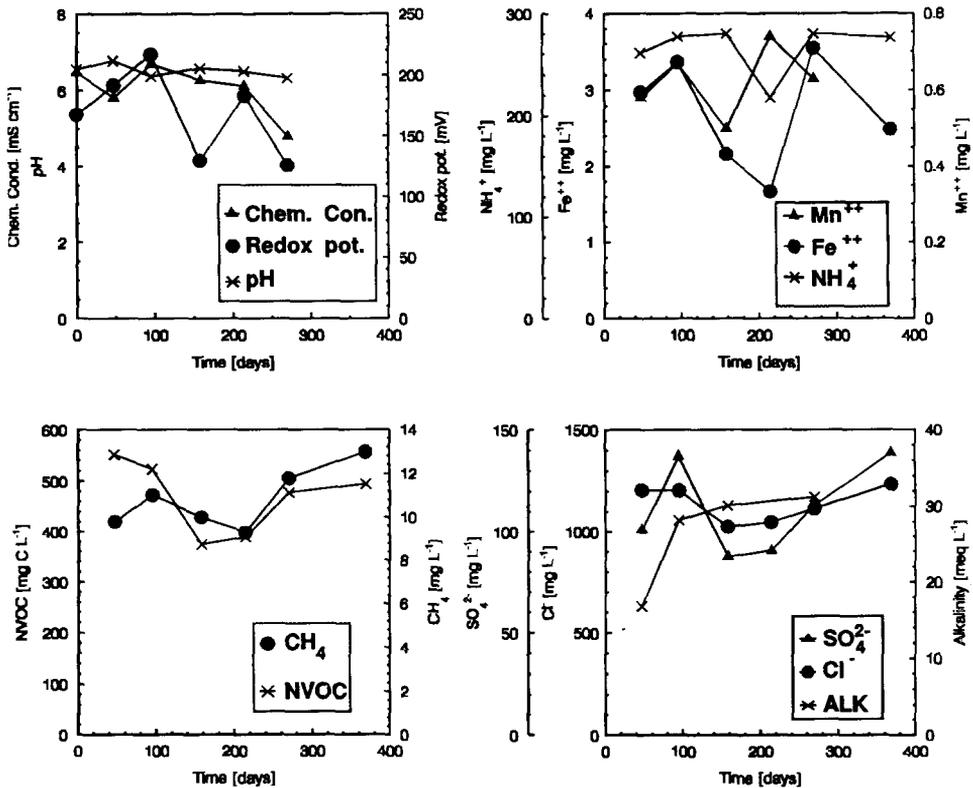


Fig. 6. Example of the time variation of some chemical species in a permanent filter 5 m downgradient of Vejen Landfill, Denmark.

sulfide was an artifact. These results indicate that sulfide disappeared from the zone near the landfill within a few months after the first mapping. The reason for this disappearance of sulfide is still unknown but precipitation with Fe in the plume may be the cause.

Groundwater parameters showed some variations in concentrations over time in the pollution plumes. Fig. 6 shows an example of this time variation for different species for a selected filter. In the permanent P-filters located within 130 m from the landfill, no oxygen, nitrate or nitrite have been detected. The groundwater in the plume has generally been very well buffered over time in all P-borings with coefficients of variation for pH in the range of 1–7% for the different filters. All other parameters show greater variance over time. Generally, the coefficients of variation are in the range of 5–50%. In a few incidents the coefficients are higher, but the reason usually is a variance among small values or one single outlier.

There have been very few changes in the assigned redox status over time (9 months) in these permanent filters. All changes in redox status have been between methanogenic and ferrogenic conditions, and all changes were based upon small variations in the sulfate concentrations around a mean value close to 40 mg L^{-1} , which, according to Table 1, is the criterion value. This consistency of redox conditions in the pollution plume justifies the assumptions of stationarity in the plume within the time scale of investigation.

CONCLUSIONS

Based on inorganic groundwater sample characterization, a sequence of redox zones was identified in the leachate pollution plume downgradient of the Vejen Landfill, Denmark. Over a 370-m downgradient distance, the redox zones changed from methanogenic, sulfidogenic, over ferrogenic, to nitrate-reducing and aerobic zones. Manganogenic zones were small and scattered. The ferrogenic zone is by far the largest zone in the leachate plume, stretching for nearly 350 m. All identified redox zones within the first 130 m from the landfill, except the sulfidogenic zone, proved to be stable within a 9-month observation period, although this period was characterized by some extremes with respect to rain fall.

The identified, thermodynamically sound sequence of redox zones downgradient from the landfill is considered to be a key factor, together with the biological activities of the zones, their hydraulic retention times and the availability of dissolved organic carbon, in understanding the fate of pollutants in the leachate plume.

A following paper (Lyngkilde and Christensen, 1992) discuss the fate of organic pollutants in view of the identified zones.

ACKNOWLEDGEMENTS

This study is part of a major research programme focusing on the effects of waste disposal on groundwater. The programme is funded by the Danish Technical Research Council, the Technical University of Denmark and the Commission of the European Communities. The technical assistance by Bent Skov, Anja Foverskov, Tage V. Andersen and Thomas Larsen is gratefully acknowledged.

REFERENCES

- Albaiges, J., Casado, F. and Ventura, F., 1986. Organic indicators of ground water pollution by a sanitary landfill. *Water Res.*, 20(9): 1153–1159.
- Barker, J.F., Tessmann, J.S., Plotz, P.E. and Reinhard, M., 1986. The organic geochemistry of a sanitary landfill leachate plume. In: D.L. Macalady (Editor), *Transport and Transformations of Organic Contaminants*. *J. Contam. Hydrol.*, 1: 171–189 (special issue).
- Barker, J.F., Barbash, J.E. and Labonte, M., 1988. Groundwater contamination at a landfill sited on fractured carbonate and shale. *J. Contam. Hydrol.*, 3: 1–25.
- Baxter, K.M., 1985. The effects of a hazardous and a domestic waste landfill on the trace organic quality of Chalk groundwater at a site in east Anglia. *Sci. Total Environ.*, 47: 93–98
- Bjerg, P.L. and Christensen, T.H., 1992. Spatial and temporal small scale variation in groundwater quality of a shallow sandy aquifer. *J. Hydrol.*, 131: 133–149.
- Champ, D.R., Gulens, J. and Jackson, R.E., 1979. Oxidation–reduction sequences in ground water flow systems. *Can. J. Earth Sci.*, 16: 12–23.
- Ehrig, H.-J., 1983. Quality and quantity of sanitary landfill leachate. *Waste Manage. Res.*, 1: 53–68
- Germanov, A.I., Volkov, G.A., Lisitsin, A.K. and Serebrennikov, V.S., 1959. Investigations of the oxidation–reduction potential of ground waters. *Geochemistry*, 3: 322–329.
- Kjeldsen, P., 1992. Groundwater pollution source characterization of an old landfill. *J. Hydrol.* (To be submitted.)
- Lindberg, R.D. and Runnels, D.D., 1984. Ground water redox reactions: an analysis of equilibrium state applied to Eh measurements and geochemical modelling. *Science*, 225: 925–927.
- Lyngkilde, J. and Christensen, T.H., 1992. Fate of organic contaminants in the redox zones of a landfill leachate pollution plume (Vejen, Denmark). *J. Contam. Hydrol.*, 10: 291–307 (in this issue).
- Macca, C. and Bombi, G.G., 1989. Linearity range of Gran plots for the end-point in potentiometric titrations. *Analyst (London)*, 114: 463–470.
- Midgley, D. and Torrance, K., 1978. *Potentiometric Water Analysis*. Wiley, Chichester, 409 pp. (see especially pp. 355 and 356).
- Pedersen, J.K., Bjerg, P.L. and Christensen, T.H., 1991. Correlation of nitrate profiles with groundwater and sediment characteristics in a shallow sandy aquifer. *J. Hydrol.*, 124: 263–277.
- Postma, D., Hansen, E.Z. and Lyngkilde, J., 1990. Evaluation and development of methods for sampling and field analysis of groundwaters containing redox sensitive components. *Inst. Geol. Geotech., Tech. Univ. of Denmark, Lyngby*, 84 pp. (in Danish, with extensive abstracts in English).
- Windholz, M., Budavari, S., Blumetti, R.F. and Ottenbein, E.S. (Editors), 1983. *The Merck Index*. Merck & Co., Inc., Rahway, NJ, 10th ed. (edition P 852), 2165 pp.