



Biogeochemical processes at the fringe of a landfill leachate pollution plume: potential for dissolved organic carbon, Fe(II), Mn(II), NH₄, and CH₄ oxidation

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Abstract

Various redox reactions may occur at the fringe of a landfill leachate plume, involving oxidation of dissolved organic carbon (DOC), CH₄, Fe(II), Mn(II), and NH₄ from leachate and reduction of O₂, NO₃ and SO₄ from pristine groundwater. Knowledge on the relevance of these processes is essential for the simulation and evaluation of natural attenuation (NA) of pollution plumes. The occurrence of such biogeochemical processes was investigated at the top fringe of a landfill leachate plume (Banisveld, the Netherlands). Hydrochemical depth profiles of the top fringe were captured via installation of a series of multi-level samplers at 18, 39 and 58 m downstream from the landfill. Ten-centimeter vertical resolution was necessary to study NA within a fringe as thin as 0.5 m. Bromide appeared an equally well-conservative tracer as chloride to calculate dilution of landfill leachate, and its ratio to chloride was high compared to other possible sources of salt in groundwater. The plume fringe rose steadily from a depth of around 5 m towards the surface with a few meters in the period 1998–2003. The plume uplift may be caused by enhanced exfiltration to a brook downstream from the landfill, due to increased precipitation over this period and an artificial lowering of the water level of the brook. This rise invoked cation exchange including proton buffering, and triggered degassing of methane. The hydrochemical depth profile was simulated in a 1D vertical reactive transport model using PHREEQC-2. Optimization using the nonlinear optimization program PEST brought forward that solid organic carbon and not clay minerals controlled retardation of cations. Cation exchange resulted in spatial separation of Fe(II), Mn(II) and NH₄ fronts from the fringe, and thereby prevented possible oxidation of these secondary redox species. Degradation of DOC may

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happen in the fringe zone. Re-dissolution of methane escaped from the plume and subsequent oxidation is an explanation for absence of previously present nitrate and anaerobic conditions in pristine groundwater above the plume. Stable carbon isotope ($\delta^{13}\text{C}$) values of methane confirm anaerobic methane oxidation immediately below the fringe zone, presumably coupled to reduction of sulfate, desorbed from iron oxide. Methane must be the principle reductant consuming soluble electron-acceptors in pristine groundwater, thereby limiting NA for other solutes including organic micro-pollutants at the fringe of this landfill leachate plume.

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1. Introduction

Processes occurring at the fringe of a pollution plume are potentially of considerable importance for natural attenuation (NA) of the entire plume. Diffusive and dispersive mixing of anoxic-polluted groundwater with (sub)oxic pristine groundwater at the plume fringe results in dilution and may enhance degradation: the degradation potential for various electron-donors like aromatic hydrocarbons is absent or limited inside plumes, but excellent in the plume fringe area, due to the presence of soluble electron-acceptors like oxygen, nitrate and sulfate. Transversal mixing of oxidized and reduced groundwaters therefore enables faster biodegradation for many compounds. For example, oxidation by nitrate reduction in a 2-m-thick fringe took the main share of the total degradation in a 20-m-thick plume consisting of phenolic compounds (Mayer et al., 2001).

High-resolution groundwater analyses of plume fringes are however limitedly present and this hampers progress in understanding NA processes at the fringe of pollution plumes. The hydrochemical gradient perpendicular to a plume fringe is often badly captured in pollution plume studies, because the vertical sampling point spacing is too large with respect to the fringe thickness. Consequently, reactive transport models cannot be validated for processes operational at the plume fringe. Conventional numerical models based on rectangular grids often overpredict mixing, resulting in associated overestimation of degradation of contaminants in the plume, and consequently, underestimation of the actual plume expansion happens (Cirpka et al., 1999). However, occurrence of transient flow, which is usually not simulated, enhances dispersive mixing and hence biodegradation (Schirmer et al., 2001).

Although the understanding of mixing processes is improving, knowledge on the biogeochemistry in the plume fringe remains behind. Hunter et al. (1998) made a distinction between primary redox reactions, where organic matter is degraded, and secondary redox reactions (SRR), which involve the oxidation of reduced redox species formed by the primary redox reactions. Besides dissolved organic carbon (DOC) and aromatic hydrocarbons, especially in landfill leachate plumes several reduced redox species (Fe(II), Mn(II), NH_4 , and CH_4) can be subject to oxidation at the plume fringe, and compete for available oxidants. Secondary redox reactions may be beneficial when the electron-donor is considered as a pollutant (ammonium), but can also be regarded as unwanted (methane) because the availability of soluble oxidants then diminishes for more

harmful pollutants. The relevance of the various SRRs is under debate (Griffioen, 1999; Hunter and Van Cappellen, 2000), and the occurrence and extent of SRRs and related geochemical processes at the plume fringe deserve more attention (Christensen et al., 2000). This knowledge needs to be developed in order to validate model simulations on degradation and dilution at the plume fringe.

Landfill leachate contains high ammonium concentrations, where nitrification of ammonium under aerobic conditions is a possible attenuation process. Recently, occurrence of anaerobic ammonium oxidation (anammox) by reduction of nitrite was proved (Jetten et al., 1998), and the occurrence of anammox coupled to nitrate reduction providing nitrite for ammonium oxidation, has been observed as well (Thamdrup and Dalsgaard, 2002). Anammox may be an important process in nature at oxic/anoxic interfaces including the fringes of landfill leachate plumes (Schmidt et al., 2002).

Ferrous iron is another competitor for both nitrate and oxygen. Anaerobic nitrate-dependent Fe(II) oxidation is a microbiological process and needs the presence of an organic cosubstrate such as acetate (Straub et al., 2001). Aerobic oxidation of Fe(II) and Mn(II) occur both microbiologically mediated and chemically (Stumm and Morgan, 1996). Re-oxidation of ferrous iron that is mobilized upon reductive dissolution of iron oxide in association with organic matter oxidation, can be beneficial, as for example benzene seems more often degraded with Fe(III) than with NO_3 as electron-acceptor (Lovley, 2000).

Finally, methane in leachate is prone to oxidation at the plume fringe, at least with oxygen (Hanson and Hanson, 1996), but possibly with other electron-acceptors, too. Anaerobic methane oxidation (AMO) has been observed with sulfate as electron-acceptor, but the process is still poorly understood (Valentine and Reeburgh, 2000). Hoehler et al. (1994) and Schink (1997) proposed the mechanism of methanogens conducting reverse methanogenesis, in association with sulfate-reducers oxidizing and maintaining low levels of hydrogen in order to make the reaction thermodynamically feasible. In theory, hydrogen-oxidizing microorganisms could also use electron-acceptors other than sulfate (e.g., NO_3 , Fe(III), Mn(IV)) to keep hydrogen levels sufficiently low for reverse methanogenesis to be favorable (Hoehler et al., 1994). However, the concept of hydrogen as the electron-shuttle during AMO is questioned. Hydrogen in combination with acetic acid (Valentine and Reeburgh, 2000), formate (Sorensen et al., 2001), and transfer of an electron carrier rather than a methane-derived carbon compound (Nauhaus et al., 2002), were proposed as alternatives. Anaerobic methane oxidation coupled to nitrate-reduction has been suggested (Bjerg et al., 1995; Van Breukelen et al., 2003), and observed to occur at field conditions (Smith et al., 1991) and in a reactor (Costa et al., 2000).

The present study was initiated to study the biogeochemistry of a pollution plume fringe (Banisveld landfill, the Netherlands), and in particular the relevance of several possible SRRs. For this purpose, the (isotope) hydrochemistry was determined across the fringe at three distances downstream from the landfill, via sampling multi-level samplers (MLS) where a vertical-sampling interval of only 10 cm was obtained. Reactive transport modelling was performed using PHREEQC-2 (Parkhurst and Appelo, 1999) in order to deduce the governing biogeochemical processes. A series of additional simulations were performed to evaluate the relative importance of the various possible SRRs at the fringe of a landfill leachate plume more generally.

2. Field site description: hydrogeology and biogeochemistry

The biogeochemistry and microbial ecology of the Banisveld landfill leachate plume were previously studied (Röling et al., 2000, 2001; Van Breukelen et al., 2003, *in press*). Here, a summary will be given. The Banisveld landfill (6 ha) is situated 5 km southwest of Boxtel, the Netherlands. Disposal of primarily household refuse (400,000 m³) occurred in a former 6-m-deep sand pit between 1965 and 1977. Artificial or natural liners are absent, while most of the waste is present below the groundwater table, which lies less than 2 m below surface.

A leachate plume was detected measuring formation conductivity via cone penetration tests (Van Breukelen et al., 2003) at a depth of about 4 to 9 m below surface to a distance of about 70 m from the landfill border in May 1998 (Fig. 1). The plume migrates through a heterogeneous unconfined aquifer, which consists of fine- to coarse-grained unconsolidated clayey sands. Groundwater observation wells (WUP, W1–W9, WF) were placed in the direction of groundwater flow within and around the plume (Fig. 1).

The “Heiloop” stream downstream of the landfill (Fig. 1) drains groundwater from the area. Groundwater flow is directed NE to N towards a nature reserve beyond the Heiloop stream. The hydraulic horizontal gradient downstream of the landfill (between screens W2b and W9b) varied seasonally between 0.0003 m/m (summer) and 0.007 m/m (winter) in the period June 1998 to October 2001 (average 0.003 m/m). Groundwater flow velocity is expected to be around 4 m per year. Iso-potential lines depicted in Fig. 1 show that the vertical component of flow is generally directed downwards (infiltration) near the landfill, and turns gradually in upward direction (exfiltration) downstream. Recharge events in the area enhance both the groundwater flow velocity in the plume (horizontal hydraulic gradient) and exfiltration velocity to the Heiloop stream (vertical hydraulic gradient; data not shown).

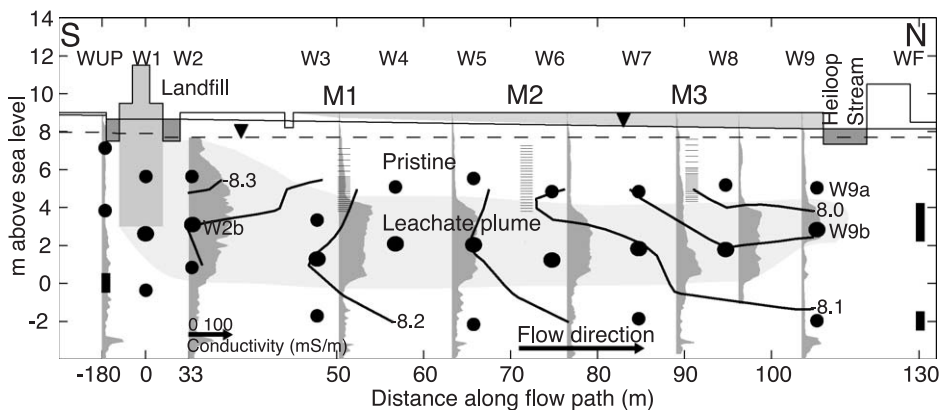


Fig. 1. Cross section of the research transect downstream of the landfill site. The leachate plume as observed in 1998 is depicted in light gray and delineated using the formation conductivity, which is plotted from left to right (dark grey). Screens of observation wells (WUP, W1–W9, WF: black dots or vertical lines) and multi-level samplers (M1–M3: thin horizontal lines) are depicted. The min and max observed water table levels and average iso-lines of hydraulic head (2000–2003, $n=6$) are shown. The soil dig off in 1999 is shown in gray.

Table 1 shows the average composition of leachate and pristine groundwater above and below the plume. Van Breukelen et al. (2003, in press) showed that degradation of DOC was coupled to iron-reduction in the core of the leachate plume. The pristine aquifer was anaerobic at about 3 m below the water table, but nitrate was present above the plume. A very positive $\delta^{15}\text{N-NO}_3$ and an elevated N_2 partial gas pressure at screen W8a indicated occurrence of nitrate-reduction in shallow groundwater (Van Breukelen et al., 2003). Stable isotope analysis of dissolved methane sampled from this screen indicated that methane degassed from the plume, re-dissolved in pristine groundwater above, and subsequently became oxidized in association with nitrate reduction (Van Breukelen et al., 2003). Sulfate may be another electron-acceptor of importance at the plume fringe. Note that the top fringe may be more reactive than the bottom fringe, since oxidant concentrations are higher there (Table 1). Principal reductants in the plume are in order of electron equivalents transferred upon oxidation (meq/l): DOC (~ 22), NH_4 (~ 21 to N_2), CH_4 (~ 9), Fe(II) (~ 1.6), Mn(II) (~ 0.04), and finally BTEX (~ 0.007).

The hydrological situation has changed since 1998. Digging off up to 1.0 m of nutrient-rich soil for nature development in the area, taking place in winter 1999–2000, resulted in a land surface dipping from the landfill towards the Heiloo stream (Fig. 1: dig off soil is shown in gray). At the same time, the amount of water led through the Heiloo was artificially reduced at an upstream point, where it was partially diverted to watercourses running north and south of the Heiloo. Less water and a wider riverbed probably have resulted in lower water levels in the Heiloo since 2000. The Heiloo may now dry up in summer, which makes surface water infiltration in the summer period impossible. Next, precipitation in the area was very high for the period 1998–2002 (880–1010 mm rain per year) compared to the long-term average (~ 800 mm/year), and the wet period was preceded by a relatively dry period of 3 years (570–680 mm/year). Lower water levels in the Heiloo in combination with a strong increase in infiltration upstream in the aquifer could have enhanced exfiltration to the Heiloo since 1998, while a wider riverbed may have extended the exfiltration zone towards the landfill.

Table 1
Composition of leachate and pristine groundwater

	O_2 (mg/l)	NO_3 (mmol/l)	SO_4 (mmol/l)	DOC (mmol/l)	Fe(II) (mmol/l)	Mn(II) ($\mu\text{mol/l}$)	NH_4 (mmol/l)	CH_4 (mmol/l)	BTEX ($\mu\text{g/l}$)
Pristine (above) 1998–1999 ^a	<0.5	0.5	1.1	1.4	0.03	5	0.2	0.1	0
Pristine (above) 2001 ^b	<1	0	0.3	8.4	0.05	17	0.007	0.03	–
Leachate 1998–1999 ^a	<0.5	0	0.1	5.4	1.6	22	7	1.1	20
Leachate 2001 ^c	<0.5	0	0.05	8.1	1.2	13	12	1.5	–
Pristine (below) 1998–1999 ^a	<0.5	0	0.2	0.8	0.14	7	0.04	0.2	0

^a Average concentrations are shown for observation wells W3–W9 for the period 1998–1999 (Van Breukelen et al., 2003).

^b Average concentrations are shown for the five upper screens at location M1 in 2001 (this study).

^c Average concentrations are shown for leachate at locations M1–M3 in 2001 (this study).

3. Sampling and analysis

3.1. Design of multi-level sampler

A permanent multi-level sampler (MLS) was designed for the present study in order to obtain cost-effectively small groundwater samples of flexible volume at small vertical spacing, with a minimum of flushing, and minimal disturbance of the biogeochemistry. Fig. 2 shows the MLS constructed for the present study. Teflon sampling tubing [inner diameter (ID) is 2 mm, outer diameter (OD) is 4 mm] and porous borosilicate glass filters (pore size is 100–160 μm , screen length is 2 cm, OD is 8 mm, manufacturer is Schott) were chosen to minimize alteration of hydrogeochemical conditions (Van Breukelen, 2003). Sounding was preferred above drilling the MLS into the ground as disturbance and costs are less and installation is easier. The high cone resistance of this aquifer (up to 50×10^6 Pa) limited the maximum diameter of the probe rods and, consequently, the diameter of the MLS system to about 36 mm. A maximum of six screens were attached using tie-ribs at a 30-cm vertical spacing interval in an indentation made at the outside of a 2-m length PVC pipe (ID is 16.5 mm, OD is 19 mm). Silicon tubing was used to seal the holes connecting the inner tubing with the outer sampling screens. In order to prohibit short-circuit flow, screens were separated by 2.5-cm-thick solid cylinders (OD is 35 mm) of bentonite (Eijkelkamp, Giesbeek, the Netherlands), wrapped in polypropylene filter sock (Eijkelkamp) and confined by PVC discs (OD is 36 mm). PVC glue (Bizon International, Goes, the Netherlands) was used to connect all parts of the system. The MLS was extended in the field using PVC pipes of 1–2-m length and 5-cm-long PVC connectors.

3.2. Installation of the MLS

Three locations (M1, M2, M3) were selected in the flow direction at 18, 39 and 58 m from the landfill border along an existing research transect (Fig. 1). Cone penetration tests (CPTs) including measurement of aquifer formation conductivity provided the depth to and height of the plume fringe in 1998 (Van Breukelen et al., 2003). In advance of placing the MLSs, additional CPTs were performed to verify the fringe position in January 2001 (Fig. 3). Fig. 3 shows that the fringe was in January 2001 about 0.6 m higher than in May 1998.

Steel pipes (ID/OD are 39/55 mm) with a stainless steel expendable point in front were pushed hydraulically to the target depth using the weight of a sounding truck. Next, the empty casing was flushed from the bottom with nitrogen gas to remove oxygen (checked with an oxygen electrode), before putting the MLS in the casing. Additional PVC extension pipe was glued to the MLS using PVC glue, connectors, and tape. After finishing the MLS construction, water was added to the casing (under a continuous flow of nitrogen gas) in order to prohibit inflow of aquifer material while the casing was retrieved. The water was a solution of 1.0 mM CaCl_2 , 1.0 mM NaHCO_3 and 0.25 mM KBr with $\text{pH}=7.9$, and was made anaerobic by flushing it with nitrogen gas just before adding it to the casing.

A cluster of four MLSs was installed at each location within a horizontal distance of 0.5 m from each other. The effective screen spacing was enhanced by placing MLSs (having a

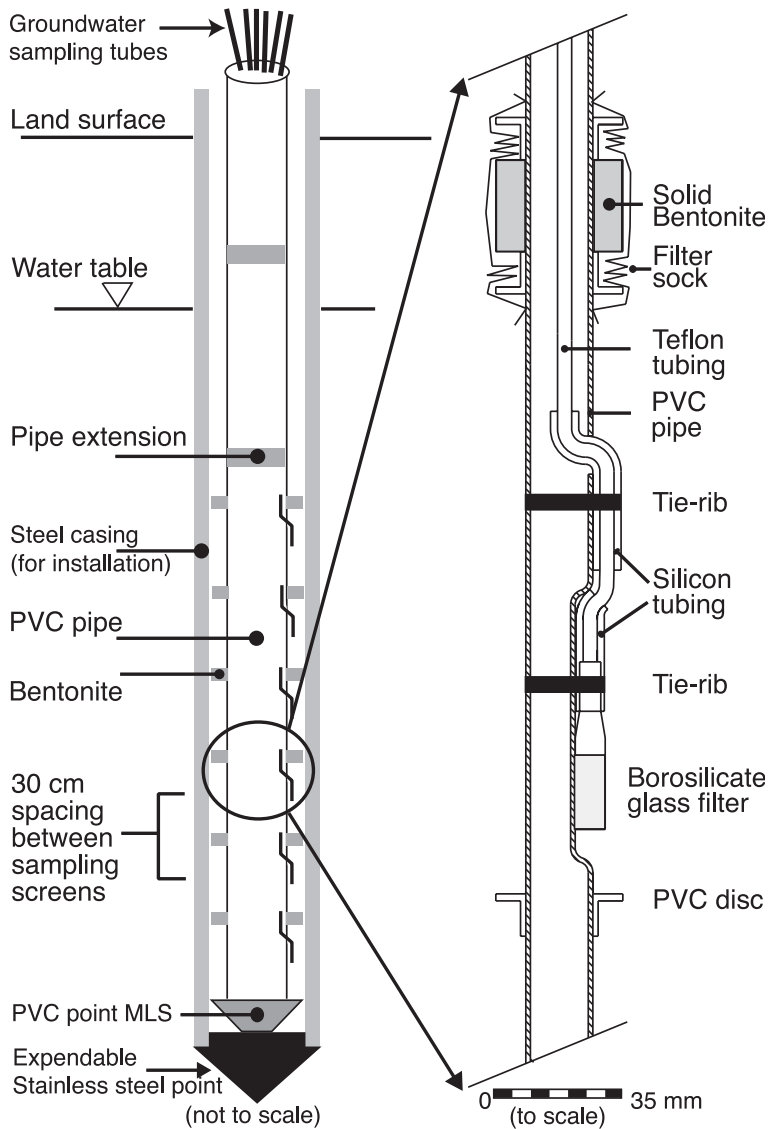


Fig. 2. Schematic diagram of multi-level sampler (MLS).

30-cm screen spacing) with a depth difference of 10 or 15 cm in order to obtain a vertical sample depth spacing of 10 cm around the plume fringe at location M1 and M3 by forming a group of three MLSs, and 15 cm at location M2 by pairing two MLSs (see Fig. 3). A single MLS was placed in pristine groundwater above the group of three at locations M1 and M3, while in total two MLS pairs were placed one above each other at location M2 to be able to capture the transition from pristine groundwater to leachate (Fig. 3). Screens

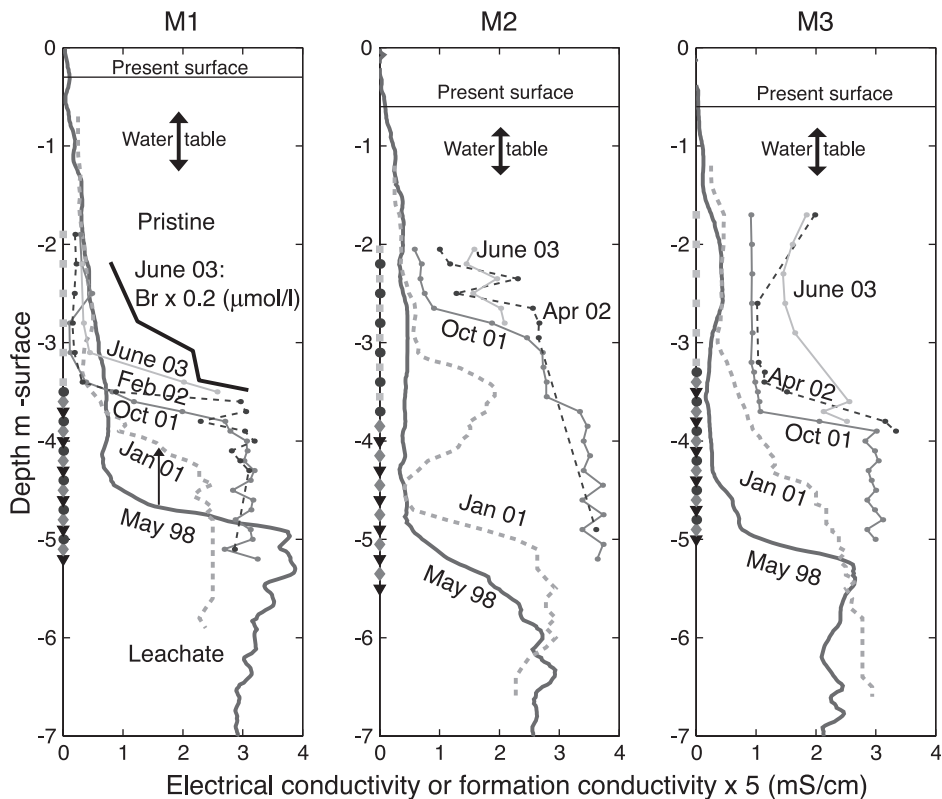


Fig. 3. Electrical conductivity and formation conductivity profiles at locations M1, M2 and M3 for the period May 1998–June 2003. The depth positions of the MLSs and screens are shown: screens from a particular MLS are depicted with identical symbols.

were placed between about 2–5 m below the original surface before soil excavations in 1999.

3.3. Groundwater sampling and analysis

All screens were sampled for a complete analysis of the hydrochemistry in October 2001. A selection of screens was sampled once more for both hydrochemistry and stable isotope analysis in February 2002 (M1) and April 2002 (M2 and M3). Finally, some samples were taken in June 2003 for Br, Cl and electrical conductivity measurements. Samples were taken using a peristaltic pump, and the amount of water sampled was minimized (<200 ml for first sampling round, where <50 ml was pumped in order to flush the sampling tubing three times) in order to obtain a sample representative for a small vertical aquifer section (<5 cm radius, taking a porosity of 0.3; ~10 cm radius for sampling round including isotope analysis). Electrical conductivity (GMH 3410, Greisinger electronic, Germany), dissolved O₂ (DO-166FT, Lazar Research Laboratories, LA,

USA) and pH (Model 1001, Sentron, Roden, the Netherlands) were measured by electrodes placed in flow cells (Lazar Research Laboratories) having a volume of less than 1 ml. Sampling, conservation and analysis of alkalinity, Cl, NO₃, NO₂, SO₄, Na, K, Mg, Ca, Fe(II), Mn(II), NH₄, PO₄, CH₄, and DOC were performed, and were described elsewhere (Van Breukelen et al., 2003). In addition, Br, Si, and Al were measured using ion chromatography (Br) and inductively coupled plasma-atomic emission spectrometry (Si, Al). Five-milliliter Venoject blood sample vials (3.0-ml groundwater, in duplicate) were used for methane analysis in 2001, while 10-ml vials (7.0-ml groundwater, in duplicate) were used during sampling in 2002.

Samples for $\delta^{13}\text{C-CH}_4$ were taken in 150-ml glass vials capped with airtight stoppers. Eight drops of an I₂-KI solution (1.5 g I₂ and 3 g KI to 100 ml aqua dest.) were added before capping. Next, vials were flushed three times with helium gas and subsequently evacuated. Three aliquots of ca. 50-ml groundwater were injected in the evacuated vials using a PE syringe. Analysis was performed at the Environmental Isotope Laboratory, University of Waterloo, Canada.

4. Results

4.1. Mixing between leachate and pristine groundwater

Three positions in the hydrochemical depth profiles (see Figs. 5 and 6) are of importance for later discussion and defined here: the pristine-end of the fringe (F1, Br or Cl concentration is 100% pristine groundwater), the leachate-end of the fringe (F2, Br or Cl concentration is 100% leachate), and the divalent-cation front (F3, concentrations of divalent cations are 100% leachate). Note that Ca, Mg, Fe(II) and Mn(II) show a concentration decrease in upward direction from F3. The height of the fringe (the distance between F1 and F2) is 0.5 m at M1 and estimated as 1 m at M2, since position F1 is above the sampling interval. The fringe has not been captured at M3, but position F3 is present.

Mixing between leachate and pristine groundwater is determined best using conservative tracers. Chloride is used preferably as conservative tracer in landfill leachate studies (e.g., Christensen et al., 2001), but alternatives exist: deuterium (Cozzarelli et al., 2000), boron (Hofer et al., 1997) and strontium isotopes (Vilomet et al., 2001). Bromide and fluoride were measured besides chloride in this study to determine their potential as conservative tracer of landfill leachate. Fig. 4 shows that chloride and bromide concentrations were several times higher in leachate than in pristine groundwater, while the correlation between chloride and bromide in leachate was high ($R^2=0.91$, $n=56$). Fluoride concentrations (0–6 $\mu\text{mol/l}$) however were not different. Both chloride and bromide were therefore used as tracer in this study. The Cl to Br molar ratio was 355 ± 25 in the leachate plume. The low bromide concentrations measured (1.6–18 $\mu\text{mol/l}$) and its molar ratio to chloride prove that water used for placement of the MLSs (Br=0.25 mmol/l and Cl to Br molar ratio of 8) has been flushed away.

Fig. 4 shows that presence and dilution of landfill leachate is better determined using chloride in combination with bromide, since chloride alone is not useable in some cases, for example, near landfills where road salts are applied (Bjerg et al., 1995). The Cl to Br

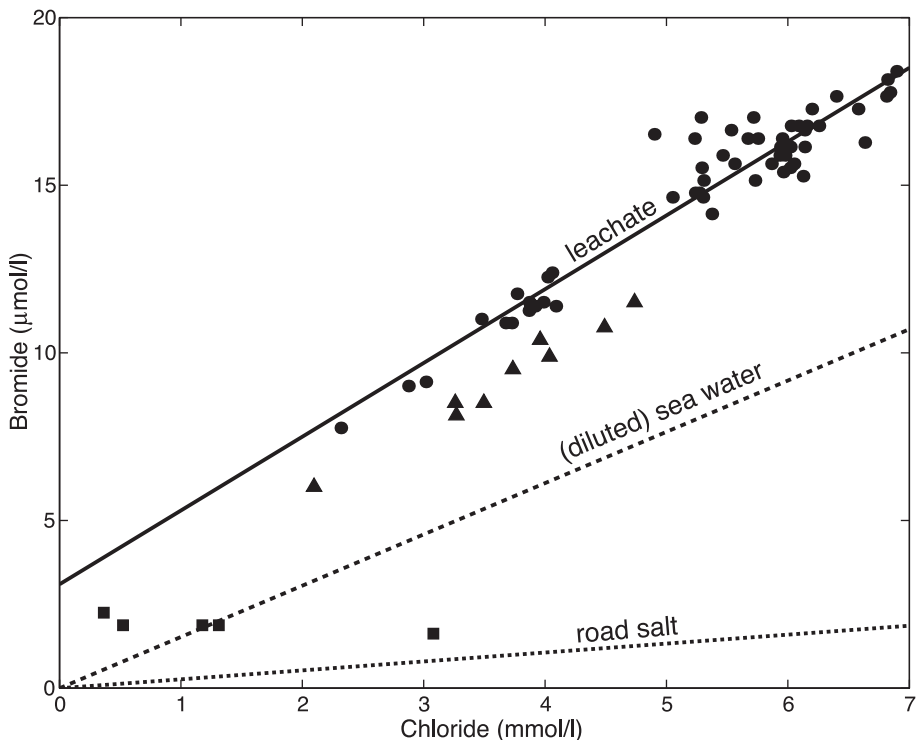


Fig. 4. Relation between bromide and chloride in leachate (●), pristine groundwater (■), and the mixing zone (▲). Mixing lines for (diluted) seawater and road salt (maximum Br/Cl ratio) are shown as well.

molar ratio of 300–400 observed in landfill leachate is significantly different from other sources: halite ($\sim 2 \times 10^3$ to 2×10^4 ; Davis et al., 1998), road salts ($\sim 4 \times 10^3$ to 4×10^5 ; Granato, 1996), sewage waste water (commonly 680–1350; Davis et al., 1998), (dilute) seawater and rain water in coastal areas (654; Davis et al., 1998), or animal waste (goats, 130; cattle, 192; horses, 330; Hudack, 2003). The Cl to Br molar ratio could therefore be a useful tracer to discriminate leachate from other sources of salt in groundwater. Degradation of soil organic matter, having a relatively high bromine to chlorine content, has been observed to lower the Cl to Br molar ratio in soil water down to 23 (Gerritse and George, 1988). Consequently, the relatively high bromide concentration in landfill leachate is possibly the result of degradation of organic carbon in the landfill body.

Leachate showed higher concentrations than pristine groundwater (present at location M1 between 1.9 and 3.1 m below surface) for the following compounds: Cl, Br, alkalinity, Na, K, Mg, Ca, Fe(II), Mn(II), NH_4 , and CH_4 (Figs. 5 and 6, and Table 1). The dissolved organic carbon (DOC) concentration was higher in leachate than in pristine groundwater in 1998–1999 (Table 1). However, the DOC concentration in pristine groundwater at M1 was exceptionally high. Pristine groundwater showed higher concentrations for SO_4 , Si and Al (results not shown for Si and Al). Its pH is slightly acidic, while leachate pH is

around 6.4. Leachate is supersaturated for siderite, in equilibrium with calcite at M1, but undersaturated further downstream (locations M2, M3; results not shown). Siderite and calcite are not present in the pristine aquifer (Van Breukelen et al., 2003). The concentration of PO_4 was below $0.3 \mu\text{mol/l}$ in all samples. Hydrochemical profiles were generally comparable for both sampling events, but sulfate concentrations in pristine groundwater at M1 decreased, while the plume moved somewhat upward (see later).

4.2. Upward movement of the leachate plume

A comparison between formation conductivity measured in May 1998 and January 2001, and electrical conductivity (EC) of groundwater as measured in October 2001, February/April 2002, and June 2003, shows that the top of the leachate plume has moved progressively in upward direction (Fig. 3). Upward advective transport in combination with geochemical processes retarding the EC (see Section 4.4) must have occurred to explain the considerable lag between the bromide/chloride front and the electrical conductivity front. Fig. 3 illustrates that the lag is about 0.3 m at M1 in June 2003. The lag is particularly large at M3, as shown in Fig. 5, where the bicarbonate concentration is indicative for the EC. Its non-conservative behavior makes EC clearly unsuitable as a mixing tracer. Since the transitions in EC were assumed to represent the fringe position, MLSs were installed somewhat too deep at M2 and M3. Consequently, the transition to pristine groundwater (position F1) was not captured at M2 and M3. The total upward movement of the fringe between 1998 and 2001 increases from 1.3 m at M1 to 3.3 m at M2 and beyond at M3 (Fig. 5).

The cause of the plume uplift might be related to an increase in rainfall and hence infiltration in the area since 1998, together with an artificially lowered water level in the Heiloo since 2000, enhancing the exfiltration towards the Heiloo stream (see Section 2; Fig. 1). The larger plume uplift as observed from location M1 towards M3 (Figs. 3 and 5), agrees with the vertical hydraulic pressure gradient increasing towards the Heiloo (Fig. 1).

4.3. Distribution of redox species and occurrence of redox processes across the fringe

4.3.1. Electron-acceptors

Oxygen was not present in leachate (detection limit estimated at 0.5 mg/l), but a concentration of $0.5\text{--}1 \text{ mg/l}$ is present in pristine groundwater at M1 (Table 1). Data were not available to determine if the upper meter of the saturated zone was aerobic. Nitrate was measured up to 1.2 mmol/l (mean $\sim 0.5 \text{ mmol/l}$) in all observation screens (W4–W9) above the leachate plume at about 4 m below surface, during three sampling rounds from June 1998 to October 1999 (Table 1). Remarkably, nitrate was absent in the MLSs up to 2 m below surface in 2001–2002, with the exception of three samples taken in 2001 from the fringe at M2. These samples showed decreasing nitrate concentrations with depth (0.26 down to 0.16 mmol/l). Therefore, nitrate has recently disappeared as electron-acceptor, while it was present at an earlier stage (Van Breukelen et al., 2003).

Alternative electron-acceptors at the fringe could be oxides of Fe and Mn, and sulfate. Low Fe(II) concentrations and undersaturation for siderite indicate that iron-reduction is

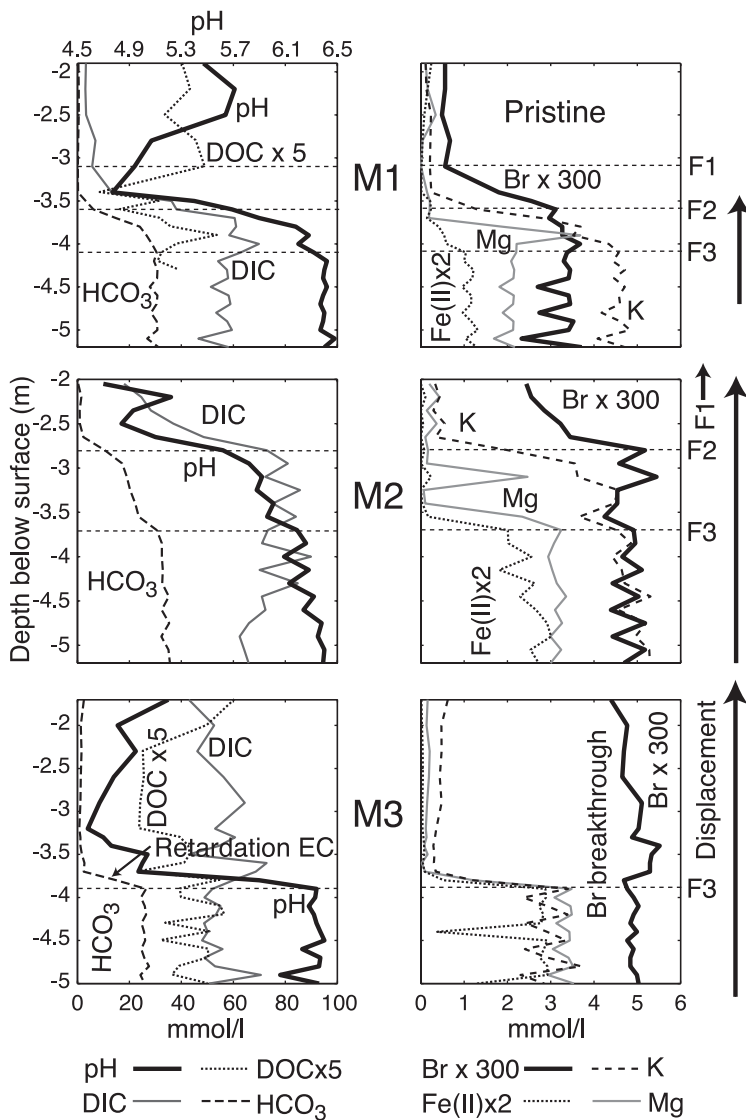


Fig. 5. Hydrochemical depth-profiles (October 2001) at locations M1–M3. Positions F1–F3 are indicated. Arrows show the total upward displacement of the fringe since 1998. Results for pH, DIC, DOC (no results M2), HCO₃, Br, K, Fe and Mg are shown.

not important at the fringe and in pristine groundwater above the fringe (Fig. 5). The Mn(II) to Fe(II) mole ratio increases from the F3 fronts towards the surface at M2 and M3. Manganese(II) even exceeds the Fe(II) concentration for two fringe samples at M2 (Figs. 5 and 6). This indicates reductive dissolution of manganese oxide in the upper part of the aquifer probably due to inflow of rising leachate.

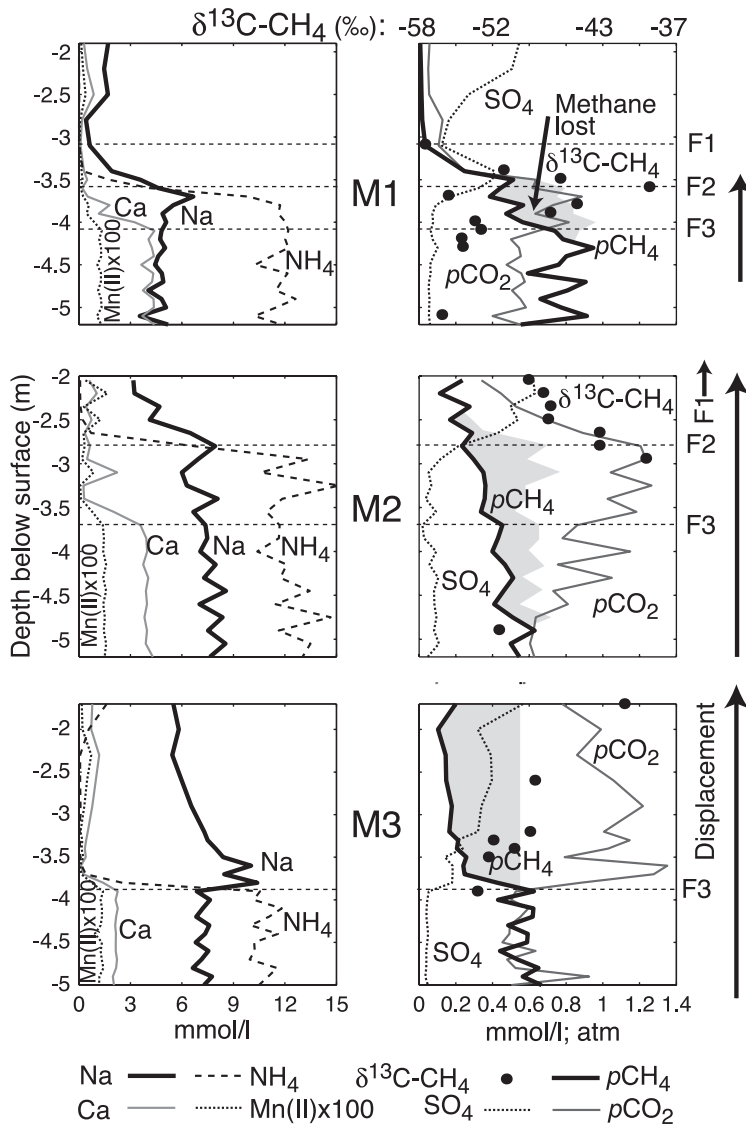


Fig. 6. Hydrochemical depth profiles (October 2001) at locations M1–M3. Positions F1–F3 are indicated. Arrows show the total upward displacement of the fringe since 1998. Results for Na, Mn, Ca, NH₄, SO₄, pCO₂, pCH₄, and δ¹³C-CH₄ are shown. Shaded area represents the methane lost corrected for dilution. Samples for δ¹³C-CH₄ were taken in 2002 (methane concentration comparable).

Sulfate-reduction may occur in pristine groundwater at M1, because sulfate decreased with depth (Fig. 6), and sulfate concentrations decreased between 2001 and 2002 with 20–60% (results not shown). The sulfate concentration remarkably peaks at the fringe zone (F1–F2) of M1 instead of leveling off to the leachate concentration. This sulfate peak may

be explained by desorption from iron oxide (surface complexation) when the rising leachate displaces slightly acidic pristine groundwater (see Section 5). Note that sulfate peak values coincide with the strong decrease in pH immediately above the F3 front at all locations. Occurrence of sulfate-reduction at the fringe is difficult to determine, since sulfate desorbs in this zone as well.

4.3.2. Electron-donors

Possible electron-donors susceptible to oxidation at the fringe are divided into three groups: (1) non-sorbing organic solutes (DOC and methane), (2) adsorbing organic contaminants (e.g. benzene), and (3) the sorbing reduced inorganic cations (Fe(II), Mn(II) and NH_4). If present, soluble electron-acceptors in pristine groundwater such as oxygen and nitrate mix with anaerobic leachate. The concentration of an electron-acceptor admixing from pristine groundwater is per definition 100% at the pristine end of the conservative tracer front (Figs. 5 and 6: F1), and zero at the leachate end of the conservative tracer front (Figs. 5 and 6: F2). Consequently, oxidation of sorbing Fe(II), Mn(II) and NH_4 is hindered compared to oxidation of non-sorbing reductants if O_2 and NO_3 were present in pristine groundwater, because retardation of cations leads to separation from the dissolved oxidants, as will be explained in more detail later.

Dissolved organic carbon (measured for M1 and M3 in 2001) showed high concentrations both for leachate and pristine groundwater at M1 (Fig. 5, Table 1). Such high DOC concentrations were previously not observed for pristine groundwater (Table 1). However, low DOC concentrations were measured for two fringe samples at M1 (1.7 and 3.2 mmol/l) suggesting that oxidation of DOC occurs at the fringe zone. High bromide concentrations showed that leachate was present in the complete depth-profile at M3. Five out of the upper eleven samples above the F3 front at M3 showed low DOC concentrations (4.8–5.1 mmol/l), while the DOC concentration at larger depth was comparable to the DOC concentration measured at M1. This indicates that DOC became partly degraded after the plume rose at M3. The other organic and non-sorbing electron-donor in leachate is methane and is present at high concentration. Processes governing the fate of methane are discussed in Section 4.5.

4.4. Impact of cation-exchange reactions and proton-buffering

The fronts of cations are clearly separated in space (Figs. 5 and 6). The following cation fronts follow with depth after the conservative tracer front (F1–F2): (1) Na, (2) NH_4 and K (NH_4 slightly before K), and (3) Ca, Mg, Fe and Mn. Front-spacing is as little as 10 cm at M1. The front spacing is larger at M2, and all cations except sodium are strongly retarded with respect to bromide at M3. This chromatographic pattern brings forward that advective transport has occurred (Appelo and Willemsen, 1987), i.e., the leachate plume has risen towards the surface. Dispersive/diffusive transport without advection results rather in a simple mixture between leachate and pristine groundwater at the fringe.

The observed chromatographic pattern is particular in the way that the K and NH_4 fronts are present closer to F1–F2 (i.e., are less retarded) than the divalent cation fronts (Ca, Mg, Fe(II), and Mn(II); see Figs. 5 and 6). This order implies that solid organic carbon (SOM) rather than clay minerals control the sorption of cations, because

monovalent K and NH₄ have a lower affinity than divalent cations for SOM (Chung and Zasoski, 1994), while this is vice versa for clay minerals especially illite (Bruggenwert and Kamphorst, 1982).

Van Breukelen et al. (in press) showed that flow of pH-neutral leachate through the slightly acidic aquifer triggers release of protons as a result of proton-buffering. All divalent cations become lowered in concentration from the divalent cation-front (F3; monovalent cations at somewhat higher elevation) towards the leachate end of the fringe (F2), and the pH decreases simultaneously over the interval F3–F2. Therefore, release of protons in exchange for cations in leachate occurs in response to a rise of the leachate plume. The results bring forward the occurrence of cation exchange including proton buffering in the fringe zone.

4.5. Fate of methane: degassing and anaerobic methane oxidation

Proton buffering causes retardation of the pH front. The pH decreases between F3 and F2, while DIC remains constant until it dilutes due to mixing with pristine groundwater between F2 and F1 (Fig. 5). The pH change results in a decrease of bicarbonate and an associated increase in dissolved carbon dioxide and partial CO₂ pressure (Fig. 6). Proton buffering also seems to occur below F3 at M2, since pH continuously increases towards the bottom of the profile. Remarkably, *p*CH₄ decreases, while *p*CO₂ increases at all three locations (Fig. 6). The CH₄ partial pressure was calculated for the situation that only conservative mixing would happen, where mixing is calculated from Br concentrations. The area is indicated where observed *p*CH₄ is below the partial methane pressure according to conservative mixing (Fig. 6). Apparently, degassing of methane compensates for an increase in total gas pressure, caused by an increase in partial CO₂ pressure upon proton buffering. Redissolution of escaped methane in pristine groundwater, followed by oxidation could be an explanation for the absence of oxygen and nitrate (see before).

Carbon-13 isotopes of methane were measured to determine if oxidation of methane occurred at the plume fringe. Previous measurements in 1999 showed that δ¹³C-CH₄ ranged between -54.4‰ to -52.7‰ (n=9) along the plume axis (6–8 m below surface), while a value of -50.3‰ was observed for one pristine, methane-containing groundwater sample above the plume (Van Breukelen et al., 2003). Current measurements showed

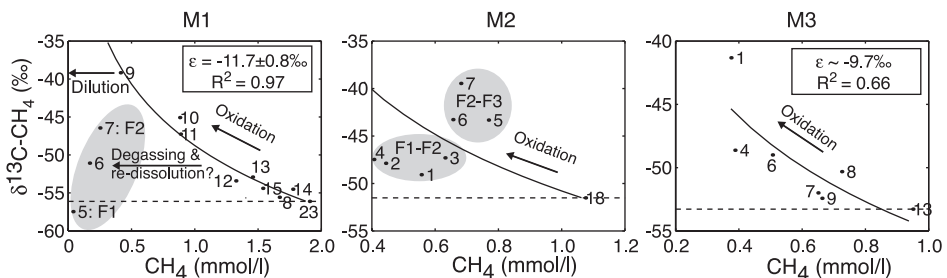


Fig. 7. δ¹³C of dissolved methane versus methane concentration in 2002. Samples are numbered from top (1) to bottom (24) for each location. Oxidation of methane will yield the curved lines in this plot. Calculated enrichment factors (ϵ) for anaerobic methane oxidation below the fringe (F2) are shown for locations M1 and M3.

lowest values at the bottom of the MLS profiles, together with lower concentrations and enriched $\delta^{13}\text{C-CH}_4$ values up to -39% closer to the surface (Fig. 6).

Recently, Grossman et al. (2002) observed a correlation between decreasing methane concentrations and increasing $\delta^{13}\text{C-CH}_4$ values downstream in the Norman landfill leachate plume, and attributed this to anaerobic methane oxidation (AMO), presumably coupled to sulfate-reduction. Here, we report evidence for AMO as well. High correlation ($R^2=0.97$) between decreasing methane concentrations and increasing $\delta^{13}\text{C-CH}_4$ values is observed at M1 for all samples below F2 (Fig. 7). The calculated enrichment factors (ϵ) of $-11.7 \pm 0.8\%$ at M1 and $-9.7 \pm 3.1\%$ at M3 were somewhat lower than observed at the Norman site (about -13% , which was at the high end of the reported range for AMO (Grossman et al., 2002). However, the enrichment factor for AMO may be underestimated at the present site because co-occurring degassing possibly lowers methane concentrations without significant fractionation ($\sim 1\%$ Bergamaschi, 1997). Degassing alone cannot account for the strong increase in $\delta^{13}\text{C-CH}_4$ values, because this process involves little fractionation (Bergamaschi, 1997; Van Breukelen et al., 2003). Removal of methane below F2 must therefore be explained by a combination of degassing and AMO.

Highest $\delta^{13}\text{C-CH}_4$ values were observed at F2, while values were somewhat lower in the fringe zone (F1–F2). Signatures would remain constant if methane at F2 is only diluted at the fringe. Possibly methane with lower signatures degassed between F2 and F3, and has re-dissolved at the fringe (F1–F2), where hydrostatic pressure exceeds total gas pressure (Fig. 8), explaining these lower signatures there (Fig. 7). Occurrence of AMO coincides with desorption of sulfate between F1 and F3 (see before and later). Anaerobic methane oxidation is therefore probably coupled to sulfate-reduction in this zone, since other major redox processes are not occurring.

5. Reactive transport modelling of the rising plume fringe

5.1. Model set-up and calibration

A reactive transport model was constructed in PHREEQC-2 (Parkhurst and Appelo, 1999) to simulate the hydrochemistry of the plume fringe at location M1, in order to verify quantitatively if proton buffering and degassing triggered by a rising plume determine the hydrochemical patterns across the fringe. Redox processes (oxidation of DOC and methane with nitrate or sulfate) and redissolution of escaped methane were not simulated. The model consisted of 100 cells each having a length of 0.05 m. Leachate was present in the lower forty cells, pristine groundwater in the upper 60 cells. Advective upward transport of leachate, displacing pristine groundwater, was simulated across the observed vertical distance of 1.3 m for the period May 1998 through October 2001. The pore water velocity was thus 32 mm/month. A transversal dispersivity of 1 mm (Klenk and Grathwohl, 2002) was adopted. The effective diffusion coefficient needed to be rather low ($5 \times 10^{-11} \text{ m}^2/\text{s}$) to obtain a best fit for bromide, indicating a high tortuosity. Mixing at the fringe was mainly diffusion controlled.

The initial leachate and pristine groundwater composition together with the composition of inflowing leachate at the lower model boundary were assumed constant. The

average of the concentrations between 3.8 and 4.9 m below surface was taken for leachate ($n=9$; excluding screens at 4.2, 4.4, 4.8 m below surface for all species except methane). The concentrations for pristine groundwater (pH, Na, K, Ca, Mg, NH_4) were optimized (see later) within the concentration ranges as observed for screens between 1.9 and 3.1 m below surface ($n=5$). The average of observed concentrations in pristine groundwater was taken for alkalinity, Cl, and Br. Pristine concentrations for Fe and Mn were allowed to be optimized below the observed minimum for pristine groundwater in order to improve the fit of the model. A groundwater temperature of 11 °C was taken.

The proton-buffering capacity (PBC) and the cation exchange capacity (CEC) were optimized between zero and maximum values, which were estimated from soil organic carbon and clay content measurements in the aquifer, respectively (Van Breukelen et al., 2003), following Appelo et al. (1998). Exchange coefficients for cations on CEC were equal to those used in a reactive transport model of the central flow path in the present plume (Van Breukelen et al., in press). Exchange coefficients for cations on the proton-buffer (PBC) were taken from the previous study as well, but were allowed to change during optimization to values 1 log unit lower than the CEC exchange coefficients.

Surface complexation was included to simulate sulfate at the fringe following the Dzombak and Morel (1990) model implemented in PHREEQC. A FeOOH content of 11 mmol/l, close to the average measured FeOOH content of 14 mmol/l (Van Breukelen et al., 2003), a specific surface area of 600 m²/g FeOOH, and 0.2 mol strong sites and 0.005 mol weak sites per mol FeOOH were taken (Dzombak and Morel, 1990). Surface complexation of the following species was simulated (note that phosphate was not detected): H^+ , Ca^{2+} , Mg^{2+} , Fe^{2+} , Mn^{2+} , SO_4^{2-} and CO_3^{2-} .

Table 2
Optimized model parameters and measured values (minimum, mean, maximum)

	pH	Ca	Mg	Na	K	NH_4	Fe	Mn	HCO_3
<i>Pristine groundwater (mmol/l)</i>									
Minimum	4.94	0.09	0.005	0.41	0.11	0.005	0.009	3×10^{-4}	0.18
Mean	5.37	0.38	0.13	1.18	0.18	0.007	0.054	0.017	0.38
Maximum	5.71	0.86	0.34	1.7	0.24	0.011	0.12	0.004	0.55
Optimum PEST	5.48	0.09	0.06	1.47	0.15	0.011	0.002	8×10^{-5}	
<i>Leachate (mmol/l)</i>									
Mean	6.39	4.3	2.1	4.8	4.6	11.9	0.58	0.011	30.4
	Sediment ^a		Exchange coefficients on proton buffer ^b						
	CEC	PBC	CaY_2	MgY_2	NaY	KY	NH_4Y	FeY_2	MnY_2
Minimum	9	1.6	-0.20	-0.40				-0.40	-0.40
Mean initial	23	4.7	0.10	-0.20	-1.00	-0.75	-0.75	-0.20	-0.20
Maximum	42	12.3				-0.30	-0.40		
Optimum PEST	0.2	8.3	-0.20	-0.40		-0.57	-0.75	-0.20	-0.20

^a Contents for the cation exchange capacity (CEC) and the proton-buffering capacity (PBC) are given in meq/kg soil. Conversion to meq/l was done for the model by multiplying with 6.2 [using a porosity of 0.3 and the specific weight of quartz (2.65 g/cm³)].

^b Values are expressed as $\log(K)$ for $\text{I}^{\text{++}} + \text{iY}^- = \text{iY}_i$.

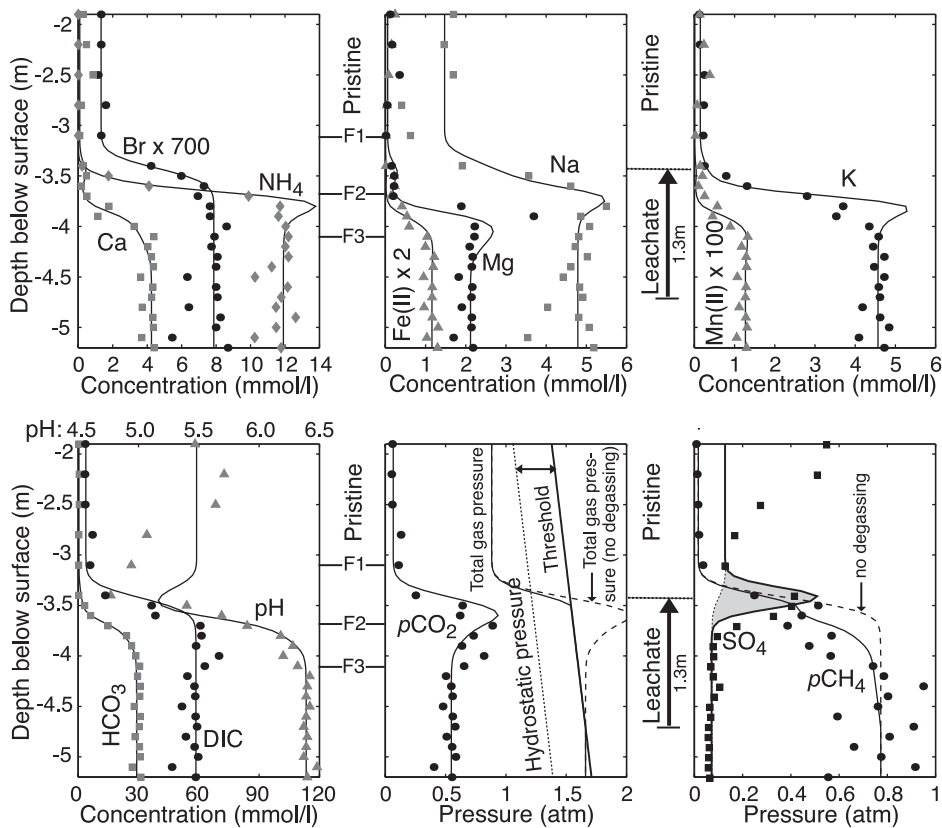


Fig. 8. Results of reactive transport model of plume fringe at location M1. Dashed lines show partial methane pressure and total gas pressure for simulations without degassing. Sulfate, desorbed by surface complexation, is shaded.

The model was calibrated using the nonlinear optimization program PEST (Watermark Computing: <http://www.sspa.com/pest>). Observations between 3.4 and 4.0 m below surface ($n=7$) for pH, alkalinity, Na, K, Ca, Mg, NH_4 , Fe, and Mn were used to constrain the model. The reciprocal of observed values was taken as weight factor. Weight for pH was multiplied with a factor 10 to better constrain on this crucial variable.

Degassing of CH_4 , CO_2 , and N_2 was simulated as described previously (Van Breukelen et al., in press). A partial N_2 pressure of 0.8 atm was adopted for pristine groundwater, while for leachate the average observed $p\text{N}_2$ of 0.34 atm (Van Breukelen et al., 2003) was taken. For each cell, a specific hydrostatic pressure was imposed, calculated using the minimum observed water table level (1.3 m below surface) in the period 1998–2001 (12 measurements) at M1. The total gas pressure exceeded the hydrostatic pressure up to some tenths of an atmosphere in the present plume (Van Breukelen et al., 2003). Therefore, bubble formation and subsequent degassing from the groundwater to the atmosphere was only allowed if the sum of the CH_4 , CO_2 , and N_2

partial gas pressures exceeded the sum of the hydrostatic pressure at a particular depth and an adopted threshold pressure of 0.32 atm.

5.2. Model results

Results of the modelling are presented in Fig. 8. The model reproduces observations well. Note that the model did not aim to capture the pH variation in pristine groundwater. An intermediate value was optimized for the PBC, while the CEC was required to be very low (Table 2). Geochemical heterogeneity of the aquifer may explain a low CEC (see before). A larger CEC to PBC ratio gives an overall higher selectivity for K and NH_4 and could therefore not reproduce the chromatographic pattern at the site.

A good model fit was achieved taking the minimum observed pristine groundwater concentrations for Ca, Fe and Mn, maximum concentrations for Na and NH_4 , and intermediate concentrations for Mg, Na and K. However, the Fe and Mn fronts were not captured well and small peaks were simulated (results not shown). A better model fit, in particular for Fe and Mn, was attained when the selectivity of Ca, Mg and also K for the proton buffer was reduced, while the Fe and Mn concentration for pristine groundwater was taken below the observed minimum (Table 2). The Fe and Mn concentrations were likely lower before plume uplift started than presently observed, since NO_3 was still present.

Chromatographic patterns observed at locations M2 and M3 were identical to those at M1, while front separation increased with increasing uplift (Figs. 5 and 6): both the uplift (~ 1.3 m at M1, ~ 3.3 m at M2) and the length of the proton-buffering zone (the distance between F3 and F1; ~ 1.0 m at M1, estimated 2.5 m at M2) were related and a factor 2.5 higher at M2 than at M1. The proton-buffering zone was largest at M3 and extended from front F3 to beyond the top of the MLS profile. Cation concentrations except for sodium changed dramatically at M3 within a 20-cm vertical distance at 3.8 m below surface. Apparently, a thin layer must be present there with a high cation exchange capacity, prohibiting breakthrough of pH and all cations except sodium, which has the lowest affinity for exchange sites (Table 2).

The simulated methane concentration overshoots observations at the proton-buffering zone a little when degassing is not included in the model (Fig. 8: dashed line). The model predicts methane observations better in this zone when simulation of degassing is included (Fig. 8: solid line). Proton buffering causes a pH decrease, which results in a peak of the $p\text{CO}_2$ pressure at 3.5 to 4 m below surface as discussed before. The model reproduces the increase in $p\text{CO}_2$ compensated by a decrease in $p\text{CH}_4$, as observed in the field, quite well (Fig. 6). The observed methane loss seems however somewhat larger than simulated. This can be explained by AMO not included in the model and may also be related to uncertainty in the threshold pressure. The calculated amount of methane degassed may consume a nitrate concentration of ~ 0.2 mmol/l in a column of pristine groundwater of 1.5 m height above the plume.

Finally, Fig. 8 shows that surface complexation results in desorption of sulfate from iron oxide, and a sulfate peak below F1 as observed, due to an increase in pH when leachate displaces slightly acidic pristine groundwater. Concentrations of other species including pH were not significantly affected by surface complexation.

5.3. General model for potential of secondary redox reactions at the fringe of a plume

A series of additional 1D PHREEQC simulations was performed to evaluate the potential of Fe(II), Mn(II), NH₄ and CH₄ oxidation at the top fringe of landfill leachate plumes in general. Oxidation can occur if the front of an electron-donor overlaps with the opposite-oriented front of a soluble electron-acceptor admixing from pristine groundwater (i.e., the electron-donor and the electron-acceptor are mixed and may react). The control of aquifer geochemistry (CEC, PBC) on the potential for occurrence of secondary redox reactions was addressed. Furthermore, effects of both a stationary and a transient fringe (seasonally upward and downward moving) were evaluated. In the case of a stationary fringe only diffusion was simulated in order to mimic transversal dispersion.

Simulations (results not presented) showed that methane has best contact with electron-acceptors in pristine groundwater, and is consequently most reactive at the top fringe of a plume, in particular when a plume moves upwards like observed in the present study. In that case, cation-exchange reactions involving NH₄, Fe(II) and Mn(II) result in a chromatographic separation with available dissolved electron-acceptors outside the plume, where the extent of separation depends on CEC and impact of proton buffering (i.e., SOM content and pH difference across fringe). This situation is comparable to the downstream edge (front) of a plume where advective transport moves the plume downstream. In contrast, sorption-induced retardation could result in contact of NH₄, Fe(II) and Mn(II) with electron-acceptors, if a plume moves downwards with sufficient amplitude. Ammonium will then be most susceptible to oxidation as it sorbs better than Fe(II) or Mn(II). Iron(II) or manganese(II) will only be the electron-donors in best contact with oxidants if the CEC is limited and the proton buffer, preferentially sorbing Fe(II) and Mn(II) over NH₄, is large. Contact for all these electron-donors with dissolved electron-acceptors in pristine groundwater is good, but decreases slightly in the order: CH₄, NH₄, Fe(II) or Mn(II), for both a transient (top/bottom) fringe at average position and a transversal-dispersion controlled, stationary fringe.

6. Discussion and conclusion

Summarizing, the plume rose gradually to the surface in the period 1998–2003. The plume uplift might be caused by enhanced exfiltration to the “Heilooop” stream due to increased precipitation over this period and an artificial lowering of the water level in the stream. Rising of the plume triggered proton buffering including cation exchange, and induced degassing of methane. Cation exchange resulted in spatial separation of NH₄ and in particular Fe(II) and Mn(II) from potential electron-acceptors outside the plume. Consequently, methane oxidation is potentially the most important secondary redox process at the fringe, and competes with DOC for available oxidants. Anaerobic methane oxidation also occurred directly below the fringe as evidenced by $\delta^{13}\text{C-CH}_4$ analysis, and was probably coupled to SO₄-reduction. Furthermore, methane can disperse further into pristine groundwater than DOC, because of its volatility. This study shows that degassing of methane happens and could result in subsequent re-dissolution in above-flowing pristine groundwater, and thereby increases the importance of methane oxidation as a process scavenging

available electron-acceptors. Methane concentrations that decrease upwards from 1 to 0.2 mg/l in pristine groundwater immediately above the plume indicate that this occurs, while oxidation of the methane is an explanation for the absence of previously observed nitrate. Degassing may also lead to entrapment of gas bubbles in the aquifer, resulting in presence of a stationary gas phase. This reduces the hydraulic permeability at the fringe and, hence, transversal mixing or further migration of the plume towards the surface.

The present study shows that NA at the fringe of this landfill leachate plume was limited, in comparison to the 40% of DOC degraded along the plume axis found by Van Breukelen et al. (2003). Limited reactivity was primarily due to depletion of O₂ and NO₃ in pristine groundwater, probably caused by oxidation of methane escaped from leachate. This finding contrasts with a study on NA of a plume with phenolic compounds, where redox reactions at the fringe were primarily responsible for degradation (Mayer et al., 2001). There, toxic contaminant levels probably impeded degradation in the core, while dilution and presence of O₂ and NO₃ in pristine groundwater resulted in degradation at the fringe. Detailed vertical sampling on 0.1-m scale was necessary to capture the hydro-chemical gradients across the plume fringe, which is typically tenths of meters to a few meters thick for a typical pollution plume. The limited length of the plume restricted the height of the fringe and, consequently, the contribution of the fringe to total NA as well. However, the size of the fringe zone seems comparable to other plumes described in literature considering its short plume length (e.g., Frind and Hokkanen, 1987; Mayer et al., 2001; Brun et al., 2002).

Re-oxidation of dissolved Fe(II) at the outskirts of a plume was proposed by Christensen et al. (2001) and Heron (1994) as an important secondary redox process leading to regeneration of the aquifer oxidation capacity (OXC). The idea for this process was speculated on a few outliers of high Fe(III)-oxide content (about triple background content) at the outskirts of the Vejen landfill leachate plume in the study of Heron and Christensen (1995). However, most measurements were not higher than background. The authors noted that these data could not reveal whether increased iron oxide content was due to re-precipitation of mobilized Fe(II) or sediment heterogeneity. Furthermore, even if this process happens, it is in essential OXC-neutral. It would indeed regenerate Fe(III)-oxide as an oxidant, but at the expense of oxygen. This must be regarded unfavorable for the degradation of aromatic hydrocarbons, which degrade better under aerobic conditions.

Occurrence of this process was initially supported by a model study by Hunter et al. (1998) who addressed the importance of secondary redox reactions at the downstream front of a hypothetical landfill leachate plume: oxidation of metal species and methane consumed a comparable quantity of oxidants at the fringe. However, cation-exchange reactions were not considered. Griffioen (1999) argued that ignoring cation-exchange reactions overestimated the importance of Fe(II) and also Mn(II) oxidation at the front of the plume. Cation-exchange reactions result in chromatographic separation of Fe(II) and Mn(II) from oxidants, especially when transport is advection instead of dispersion controlled. Results of the present study show that this indeed occurs, and is the case for ammonium as well. A reactive transport model of the Vejen landfill leachate plume incorporating cation exchange did also not predict re-precipitation of dissolved Fe(II) at the downstream plume front (Brun et al., 2002). Note that the type of cation-exchanger present determines the extent of retardation of NH₄ versus Fe(II) and Mn(II), where illite-

type of clay minerals yield high retardation for NH_4 , while SOM yields high retardation factors for divalent and trivalent metals (together with H^+).

Reductive dissolution of manganese-oxide by Fe(II) is another mechanism within the plume which prohibits re-oxidation of Fe(II) by dissolved O_2 and NO_3 at the fringe, and is observed at the Grindsted landfill (Bjerg et al., 1995). The redox chemistry at the fringe of that plume was exclusively determined by secondary redox reactions, since DOC was completely degraded within the plume. Indications for ammonium and methane oxidation at the plume fringe were found. The observation that the methane plume was contained within a larger ammonium plume, suggests that oxidation of methane was preferred. Manganese concentrations were elevated with respect to background in the plume including the fringe. This points out that Mn-oxide can be regarded as a fringe-oxidant next to O_2 and NO_3 . Elevated Mn to Fe ratio at the fringe of the present site supports this. In conclusion, current evidence and theory shows that the process of re-oxidation of Fe(II) at the fringe of a landfill leachate plume is less significant than hypothesized by Heron (1994). However, the process could be general for hydrocarbon pollution plumes, which lack ammonium, contain usually less or no methane, and where DOC (hydrocarbons) is not conservative and retards likely more than the Fe(II) formed by iron-reduction.

The relevance of methane oxidation at the fringe would lessen if anaerobic methane oxidation (AMO) inside a leachate plume occurs (Griffioen, 1999). Anaerobic methane oxidation coupled to sulfate-reduction has been observed in marine environments (Valentine and Reeburgh, 2000), but could thermodynamically be coupled to reduction of iron oxide as well (Hoehler et al., 1994). Stable isotope analysis (SIA) of methane indicated occurrence of AMO presumably coupled to sulfate-reduction inside and at the fringe of the Norman landfill leachate plume (Grossman et al., 2002). This process seems to happen at and directly below the fringe zone of the present landfill leachate plume as well. However, methane stable isotope analysis indicated absence of AMO in the core of the present plume (Van Breukelen et al., 2003), and inside a petroleum hydrocarbon plume (Revesz et al., 1995). In conclusion, current evidence shows that AMO inside contaminated plumes will usually not result in absence of methane at the fringes.

A typical landfill leachate methane concentration of 1 mmol/l is capable of consuming 0.35 mmol/l O_2 (groundwater in equilibrium with atmosphere at 10 °C) together with a considerable nitrate concentration of 1.3 mmol/l. Methane oxidation can be the most important redox process at the fringe of a leachate plume, if AMO inside the plume does not considerably attenuate methane, sorption-reactions retard cations in a reduced state, and depth-fluctuation of the fringe is small (i.e. Fe(II) and NH_4 retard and may become oxidized instead of CH_4 if a plume fringe moves downward). Then, methane can consume all available oxygen and nitrate in pristine groundwater, and thereby reduces NA at the fringe for other solutes to dilution only.

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