ground water

Review Paper/

Biogeochemical Evolution of a Landfill Leachate Plume, Norman, Oklahoma

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Abstract

Leachate from municipal landfills can create groundwater contaminant plumes that may last for decades to centuries. The fate of reactive contaminants in leachate-affected aquifers depends on the sustainability of biogeochemical processes affecting contaminant transport. Temporal variations in the configuration of redox zones downgradient from the Norman Landfill were studied for more than a decade. The leachate plume contained elevated concentrations of nonvolatile dissolved organic carbon (NVDOC) (up to 300 mg/L), methane (16 mg/L), ammonium (650 mg/L as N), iron (23 mg/L), chloride (1030 mg/L), and bicarbonate (4270 mg/L). Chemical and isotopic investigations along a 2D plume transect revealed consumption of solid and aqueous electron acceptors in the aquifer, depleting the natural attenuation capacity. Despite the relative recalcitrance of NVDOC to biodegradation, the center of the plume was depleted in sulfate, which reduces the long-term oxidation capacity of the leachate-affected aquifer. Ammonium and methane were attenuated in the aquifer relative to chloride by different processes: ammonium transport was retarded mainly by physical interaction with aquifer solids, whereas the methane plume was truncated largely by oxidation. Studies near plume boundaries revealed temporal variability in constituent concentrations related in part to hydrologic changes at various time scales. The upper boundary of the plume was a particularly active location where redox reactions responded to recharge events and seasonal water-table fluctuations. Accurately describing the biogeochemical processes that affect the transport of contaminants in this landfill-leachate-affected aquifer required understanding the aquifer's geologic and hydrodynamic framework.

Introduction

The transport of potentially toxic contaminants in leachate, from both old and modern landfills, is a serious environmental problem. In the United States alone, approximately 135 million tons of municipal solid waste (MSW) was deposited in landfills in 2008, making landfills the most common method of MSW disposal (USEPA 2009). Approximately 1653 operational landfills were active during 2004 in the United States (Simmons et al. 2006), which is a decrease from 7683 active landfills in 1982. Of greater concern are the closed landfills in the United States, estimated at more than 90,000 two decades ago (Suflita et al. 1992). These closed landfills are typically unlined so that exposure of buried waste to precipitation and groundwater seepage is expected to create leachate plumes containing complex mixtures of organic and inorganic contaminants (Bjerg et al. 2003). Past practices commonly located landfills near wetlands and surface water bodies, increasing the potential impact of leachate on nearby ecosystems. In addition, landfills alone accounted for approximately 23% of total U.S. anthropogenic methane (CH_4) emissions to the atmosphere in 2007

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(http://epa.gov/climatechange/emissions/downloads09/Waste.pdf).

One approach to managing landfill contaminant plumes is monitored natural attenuation (MNA) (Christensen et al. 2000; Bjerg et al. 2003, 2009). MNA involves monitoring the processes that transform contaminants to less harmful forms, or immobilize contaminants so they are less of a threat to the environment (National Research Council 2000). MNA can be a less-expensive alternative to active remediation methods such as extracting contaminated groundwater for treatment, but only where MNA is sufficient to limit plume migration. Despite the importance of MNA, there have been few long-term investigations (Baun et al. 2003) that focus on the integration of natural biogeochemical processes in complex subsurface systems such as leachate-affected surficial aquifers.

Microbial processes in contaminant plumes evolve over time in response to changing conditions. As a result, rates of contaminant degradation are also modified. For example, at the Grindsted Landfill in Denmark, Lønborg et al. (2006) reported that first-order degradation rates of six volatile organic compounds (VOCs) (benzene, toluene, ethylbenzene, *o*-xylene, *m*, *p*-xylene, and naphthalene) in the methanogenic/sulfate- and iron-reducing zones varied substantially with redox zone. Within the anoxic center of the Grindsted plume, highest rates of biodegradation of most of the compounds were found in the Fe-reducing zones, whereas only *o*-xylene and toluene were biodegraded substantially in the methanogenic/sulfate-reducing environment. Clearly, the availability of electron acceptors, such as oxygen (O_2), ferric iron (Fe(III)) oxides, and sulfate (SO_4^{2-}), is an important factor for evaluating the efficacy and sustainability of intrinsic bioremediation in landfill-contaminated aquifers. In another paper in this volume, Bjerg et al. (2009) use results from three Danish landfills to illustrate complexities involved in applying MNA as a remediation option for landfill leachate plumes.

In this article, we summarize results of a 10-year study of the geochemical evolution of a leachate plume at the Norman Landfill Research Site (Norman, Oklahoma, USA) as it moved through generally anoxic alluvial sediments toward the Canadian River, and we review previously published processes-oriented studies from the field and laboratory that provide insight into the cycling of C, N, H, S, Fe, and O species in this system. The focus of the Norman investigations was on understanding the biogeochemical processes associated with degradation of organic and inorganic contaminants in the leachate plume. Through long-term research and identification of processes resulting from the contaminant plume mixing with background groundwater and exposure to aquifer solids, insight was gained into what types of contaminants are released from the Norman Landfill and other similar sites and how these sources of contamination change over time. In addition, we evaluated the effect of the contaminants on the geochemical composition of the aquifer itself. The resulting knowledge and methods developed from research at the Norman Landfill Research Site can improve the effectiveness and may reduce the cost of characterization and remediation at other contaminated sites.

Our main goal with this article is to provide a comprehensive understanding of how the Norman Landfill leachate plume evolved as the leachate components moved through the aquifer and the dissolved constituents reacted with each other and with dissolved and solid phases in the aquifer. Elucidating these processes and their effects required observations at different scales. Two complementary approaches were taken at the Norman Landfill Research Site to assess how biogeochemical zonation in the aquifer, downgradient from the landfill, changed over time and how those changes were related to natural attenuation of leachate components. One approach focused on the long-term evolution of redox zones at the plume scale by sampling on an annual or biennial time scale and another focused on seasonal variability by sampling on a monthly time scale at particular spatial locations where enhanced chemical reactions were expected. Plume-scale studies revealed that some contaminants moved through the aquifer with little attenuation, whereas others were attenuated by various processes including sorption and biogeochemical interactions with aquifer solids. Smaller-scale temporal studies revealed the effects of dynamic hydrologic and chemical conditions at the interfaces between the plume and overlying recharge water and at a discharge interface in a shallow wetland (referred to as a slough). Stable isotope data were used to differentiate water masses and compare processes affecting plume constituents such as ammonium (NH_4^+), SO_4^{2-}, and CH_4 in the center of the plume relative to processes active at the plume boundaries.

The Norman Landfill Research Site

The Norman Landfill Research Site is a closed municipal solid waste landfill, formerly operated by the city of Norman, Oklahoma. The Norman Site is located south of the city of Norman on alluvial deposits of the Canadian River (Figure 1). The site is a research location for the Toxic Substances Hydrology Program of the U.S. Geological Survey (USGS) (http://toxics.usgs.gov/). Scientists from the USGS, other federal agencies, and numerous universities have installed a network of groundwater sampling devices and instruments to investigate the chemical, biological, and hydrologic processes in groundwater and surface water affected by landfill leachate (http://ok.water.usgs.gov/projects/norlan/pubs.html).

The site began as an open dump in the early 1900s and became a sanitary landfill (which required more stringent engineering-controlled disposal and soil-covering practices) as regulatory controls increased in the 1960s through 1980s. No restrictions were placed on the type of material dumped at the landfill. The waste in the landfill is predominantly residential and commercial solid waste, although the landfill closure report documents several incidents of suspected hazardous waste disposal (Dixon 1992). In the 1960s and early 1970s, waste was

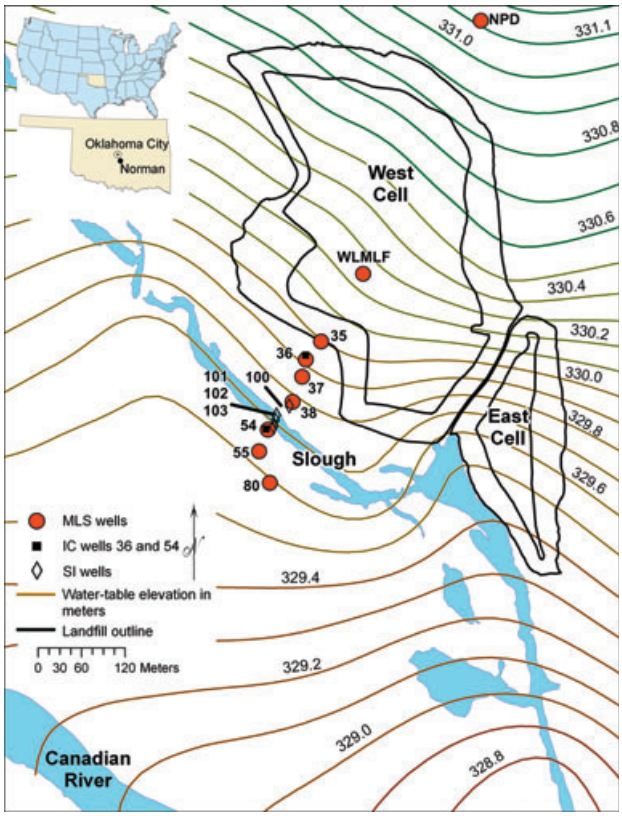

Figure 1. Map showing the location of the Norman landfill and MLS35-80 monitoring well transect, with water-level contours measured in 1998 (0.1-m intervals). Groundwater flow direction is generally southwest between the landfill and the slough, perpendicular to the water-level contours and parallel to the well transect. MLS, multilevel well clusters, extend to the base of the aquifer.

dumped into trenches about 3 m deep that contained 1.5 to 2.5 m of water because of the shallow water table. The waste was subsequently covered with 15 cm of sand. Waste handling was modified in the late 1970s and early 1980s to deposit the wastes on lifts of sand that were covered by surrounding sediment; this operation led to the construction of elevated mounds. In response to the passage of more stringent regulations in Subtitle D of the Resource Conservation and Recovery Act (RCRA), the landfill was closed in 1985, and the mounds were covered with local clay and silty sand and grass vegetation. The capped landfill includes two cells, the east cell and the west cell (Figure 1). The base of the landfill area is about 314,000 m^2 and the capped area is 186,000 m^2. The total mass of buried waste is estimated at approximately 2.6 million tons and the cap rises to an elevation 12 to 15 m above the surrounding alluvium.

The Canadian River flows southeast and, in 2010, was about 600 m southwest from the edge of the landfill. The river is separated from the landfill by a relatively flat area, with low sand dunes vegetated with small willow and cottonwood trees, shrubs, and native grasses. The water table in the Canadian River alluvium fluctuates in response to rainfall and seasonal evapotranspiration, and is usually less than 2 m below land surface near the landfill (Scholl et al. 2004). Average annual precipitation is approximately 96 cm/year. May and June typically have the most rainfall, with a secondary maximum in September and October (Jaeschke et al. 2010). Evapotranspiration during the growing season limited the recharge amounts which averaged approximately 0.55 m/year between 1998 and 2000 (Scholl et al. 2004). A shallow stream, with ponded wetland areas caused by beaver dams (subsequently referred to as the slough), has an average depth of about 0.75 m, runs parallel to and about 100 m from the edge of the landfill, and has an elevation of approximately 330 m (Figure 1).

The Canadian River alluvium, which is 10 to 12 m thick, is predominantly pale red, fine- to medium-grained sand beds with interbedded, discontinuous layers of red-brown clayey silt and gravel. A discontinuous low hydraulic-conductivity interval that consists of silt and clay was detected at elevations between 326 and 328 m beneath much of the study area. A high hydraulic-conductivity layer containing coarse sand and gravel is located near the base of the alluvium at an elevation of 319 m. Low-permeability shale and siltstone in the Hennessey Group of Permian age act as a lower boundary to vertical groundwater flow beneath the alluvium. The red color of the alluvium is attributed to very fine grained (less than 0.1 μm) disseminated hematite that originated with the detrital sediments from the abundant red beds in the drainage basin. Sand layers are comprised of quartz, illite-smectite, feldspars, and minor calcite and dolomite; mud layer mineralogy is similar but with greater amounts of clays that include illite-smectite, smectite, kaolinite, and chlorite (Breit et al. 2005). Authigenic phases in the aquifer include FeS, pyrite (FeS_2), barite ($BaSO_4$), and very fine (less than 0.1 μm) Fe(III) oxides. Mirabilite ($Na_2SO_4 \cdot 10H_2O$) and gypsum ($CaSO_4 \cdot 2H_2O$) occur in trace amounts as ephemeral accumulations on the land surface (Tuttle et al. 2009).

Methods

The monitoring well network at the Norman Landfill site consists of multilevel well clusters with screens set at different elevations (Figure S1, Supporting Information). The MLS (multilevel wells extending to the base of the aquifer), IC (closely spaced multilevel wells spanning the water-table reactive zone), and SI (multilevel wells in the slough area) networks follow a transect parallel to the regional groundwater flow path. Extensive geochemical studies were conducted along a transect that begins at MLS35, near the toe of the landfill, extends across the slough, and ends at MLS80 downgradient from the slough (Figure 1). Details of the placement of the monitoring wells and their construction specifications are provided in the Supporting Information. Plume-scale studies along the transect were conducted between 1997 and 2006, and local time-series studies were conducted on a monthly or semimonthly time scale between 1998 and 2008. Samples for characterization of VOC, common domestic waste water constituents, and dissolved gasses were also

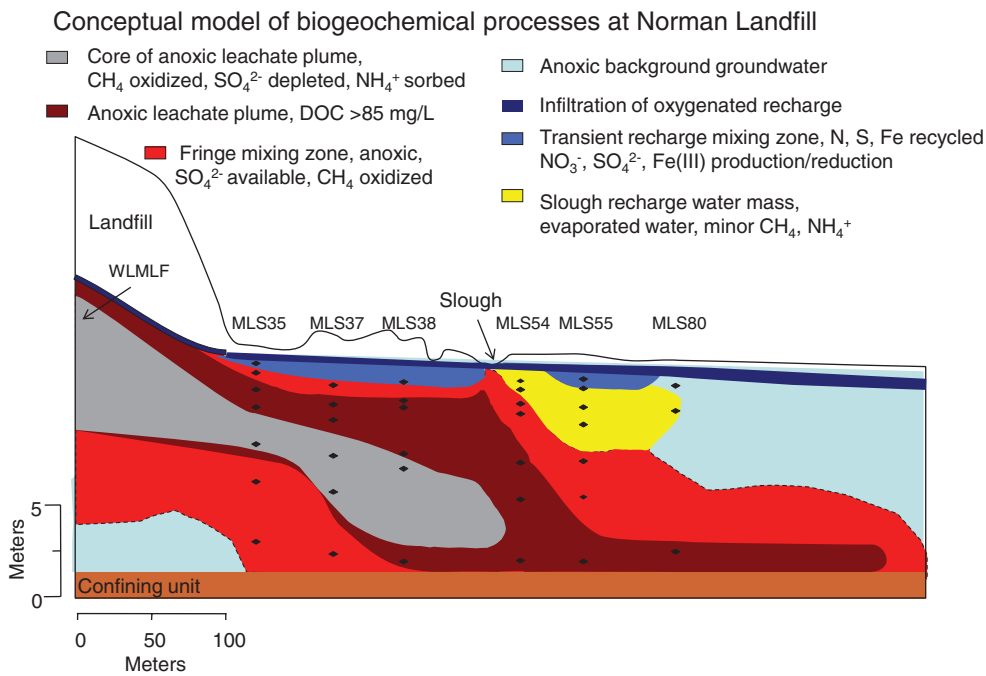

Figure 2. Model of the important hydrologic and geochemical features of the leachate plume in the alluvial aquifer downgradient from the Norman Landfill.

collected. Cores were collected and analyzed to determine grain size and the abundance of extractable Fe and S species (Breit et al. 2008; Tuttle et al. 2009). Details of the water and sediment sample collection and analyses are provided in the Supporting Information.

Results and Discussion

Conceptual Model of Plume Processes

Dynamic hydrologic conditions at Norman Landfill have created a leachate plume that interacts with a shallow wetland and also migrates underneath the wetland toward the Canadian River. Spatial and temporal variability in the rates of processes in the shallow aquifer affect the plume-scale migration of leachate constituents. Figure 2 shows a generalized conceptual model of these processes. This model shows the relationship between the hydrologic, geochemical, and microbiological processes in this system and informs our understanding of the natural attenuation potential of the landfill-leachate-affected aquifer. In the following section specific aspects of this model and the major processes represented are described in detail.

Hydrologic Characteristics Influencing Movement of the Leachate Plume

The leachate-contaminated groundwater plume is maintained by precipitation recharge that infiltrates through the landfill and is incorporated into the regional groundwater flow system, where it sinks as it moves toward downgradient discharge areas. Substantial floods of the Canadian River occurred on October 5, 1986 and again on May 29, 1987 (http://nwis.waterdata.usgs.gov/ok/nwis/peak/?site_no=07229200&amp), causing the Canadian River channel to relocate from a position at the toe of the landfill to 600 m to the south. Movement of the main river channel left a remnant channel now identified as a slough (Schlottmann 2001; Curtis and Whitney 2003). Prior to the relocation of the Canadian River the plume presumably would have discharged directly into the river near the current location of the slough. A potentiometric-surface map prepared by Scholl and Christenson (1998), after the relocation of the river channel, showed that groundwater flows generally south under the landfill and slough toward the Canadian River (Figure 1). The relocation of the Canadian River substantially increased the area of aquifer available for reaction with the leachate plume. In 1996, the plume (as defined by the distribution of specific conductance) underlaid an area of approximately 51,000 m^2 with the downgradient leading edge approximately 200 m from the landfill toe. In 2009, the plume extended beneath an area of 181,000 m^2 with the downgradient edge mixing and discharging with regional groundwater beneath the Canadian River.

Currently, the slough overlies the leachate plume. The slough does not have a distinct surface water input or output but is connected with shallow groundwater. Mendoza-Sanchez et al. (2009) determined that water input to the slough was primarily from groundwater discharge (greater than 80%) that occurred shortly after rain events, with the balance supplied by direct precipitation and runoff (less than 20%). The greatest water output from the slough, about 70%, is from evaporation (Masoner et al. 2008). A fraction of the slough water, about 20%, recharges the aquifer. Potentiometric-surface measurements and geochemical data show that leachate-containing groundwater

discharges into the slough from its NE bank and slough water recharges the aquifer along the SW bank most of the time.

Calculated groundwater velocities in the area between the landfill toe and the slough had a median value of 15 m/year (Table S1, Supporting Information). The area between the slough and the Canadian River had hydraulic gradients that were less than the hydraulic gradients between the landfill toe and the slough resulting in groundwater velocities with a median value of 8.3 m/year. A conservative tracer that moves linearly in a connected high permeability flow path will take 4.5 years to cross the transect distance of 230 m based on maximum hydraulic conductivities of 2.8×10^{-4} and a median hydraulic gradient of 3.1×10^{-3}. Travel times through median hydraulic-conductivity layers (6.6×10^{-5}) would take approximately 20 years to move the same distance, which underscores the complexity of estimating transport rates in the aquifer. Moreover, hydraulic gradients and groundwater flow directions along the MLS transect varied temporally (Figure S2). Groundwater flow directions varied at different times by around 35° between the Norman Landfill and the slough, and by up to 85° downgradient from the slough (Figure S2). Other landfill leachate plumes also have exhibited large transient changes in flow direction, for example, 20 to 70° at the Sjoelund and Grindsted sites in Denmark (Bjerg et al. 2009). Depths to water from land surface between the landfill and the Canadian River ranged from 0 to 2.1 m. Minor water-table mounding occurred beneath the landfill as a result of infiltration through the vegetated landfill cap. The water table in a well beneath the waste mound (WLMLF) ranged from 1 to 13 cm higher than the water table interpolated from wells surrounding the landfill (Christenson et al. 1999).

Chemical Characteristics of Leachate-Contaminated Groundwater

Many dissolved constituents of the leachate were derived from dissolution and degradation of buried waste material. Leachate recharging the underlying aquifer contained high nonvolatile dissolved organic carbon (NVDOC), HCO_3^-, NH_4^+, B, Cl^-, Fe^{2+}, and CH_4 concentrations, high $\delta^2H_{H_2O}$ values, and low SO_4^{2-}, Ar, and N_2 concentrations (Table 1). Arsenic, barium, cadmium, chromium, cobalt, nickel, and strontium also had substantially higher concentrations in wells downgradient from the landfill than in background wells. The NVDOC concentration is a useful measure of the bulk organic contaminant compounds in the leachate. The NVDOC, which reached a maximum concentration of 300 mg/L in WLMLF, is a highly heterogeneous mixture of nonvolatile organic components and fragments from proteins, lignin, cellulose, hemicellulose, polysaccharides, lipids, and waxes that have undergone extensive biological and chemical reactions (Nanny and Ratasuk 2002; Leenheer et al. 2003). The NVDOC contains fulvic and humic acids that can facilitate the transport of other contaminants and affect redox processes. The fulvic acid fraction of the Norman Landfill leachate NVDOC is highly aliphatic, with 10% or less aromatic (Nanny and Ratasuk 2002). The aliphatic content of this fulvic acid fraction consists primarily of branched methyl groups and quaternary aliphatic carbon structures indicating terpenoid hydrocarbon precursors thought to originate from resin acid paper sizing agents associated with disposed paper and paper products (Leenheer et al. 2003). The chemical structure of the fulvic acid fraction can facilitate transport of other dissolved organic compounds and metals (Larsen et al. 1992; Guggenberger et al. 1994; Gadad et al. 2007) which underscores the importance of characterizing the NVDOC. Moreover, changes to the physical and chemical properties of the waste with progressive decomposition can alter the composition and transport properties of mobile organic contaminants in the leachate over time. For example, degraded newsprint in the Norman Landfill, which accounts for greater than 30% of the MSW typically buried in a landfill of this age, has five times the sorptive capacity of undegraded newsprint for compounds such as toluene (Chen et al. 2004).

Organic contaminants identified in the Norman Landfill leachate reflect the residential and commercial origin of the wastes in the landfill. In 2000, leachate near the edge of the landfill contained numerous organic waste water contaminants (OWCs), including detergents, insect repellents, plasticizers, fire retardants, polycyclic aromatic hydrocarbons, and fecal indicators (Barnes et al. 2004). A similar composition and distribution of OWCs were detected in wells between the landfill and the slough in 2009 (Figure 3). Although the concentrations of OWCs generally decreased downgradient from the landfill, higher concentrations of some OWCs, and a larger number of detected OWCs, were observed at 95 m downgradient (MLS38) than at the toe of the landfill (MLS35) in 2009 (Figure 3). The same pattern was observed in 2000, indicating that well MLS38 is completed in the most concentrated part of the leachate plume (Barnes et al. 2004) and likely receives input from another source in the landfill. Several compounds were detected downgradient from the landfill but not in the landfill well (WLMLF), indicating that WLMLF was not fully representative of the heterogeneous distribution of leachate constituents within the landfill (Figure 3). OWCs detected in MLS38 and MLS35 during both the 2000 and 2009 sampling events include bisphenol A (a plasticizer), *p*-cresol (a disinfectant), DEET (an insect repellent), and tri(2-chloroethyl) phosphate (a fire-retardant) (Table 2). Persistence of these compounds 95 m downgradient from the landfill toe and over a 9-year period indicates that natural attenuation was relatively slow for these contaminants and that the landfill was a continuing source of OWCs. Buszka et al. (2009) identified similar waste-indicator and pharmaceutical compounds in landfill leachate-affected groundwater near Elkhart, Indiana. Pharmaceuticals and their metabolites detected in that study included acetaminophen, caffeine, cotinine (a nicotine metabolite), 1,7-dimethylxanthine (a caffeine metabolite), fluoxetine, and ibuprofen.

Table 1
Summary of Chemical and Isotopic Data for Background Groundwater, Groundwater Near the Source, and Groundwater from the Center of the Plume (Collected from 1997 to 2008 at the Norman Landfill Research Site)

	Background				Landfill Source				Downgradient			
	n	Min	Median	Max	*n*	Min	Median	Max	*n*	Min	Median	Max
Water temperature (°C)	9	15.1	16.9	18.7	10	21.8	22.5	24.2	10	18.2	19.5	20.8
Specific conductance (μs/cm)	9	1092	1461	1628	10	5246	8832	9256	10	3580	5025	5785
pH (standard units)	9	6.9	7.1	7.2	10	6.6	7.0	7.0	10	6.5	6.8	6.9
Alkalinity as bicarbonate (mg/L)	8	574	604	677	9	3289	3987	4269	11	1762	2107	2702
Nonvolatile organic carbon (mg/L)	6	3.1	3.3	3.9	10	189	227	299	9	52.5	87.3	113
Dissolved argon, Ar (mg/L)	3	0.56	0.63	0.64	3	0.00	0.03	0.05	6	0.13	0.15	0.20
Dissolved nitrogen, N_2 (mg/L)	3	21.8	21.9	22.5	3	0.56	1.15	2.48	6	4.45	5.49	5.91
Dissolved oxygen, O_2 (mg/L)	8	<0.01	0.14	0.49	6	<0.01	0.1	0.1	6	<0.01	0.1	0.5
Hydrogen sulfide (mg/L)	5	<0.01	<0.01	0.02	5	<0.01	0.1	0.2	5	<0.01	<0.01	<0.01
Methane (mg/L)	5	0.01	0.06	0.10	6	5.9	8.2	16.2	6	0.3	3.7	14.2
Chloride (mg/L)	8	29	147	172	9	705	931	1032	10	370	551	848
Nitrate as N (mg/L)	7	<0.05	<0.25	<0.98	4	<0.05	1.1	2.7	4	<0.05	0.7	5.3
Sulfate (mg/L)	8	86.1	124	205	9	1.0	8.1	25.4	6	0.0	0.5	30.4
Ammonium as N (mg/L)[1]	8	1.6	2.1	4.0	8	209	562	650	17	127	151	200
Calcium (mg/L)	7	102	132	158	8	92.0	104	136	8	102	245	344
Magnesium (mg/L)	7	45.5	59.1	75.4	8	89.6	105	112	8	99	119	165
Sodium (mg/L)	7	87.6	109	116	8	785	850	870	8	496	630	660
Potassium (mg/L)[1]	7	1.7	2.2	5.4	8	315	414	472	6	165	198	233
Arsenic (μg/L)	10	<1.0	2.2	7.9	2	13.0	13.5	14.0	5	6.0	8.0	12.0
Barium (mg/L)	12	1.2	0.2	0.3	12	1.4	3.4	6.3	12	1.8	11.5	15.4
Boron (mg/L)	7	0.3	0.4	0.5	7	1.4	1.8	3.2	7	3.1	3.3	3.7
Bromide (mg/L)	7	0.1	0.8	0.9	9	1.6	6.7	7.8	10	1.1	4.2	6.7
Cadmium (μg/L)	7	<0.5	<0.5	<0.5	4	<0.5	<0.5	0.6	8	<0.5	<0.5	<0.5
Chromium (μg/L)	5	1.0	2.0	4.0	4	10.0	10.5	13.3	6	3.0	5.5	9.0
Cobalt (μg/L)	9	<0.5	1.7	2.2	4	19.6	20.6	25.1	8	10.3	14.3	15.9
Iron (mg/L)	7	2.3	2.7	3.1	8	2.6	5.1	15.6	8	7.6	10.5	16.0
Manganese (mg/L)	7	1.0	1.1	1.4	7	0.1	0.1	0.3	8	0.1	0.5	1.0
Nickel (μg/L)	9	<0.1	<0.1	1.8	4	20.0	26.6	39.7	7	8.6	13.0	15.6
Silicon (mg/L)	6	11.8	12.3	12.9	6	13.5	14.4	21.7	7	14.3	16.7	18.6
Strontium (mg/L)	19	0.8	1.0	1.9	12	1.3	2.1	2.5	11	2.7	4.3	6.4
δ^2H of water (‰)	8	−31.3	−30.3	−26.1	9	−3.5	10.5	12.6	9	−18.9	−15.0	−8.1
δ^{18}O of water (‰)	8	−5.2	−5.0	−4.6	9	−6.3	−6.0	−5.7	9	−5.6	−5.4	−5.1
δ^{15}N of ammonium (‰)[1]	5	5.0	5.6	6.2	4	5.2	5.8	7.2	17	6.6	7.0	7.9

Note: Background groundwater corresponds to MLSNPD-4, landfill source groundwater corresponds to WLMLF, and downgradient groundwater corresponds to MLS35-5. *n* corresponds to number of observations used in calculating summary statistics.
[1]Values for downgradient water computed from MLS35-3.

VOCs in the Norman Landfill leachate plume were measured in 1995 and 1996 in samples collected from temporary drive-point piezometers along the current MLS35-80 transect (Eganhouse et al. 2001). In 2009, VOCs were measured in the landfill well (WLMLF), at the toe of the landfill (MLS35), and at 230 m downgradient (MLS80). Some of the compounds identified by Eganhouse et al. (2001) were still detectable in the leachate 14 years later, including those identified as good molecular markers of the leachate because of their apparent persistence within the core of the anoxic leachate plume—cholorobenzene, 1,4-dichlorobenzene, and isopropylbenzene (Table 3). In both 1995 through 1996 and 2009, naphthalene had the highest concentration of the VOCs detected (99.6 μg/L in WLMLF), and benzene was the only VOC with a concentration that exceeded the USEPA drinking water standard (Table 3). Low VOC concentrations in the leachate plume at Norman landfill are similar to those of other "old" municipal landfills that were not used for disposal of large quantities of industrial chemicals (Eganhouse et al. 2001).

Given estimated groundwater velocities in the aquifer (Table S1), mobile VOC constituents would have been transported beyond the extent of the transect in the 14 years between samplings, so their presence throughout the transect indicates continued release from the buried waste. Natural attenuation of some VOCs was indicated by decreasing concentrations of several constituents from WLMLF to MLS35-5 in 2009 (Table 3). Nonetheless, uncertainty remains as to whether WLMLF was

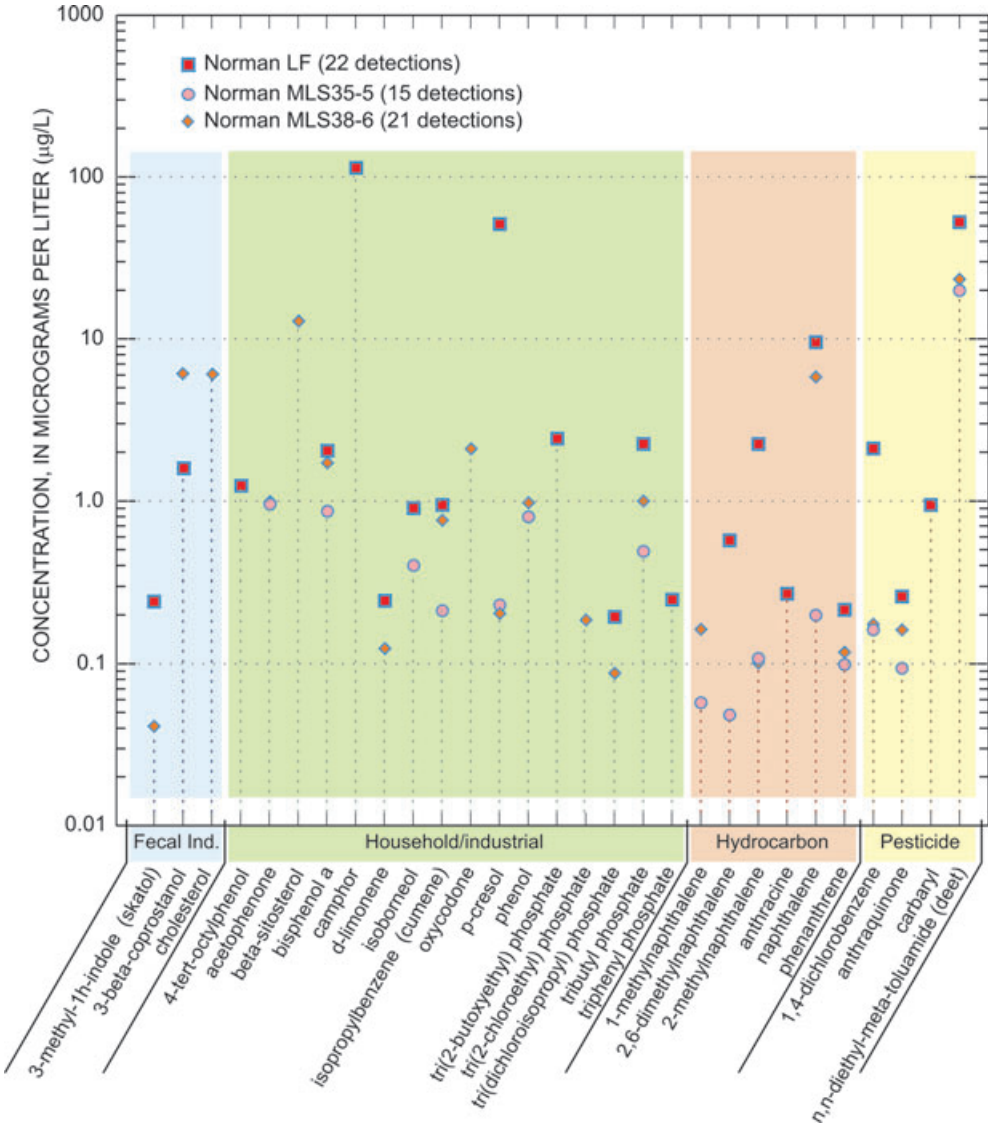

Figure 3. Nonvolatile dissolved organic compounds (NVDOC) measured in 2009 in the landfill well (WLMLF), at the toe of the landfill (MLS35, level 5, elevation 325.7 m) and 95 m downgradient from the edge of the landfill (MLS38, level 6, elevation 323.7 m).

representative of all sources within the landfill and if there is temporal variability in VOC release from the landfill. The apparent dilution factors for the conservative constituent, Cl^-, from WLMLF to MLS35 and MLS80 were 1.2 and 1.4, respectively. In contrast, concentrations of benzene, 1,3,5-trimethylbenzene, 1,4-dichlorobenzene, and naphthalene, respectively, declined by factors of 48, 5, 11, and 52 from WLMLF to MLS35 in 2009. Eganhouse et al. (2001) demonstrated that biodegradation was the dominant process controlling attenuation of VOCs in the Norman landfill leachate plume. Baun et al. (2003) studied the persistence of xenobiotic compounds in landfill leachate at the Vejen Landfill in Denmark. Although many compounds degraded in the anoxic plume, benzene and the herbicide Mecoprop (MCPP) were persistent. The persistence of benzene at low concentrations in the Vejen and Norman leachate plumes may indicate it was present at concentrations below which it is degraded; Cozzarelli et al. (2010) demonstrated a similar limitation was applicable to the biodegradation of hydrocarbons in an anoxic plume at a crude-oil spill site.

In the Vejen Landfill leachate plume (Baun et al. 2003) naphthalene has an attenuation factor of approximately 50 after adjustments for dilution, similar to that at the Norman Landfill. However, benzene degradation was not observed at the Vejen Landfill or in experiments related to two other landfill leachate plumes (Baun et al. 2003). Despite various degrees of natural attenuation for different compounds at the Norman Landfill and their continued release from the landfill, VOCs were largely attenuated within 200 m downgradient from the landfill toe in both in 1995 through 1996 (Eganhouse et al. 2001) and in 2009 (Table 3). Naphthalene, which had the highest concentration in the landfill well, was the only VOC that was still detectable at site MLS80, 230 m downgradient from the edge of the landfill (Table 3).

Table 2
Concentrations (Micrograms per Liter) of OWCs Detected in the Leachate Plume in September 2000 and February 2009

OWC	Classification	WLMLF 2009	MLS35-5 2000[1]	MLS35-5 2009	MLS38-6 2000[1]	MLS38-6 2009
Cholesterol	Fecal indicator	<0.8	0.04	<0.8	0.04	6.1
Bisphenol A	Household/industrial	2.0	0.8	0.9	0.5	1.7
p-Cresol	Household/industrial	51.2	0.2	0.2	0.5	0.2
Tri(2-chloroethyl) phosphate	Household/industrial	<0.2	0.4	<0.2	0.7	0.2
n,*n*-Diethyl-meta-toluamide (DEET)	Pesticide	52.6	8.1	19.9	13.0	23.4

[1]From Barnes et al. (2004).

Delineation of the Leachate Plume in Groundwater

Although leachate is chemically distinct from regional groundwater (Schlottmann 2001), some leachate-induced geochemical features can be difficult to identify because reactive electron donors and carbonate minerals in the aquifer sediment cause background samples to share some features with leachate, such as low O_2 and high alkalinity. Nonetheless, high concentrations of several dissolved constituents including Cl^-, B, Fe^{2+}, and NVDOC distinguish the leachate from ambient groundwater; the latter also tends to have higher concentrations of dissolved SO_4^{2-}. Figures 4 through 9 illustrate a time-series (1997 through 2006) of plume-scale concentrations and isotopic compositions of important inorganic and organic constituents in groundwater along the vertical longitudinal profile from MLS35 to MLS80 (Figure 1). Chloride is considered a conservative tracer of the leachate (Figure 4A). The distribution of Cl^- indicates the major body of the plume sank as it moved downgradient, likely because of recharge along the upper boundary, the presence of a high permeability gravel layer at the base of the aquifer, and greater density of leachate relative to uncontaminated groundwater. Irregularities in the plume boundary as defined by Cl^- concentrations were caused by a combination of source variation, aquifer heterogeneity, and hydrologic variability. Low Cl^- concentrations in the deeper parts of the aquifer near well MLS36, and persistently high Cl^- concentrations in the center of the aquifer near MLS38 (Figure 4A), may indicate that the transect was not exactly parallel to flow. Variations in hydraulic gradient and flow direction occurred throughout the study period (Figure S2), and the MLS35-80 transect may have intersected

Table 3
Concentrations (Micrograms per Liter) of VOCs Detected in the Leachate Plume in February 2009, and Comparison to Maximum Concentrations Detected Along Transect MLS35-80 in November 1995 and April 1996

VOC	1995 and 1996[1] Maximum	2009 WLMLF	2009 MLS35-5	2009 MLS80-6
Trichloroethene	0.7	0.19	0.43	<0.20
Chlorobenzene	NQ	<0.20	3.85	<0.20
2-Chlorotoluene	NQ	<0.20	0.31	<0.20
1,1-Dichloropropene	ND	0.23	0.24	<0.20
1,4-Dichlorobenzene	5.6	6.84	0.62	<0.20
1,2-Dichlorobenzene	NQ	0.88	<0.20	<0.20
Benzene	10	20.3	0.42	<0.20
Toluene	3.5	0.84	<0.20	<0.20
1,3,5-Trimethylbenzene	0.6[2]	2.03	0.41	<0.20
1,2,4-Trimethylbenzene	0.6[2]	2.05	<0.20	<0.20
Isopropylbenzene	1.24	<0.20	0.26	<0.20
p-Isopropyltoluene	ND	0.60	<0.20	<0.20
n-Butylbenzene	NQ	1.28	<0.20	<0.20
sec-Butylbenzene	NQ	0.87	<0.20	<0.20
Naphthalene	38	99.6	1.91	0.60

Note: nd, not detected; NQ, detected but not quantified.
[1]Maximum concentration reported for 1995 and 1996 (Eganhouse et al. 2001).
[2]Total trimethylbenzenes.

water that moved from upgradient locations not directly on trend with the transect.

Another relatively conservative and mobile indicator of the landfill leachate plume is the isotopic composition of water (Figures 4B and 5A). Landfill leachate water (H_2O) commonly is relatively enriched in ^2H in comparison to meteoric water, presumably because ^1H is transferred preferentially from H_2O to CH_4 or H_2 during methanogenesis (Baedecker and Back 1979; Hackley et al. 1996). At the Norman Landfill site, precipitation in 1996 to 2000 had δ^2H and $\delta^{18}O$ values consistent with a local meteoric water line described by: $\delta^2H = 7.5 \times \delta^{18}O + 11.7$ (Scholl et al. 2006). Background groundwater upgradient from the landfill had mean δ^2H and $\delta^{18}O$ values of -30.2 ± 1.6 and $-5.1 \pm 0.3‰$, respectively ($n = 58$). Water from landfill well WLMLF was substantially enriched in ^2H. Downgradient leachate plume samples had various ^2H enrichments that may reflect various amounts of methanogenesis in different parts of the landfill as well as mixing of leachate with background groundwater (Figure 10). Relative ^2H enrichments can be represented by convention as displacements from a hypothetical δ^2H-$\delta^{18}O$ correlation line with slope of 8 (Dansgaard 1964; Gat and Gonfiantini 1981):

$$\text{d-excess} = \delta^2H - 8 \times \delta^{18}O.$$

Upgradient meteoric groundwater with average d-excess of $+10.8 \pm 1.4‰$ (Figure 10) was displaced by leachate-plume water with d-excess values as high as $+30‰$ or more (Figure 9). The ^2H enrichments in many groundwater samples are too large to be explained by isotopic exchange with the amount of measured CH_4 in the groundwater. This is consistent with other evidence, presented below, indicating that most of the methanogenesis and H isotopic alteration of H_2O must have occured in the landfill while CH_4 escaped to the atmosphere or was oxidized in the unsaturated zone. The isotopically altered H_2O then moved into the aquifer, transporting a small fraction of the CH_4 produced. The H_2O isotopic anomaly persisted in the downgradient groundwater where methanogenesis was less active and CH_4 oxidation occurred (Grossman et al. 2002).

For the most part, the distribution of elevated δ^2H and d-excess values coincided with the distribution of high Cl^- concentrations. An important exception is downgradient from the slough, where H_2O exhibited relative ^{18}O enrichment and d-excess values were less than $+8‰$ (Figures 9 and 10). These isotopic features are attributed to evaporation of surface water in the slough, followed by recharge of the evaporated water to the shallow aquifer beneath the slough (Gat and Gonfiantini 1981). Evaporated slough water can be traced in the aquifer above the downgradient extension of the landfill leachate plume (Figures 5A and 9). In a detailed study of the geochemistry of the slough and shallow groundwater, Lorah et al. (2009) showed that interactions between the slough pore water and shallow aquifer varied seasonally. The evaporated isotopic signature of slough surface water was most evident in the shallow slough sediments under dry conditions (low water table), but the evaporated isotope water mass was a relatively stable feature of downgradient groundwater overlying the leachate plume.

Another common feature of landfill leachate plumes is elevated tritium (^3H) concentrations, presumably derived in part from luminescent paints (Hackley et al. 1996). Limited data ($n = 12$) from the Norman leachate plume indicate a positive correlation between ^3H and d-excess (Figure S3), consistent with mixing between background groundwater with $^3H = 5$ to 8 tritium units (TU) and leachate with $^3H \geq 240$ TU.

In general, the high Cl^- concentrations and δ^2H (and d-excess) values within the leachate plume appear to have decreased during this study, possibly because the contaminant source materials in the landfill were progressively depleted by passage of successive volumes of recharge water. Other relatively conservative leachate indicators included boron and NVDOC (Figure 5B, discussed in the preceding paragraphs). Conservative compounds showed spatial variability in concentrations, including dilution near the plume margins caused by dispersion and mixing.

Plume-Scale Transport of Major Reactive Constituents

In contrast to the distribution of Cl^- and H_2O isotopes that define the extent of transport and mixing of the leachate plume, other contaminants, such as CH_4 and NH_4^+, were attenuated by various combinations of sorption and reaction. Groundwater within the plume between the landfill and the slough was largely anoxic (less than 0.2 mg/L dissolved oxygen) and therefore, the reactions that dominate within the plume were anaerobic. The concentrations of major redox-sensitive components (C, N, S, and Fe) in the plume and aquifer sediment varied as a result of heterogeneity of the alluvium sediment, mixing of leachate with oxic and suboxic groundwater at the margins of the plume, and biogeochemical processes (Figures 2, 4 through 8).

Plume-Scale Carbon Transport and Reaction

The major C components in groundwater were NVDOC, CH_4, and dissolved inorganic carbon (DIC). Previous investigations of natural attenuation by Cozzarelli et al. (2000) indicated little change in the bulk NVDOC concentrations with distance along the center of the Norman Landfill plume, indicating that many components of the NVDOC were recalcitrant to degradation in the anoxic aquifer. This observation is consistent with the leachate being from an older methanogenic landfill (Christensen et al. 2001). The longer term study presented here shows an apparent decrease in the maximum NVDOC concentrations in the center of the plume that mimics the decrease in the Cl^- concentrations, indicating little differentiation between NVDOC and a conservative component (Figures 4A and 5B). A focused investigation of the pore water geochemistry in the slough indicated that NVDOC also was recalcitrant to degradation in these anoxic sediments, which has important implications for the many

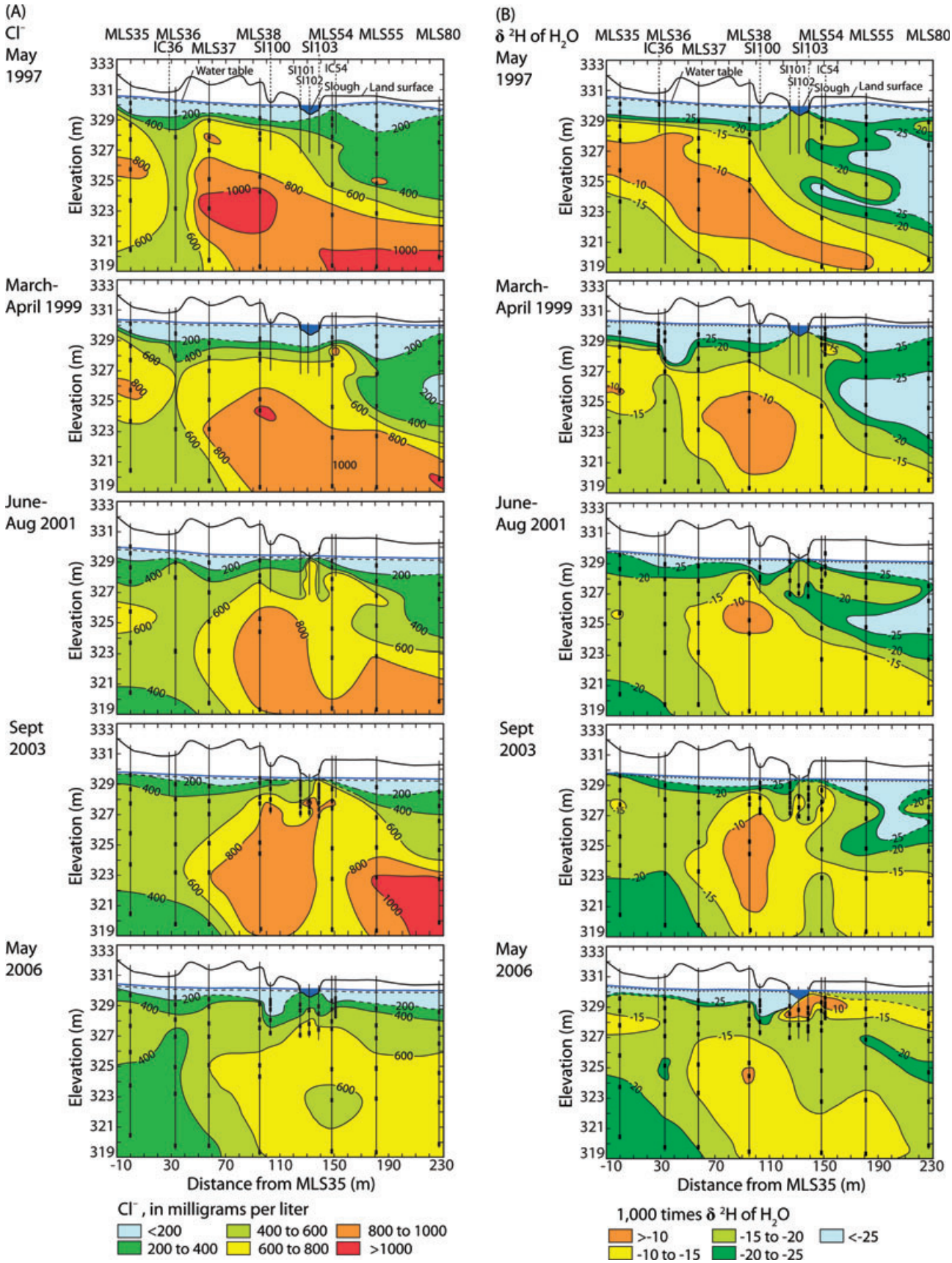

Figure 4. Distribution of (A) chloride concentrations (mg/L as Cl^-) and (B) δ^2H values of H_2O (‰) in a vertical groundwater transect approximately parallel to flow in May 1997, March through April 1999, June through August 2001, September 2003, and May 2006. The locations of the wells on transect MLS35-80 are shown in Figure 1.

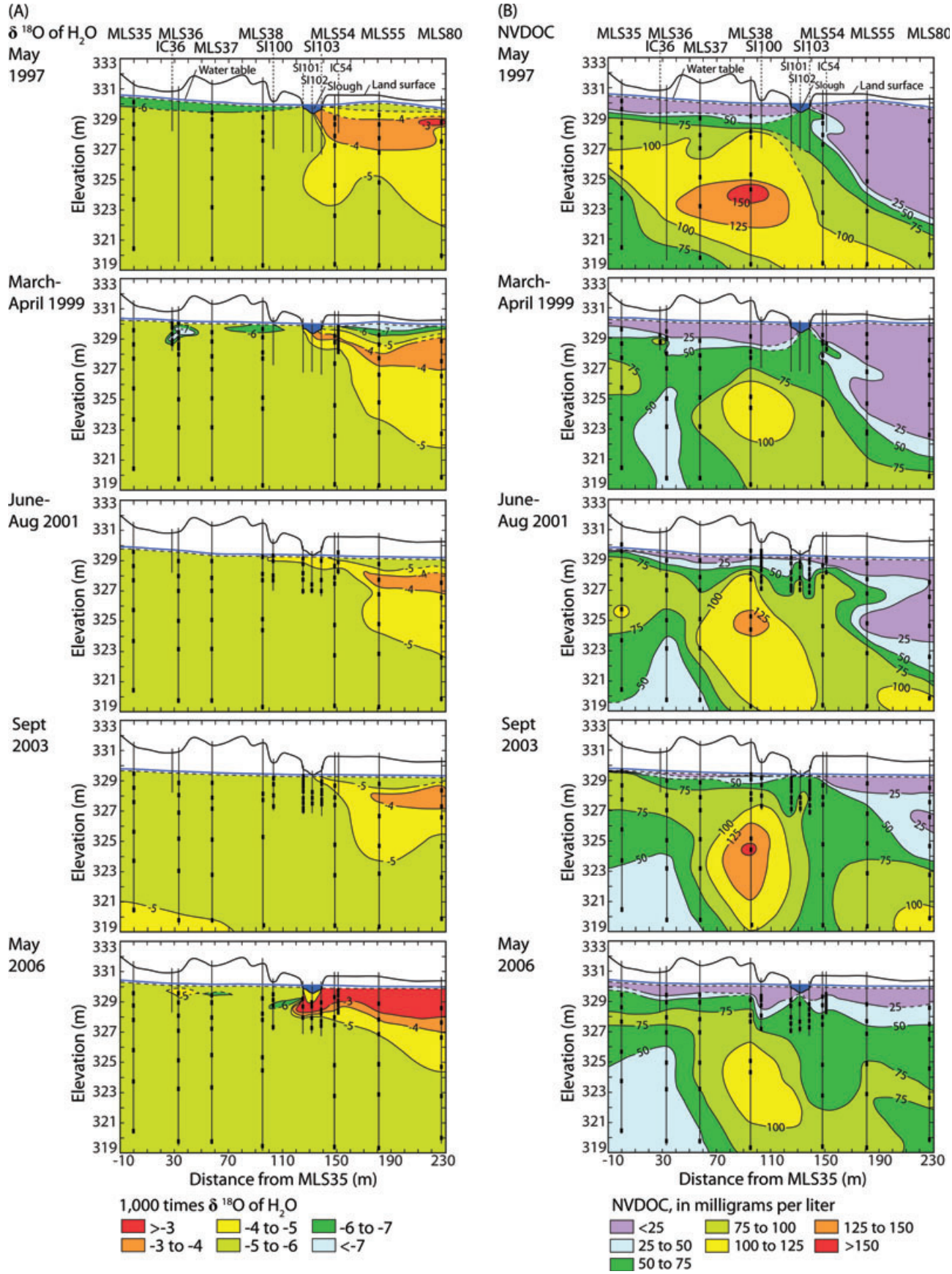

Figure 5. Distribution of (A) $\delta^{18}O$ values of H_2O (‰) and (B) NVDOC concentrations (mg/L as C) in a vertical groundwater transect approximately parallel to flow in May 1997, March through April 1999, June through August 2001, September 2003, and May 2006. The locations of the wells on transect MLS35-80 are shown in Figure 1.

landfills located near wetlands, streams, or rivers (Lorah et al. 2009).

The biodegradability of NVDOC at the Norman Landfill site has been studied to assess the reactivity of this material. Weiss et al. (2005) used a bioassay technique to determine the relative concentration of biodegradable NVDOC in the anoxic plume. In experiments in which leachate-contaminated groundwater was inoculated with an enriched sulfate-reducing microbial consortium, the maximum fraction of readily degradable NVDOC was 9 to 10% of the total NVDOC. Differences in carbon biodegradability along the MLS35-80 transect were related to the physiological profile of the microbial community. The highest diversity of microorganisms is in the landfill mound, which is also the site with the highest fraction of biodegradable carbon. These observations are consistent with those of Harris et al. (2006), who conducted *in situ* experiments to identify rate-limiting factors for SO_4^{2-} reduction in the contaminant plume. Using a combination of push-pull tests and laboratory incubations, Harris et al. (2006) found that poor biodegradability of the NVDOC in the distal regions of the plume limited SO_4^{2-} reduction rates. Detailed studies of electron acceptor availability show that, whereas oxidation capacity is greatest at the boundaries of the plume, NVDOC appears to behave conservatively at those interfaces (Scholl et al. 2006). The apparently conservative behavior of NVDOC likely results from a combination of poor reactivity and the large pool size of the NVDOC, making small concentration changes difficult to quantify.

Figure 6A shows the distribution of CH_4 along the MLS35-80 transect. Concentrations of CH_4 were highest near the center of the anoxic plume, slightly beneath the top of the SO_4^{2-} depleted zone (Figures 6A and 7B). The distribution of CH_4 did not change appreciably over 7 years, indicating that attenuation mechanisms balanced the production and transport of CH_4.

The methane-rich landfill leachate plume had anomalously low concentrations of Ar and N_2, compared to background groundwater. Ar and N_2 concentrations were directly correlated with each other, and inversely related to CH_4 concentrations (Figure 11). The gas data can be explained as a result of (1) displacement of atmospheric gases by CH_4 in the landfill; (2) mixing (dilution) of plume water with surrounding groundwater; and (3) partial CH_4 oxidation. Total calculated equilibrium pressures of major dissolved gases (N_2, Ar, CH_4, and CO_2) in the leachate plume ranged from about 0.44 to 1.07 atm and generally were less than hydrostatic pressures at the well screens. The pressures support the hypothesis that methanogenesis and atmospheric gas stripping occurred predominantly within the landfill, above and near the water table, and not at depth within the groundwater leachate plume. Atmospheric gas stripping is common in landfills, but the relative importance of methanogenesis and degassing within the saturated zone downgradient from landfills may differ from site to site. Van Breukelen et al. (2003) described degassing at depth in the Banisveld Landfill plume where pH values were lower, and calculated pCO_2 values were higher, than at Norman. At the Norman Landfill, upgradient groundwater and some of the shallowest downgradient samples above the plume had relatively normal dissolved atmospheric gas concentrations. Some of these samples may have had minor amounts of excess N_2 produced by denitrification, as they plot to the right of the air-saturation curve (Figure 11A), although dissolved excess air entrained in recharge also may have contributed to this effect (Heaton and Vogel 1981).

Methane in the Norman Landfill leachate plume was attenuated by (1) anaerobic oxidation within the center of the plume and (2) aerobic oxidation near the water table (described in the section on *Monitoring Seasonal Variation*). Anaerobic CH_4 oxidation was estimated to be a major CH_4 sink behind the leading edge of the leachate plume (Grossman et al. 2002). Methane oxidation was indicated by increasing $\delta^{13}C$ of CH_4 coupled with decreasing CH_4 concentrations in the downgradient direction (Figure 12). This is also consistent with the observation that some samples with low CH_4 concentrations were depleted in Ar and N_2, indicating these samples were degassed in an upgradient location where CH_4 concentrations were higher and subsequently lost CH_4 during transport (Figure 11B).

The highest $\delta^{13}C$ values in CH_4 occurred around the plume margins (Figure 9B) where mixing may have introduced ambient groundwater containing dissolved electron acceptors, such as SO_4^{2-}. However, $\delta^{13}C$ values in CH_4 also increased downgradient in the center of the plume, where dissolved electron acceptors were essentially absent, suggesting the importance of solid-phase electron acceptors such as barite ($BaSO_4$) or Fe(III) oxides in the sediment within this zone. High concentrations of dissolved barium (greater than 10 mg/L in some cases), and dissolution features observed by SEM on barite grains, indicate barite dissolution may be an important source of SO_4^{2-}. Grossman et al. (2002) estimated that 27% of the CH_4 was oxidized in the core of the plume with an average oxidation rate of 56 μM/year. Using the estimate of barite stores calculated by Ulrich et al. (2003), if all the CH_4 oxidation were coupled to the dissolution of barite and subsequent reduction of SO_4^{2-}, the barite within this region of the aquifer would be consumed in 116 years. Oxidation of CH_4 coupled to Fe(III)-oxide reduction was not considered an important process because Fe(III) reduction was not detected in laboratory microcosm experiments conducted with sediments from this zone (Cozzarelli et al. 2000). Although the precise mechanism of CH_4 oxidation was not determined, it is concluded that anaerobic CH_4 oxidation with both aqueous and sediment-bound electron acceptors needs to be considered when assessing or predicting transport of landfill-derived CH_4.

Alkalinity values (as HCO_3^-) are shown in Figure 7A. Although Cl^- concentrations in the leachate plume generally decreased over time, alkalinity values apparently were more stable, indicating sustained oxidation of organic carbon to DIC. There are several potential sources of reduced carbon in the aquifer system, including NVDOC and

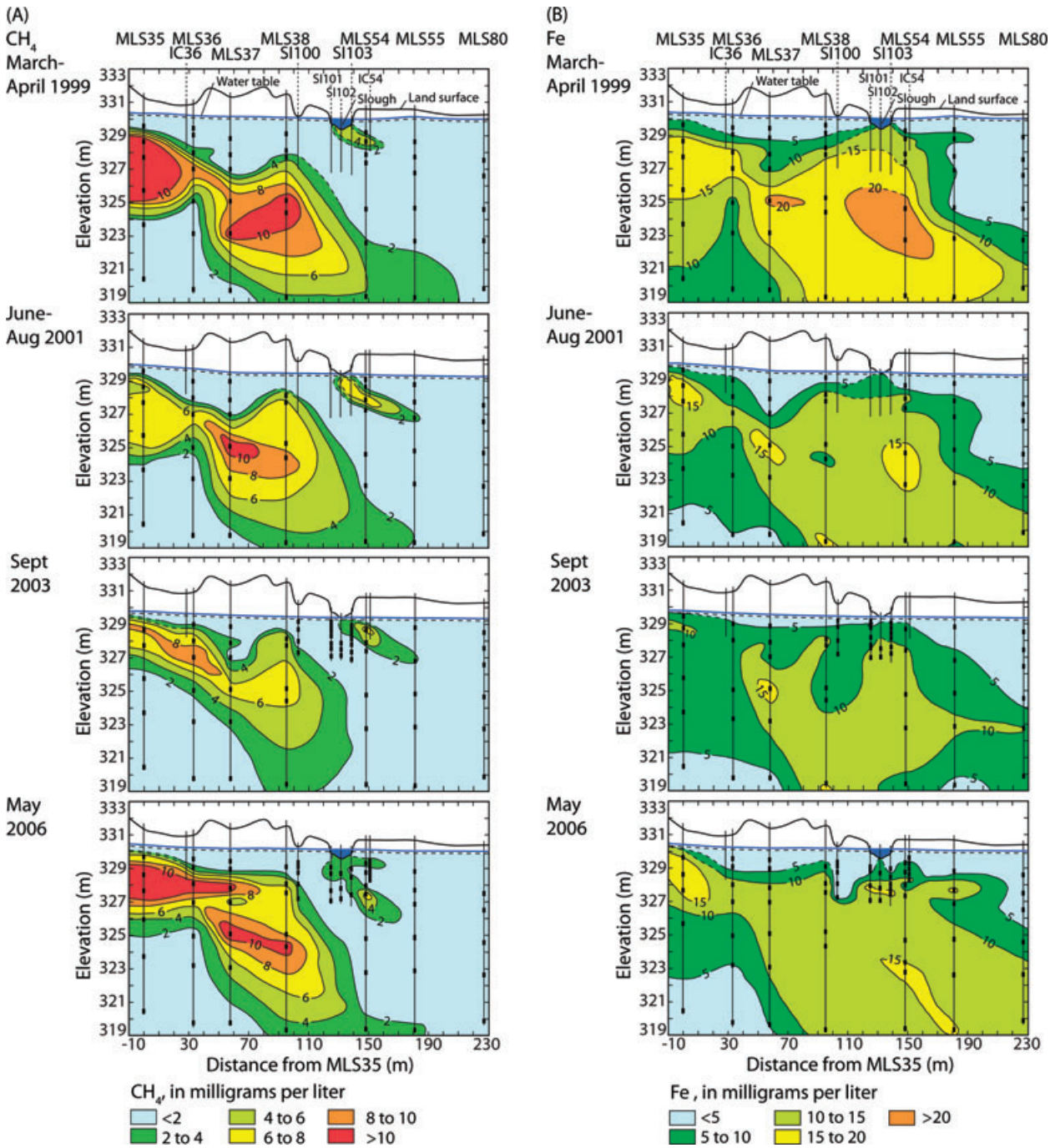

Figure 6. Distribution of (A) dissolved methane concentrations (mg/L as CH_4) and (B) dissolved iron concentrations (mg/L as Fe^{2+}) in a vertical groundwater transect approximately parallel to flow in March through April 1999, June through August 2001, September 2003, and May 2006. The locations of the wells on transect MLS35-80 are shown in Figure 1.

CH_4 from the landfill, bacterial cells (Harris et al. 2006), detrital organic matter deposited with the aquifer sediment, and decomposition products from modern leaf litter (Tuttle et al. 2009). Groundwater samples with the largest ^2H enrichments also had elevated $\delta^{13}C$[DIC] values (as high as +12‰), much higher than those typical of upgradient groundwater in the study area (−11‰; Cozzarelli et al. 2000) or shallow groundwater in the region (−18 to −12‰; Parkhurst et al. 1993). The high $\delta^{13}C$[DIC] values in the leachate likely resulted from biogenic CH_4 production coupled to CO_2 reduction (Baedecker and Back 1979). Decreasing $\delta^{13}C$[DIC] with decreasing CH_4 concentration in downgradient areas of the plume (open symbols, Figure 12) may be related to subsequent oxidation of CH_4 and organic C components within the plume, as well as mixing with normal groundwater.

A secondary CH_4-rich water mass (Figure 6A) with low $\delta^{13}C[CH_4]$ (Figure 9B) was present downgradient from the slough where it overlies the oxidized (isotopically fractionated) leachate plume CH_4. This

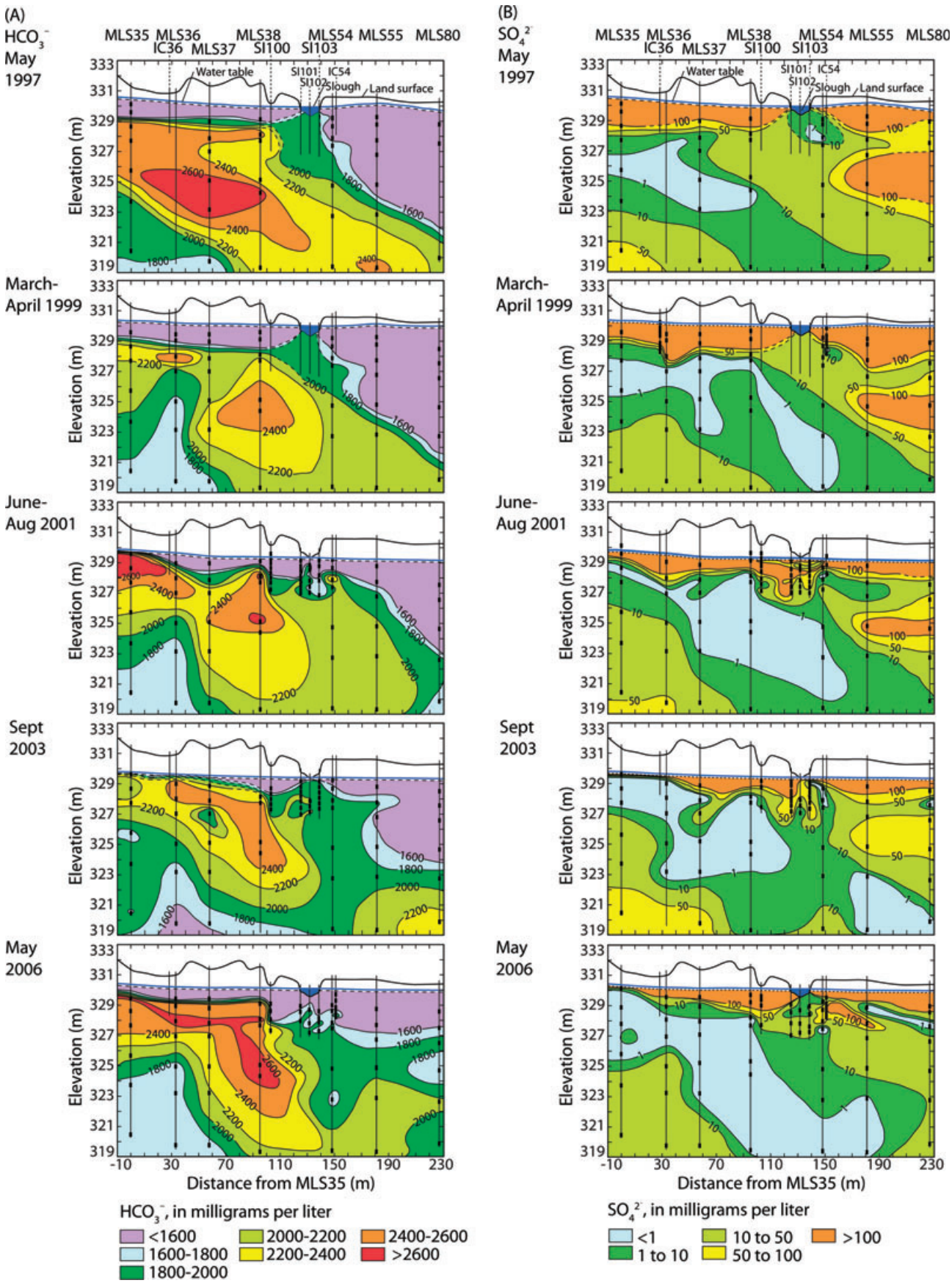

Figure 7. Distribution of (A) alkalinity (mg/L as HCO_3^-) and (B) sulfate concentrations (mg/L as SO_4^{2-}) in a vertical groundwater transect approximately parallel to flow in May 1997, March through April 1999, June through August 2001, September 2003, and May 2006. The locations of the wells on transect MLS35-80 are shown in Figure 1.

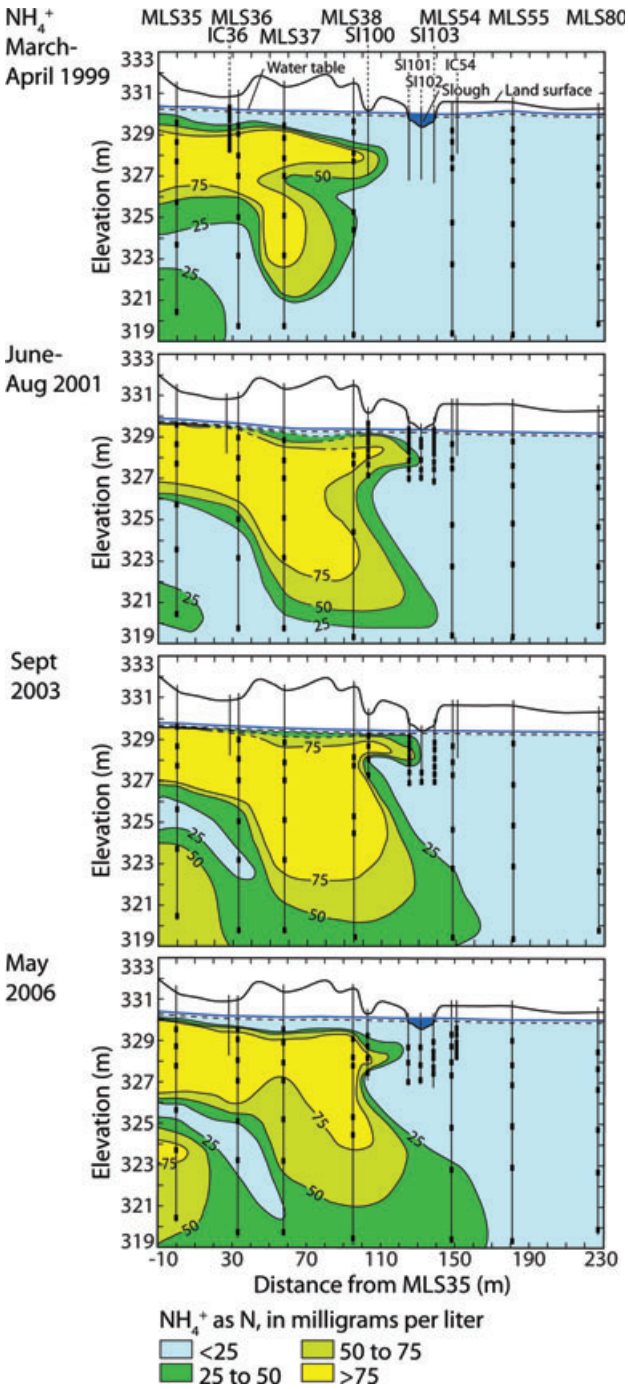

Figure 8. Distribution of ammonium (NH_4^+) concentrations (in mg/L as N) in a vertical groundwater transect approximately parallel to flow in March through April 1999, June through August 2001, September 2003, and May 2006. The locations of the wells on transect MLS35-80 are shown in Figure 1.

shallow CH_4-rich zone was associated with partially evaporated slough recharge water (Figures 5A and 9A) and probably indicates minor methane production in the slough bed sediments.

Plume-Scale Iron Transport and Reaction

Although dissolved Fe^{2+} may be partly derived from wastes buried in the landfill, the highest concentration of 23 mg/L was measured in the plume-affected aquifer and likely resulted from reaction of the plume with sediment-bound Fe(III) oxides that are responsible for the pervasive red-brown color of the sediment (Figure 6B). The reactivity of Fe sources in the sediment was tested by sequential extractions with 0.5 N HCl and Ti^{3+}-EDTA (Breit et al. 2005, 2008). The HCl extraction was expected to dissolve poorly crystalline Fe(III) oxides, carbonates, and FeS, whereas the Ti^{3+}-EDTA targeted more crystalline Fe(III) oxides (goethite and hematite) (Heron et al. 1994). In the unsaturated zone and upper 50 cm of the saturated zone, HCl-extractable Fe(III) was present in permeable sandy sediment at concentrations of 1 to 6 μmol/g; whereas Ti^{3+} extractable Fe(III) ranged from 6 to 50 μmol/g. Deeper sands had substantially lower HCl-extractable Fe(III) (less than 1 μmol/g) and lower Ti^{3+}-extractable Fe(III) (less than 1 to 23 μmol/g). HCl-extractable ferrous iron (Fe(II)) in the saturated zone sands ranged from less than 1 to 8 μmol/g. Red, muddy silt, and mud clasts in the alluvium typically contained nearly 5 to10 times more extractable total Fe than the sandy sediment. Therefore the less permeable, muddy sediment is considered to contain a greater store of potential electron acceptors; however, the availability of Fe(III) oxides intercalated with the clays for reaction with plume constituents may be limited by diffusion. The amounts of extractable Fe(III) in the Canadian River alluvium are similar to those reported by Heron et al. (1998) near the Grinsted landfill, Denmark, but lower than reported in some other leachate-affected aquifers (Jakobsen and Postma 1999).

The low concentrations of both HCl-extractable Fe(III) and Ti^{3+}-EDTA extractable Fe in sandy sediments from below the water table was characteristic of both background and leachate-contaminated sites. This consistent depletion reflects the pervasive reducing conditions in the saturated Canadian River alluvium. The concentrations of HCl-extractable Fe(II) and Ti^{3+}-EDTA extractable Fe were slightly greater in leachate-affected than in background sediments. The increase of sediment-bound Fe(II) was an expected result of the prolonged reaction of the contaminated sediment with the reducing components of the leachate plume. The origin of the slightly higher concentrations of Ti^{3+}-EDTA extractable Fe in the contaminated sediment is uncertain, but is consistent with slightly greater clay content in the leachate-affected sands relative to sands from background sites.

The abundance of reducible iron generally decreases with depth within the saturated zone sediment. The decrease is consistent with the longer residence of the deeper sediment in a reducing environment. Oxidation of leachate contaminants by residual Fe(III) oxides in the deeper sediment is expected to be slow because these Fe particles are likely to be slowly reactive coarse particles or isolated among the clay particles. Complete reduction of Fe(III) oxides in these sediments is possible as indicated by the sparse intervals of gray alluvium (including mud clasts) recovered in sediment core. These gray zones are not a product of reaction with leachate, but instead are the result of post-depositional

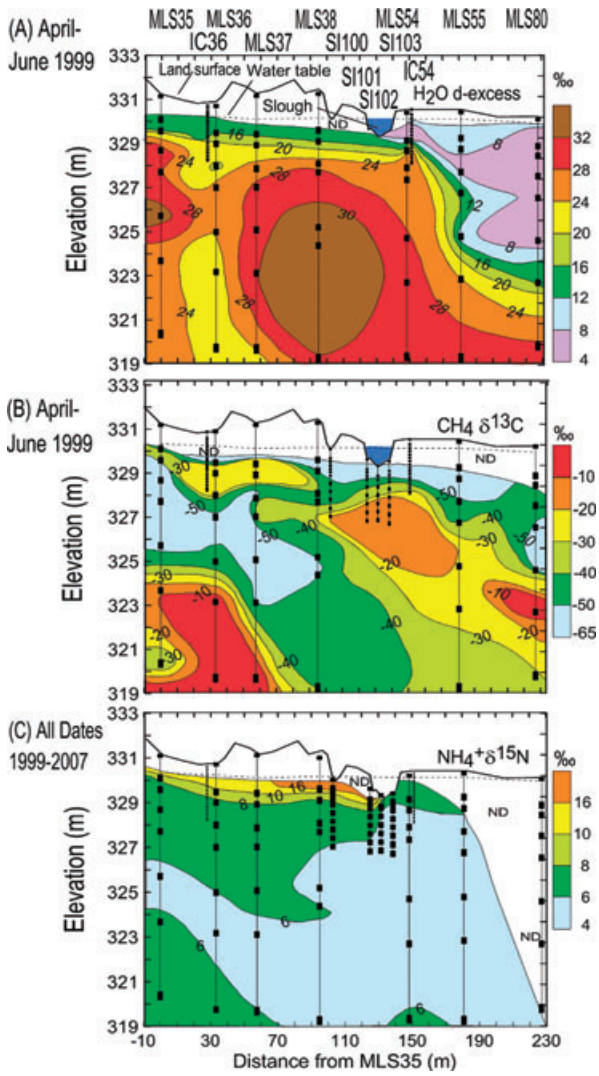

Figure 9. Distribution of isotopic indicators of plume reactions in a vertical groundwater transect approximately parallel to flow (A) "d-excess" parameter (‰) in April through June 1999, (B) $\delta^{13}C$ values of CH_4 in April through June 1999, and (C) $\delta^{15}N$ values of NH_4 from 1999 to 2007 (including mean values for re-sampled sites). The locations of the wells on transect MLS35-80 are shown in Figure 1. ND = no data.

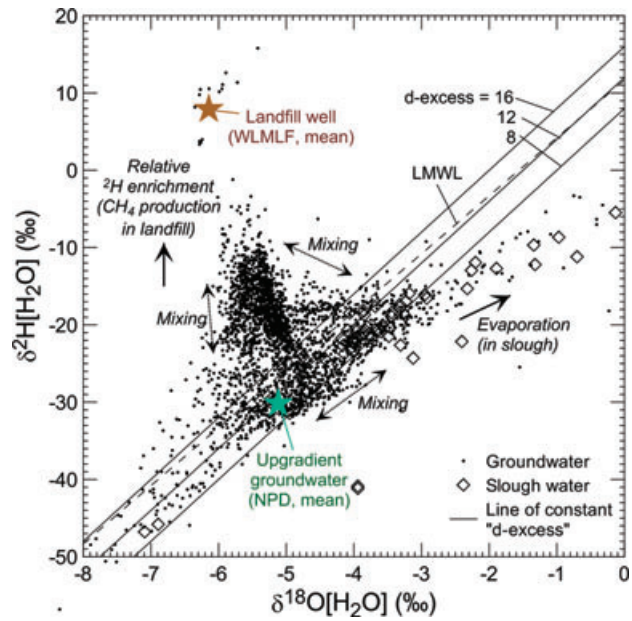

Figure 10. Variation of δ^2H and $\delta^{18}O$ values of H_2O in groundwater and slough water. Arrows indicate major processes thought to be responsible for variations (Figures 4B and 5A). The dashed line is a local meteoric water line (LMWL) derived from precipitation date (Scholl et al. 2006). Solid lines are parallel to the global meteoric water line with "d-excess" values of 8, 12, and 16, which bracket the meteoric groundwater values at the Norman Landfill Research Site.

alteration. An environment of strong reduction formed near accumulations of entrained plant fragments, which likely favored reductive dissolution of Fe(III) oxides during the thousands of years of burial.

The results of this analysis suggest that reductive dissolution of detrital Fe(III) oxides in reducing environments within the alluvium continues both within the leachate and in the generally anoxic background groundwater, but at a slow rate. More rapid Fe reduction is expected in the shallow alluvium where fine-grained and poorly crystalline Fe(III) oxides are regenerated in response to water-level fluctuations. At this mixing interface, the seasonal lowering of the water table can expose labile Fe(II)-containing phases to re-oxidation, thereby renewing the supply of Fe(III) as an electron acceptor when the water table rises again.

High concentrations of dissolved Fe^{2+} persisted along the length of the plume throughout the study period (Figure 6B), consistent with transport under reducing conditions. High dissolved Fe^{2+} concentrations in wells downgradient from the landfill do not correlate with Fe-reducing activity in local aquifer material and the source of the Fe^{2+} in the plume is thought to be largely from dissolution and reduction of Fe(III) oxides farther upgradient or from dissolution of Fe in the landfill waste (Cozzarelli et al. 2000). Laboratory experiments with sediment from MLS35, below an elevation of 324 m, near the interface of the plume with underlying background groundwater, indicated Fe reduction at a rate of 2 nmol/g-sed/d, whereas Fe(III) reduction rates measured near the water table at an elevation of 329.4 m were 6.5 nmol/g-sed/d (Cozzarelli et al. 2000). Iron(III) reduction rates in sediment from the center of the plume were too low to measure. These observations are consistent with the hypothesis that Fe(III) reduction induced by the leachate within the alluvium occurred largely at the boundaries of the plume. On the basis of the rate of Fe reduction measured near the plume—background groundwater mixing interface and a typical Fe(III) content of sandy sediment, Fe(III)—oxide reduction would be expected to deplete the reducible Fe(III) in only 5 to 10 years. Measurable rates of Fe reduction in the alluvium more than 10 years after the landfill was closed are consistent with the advance of the leachate plume into sediments in which relatively labile Fe(III) oxides were

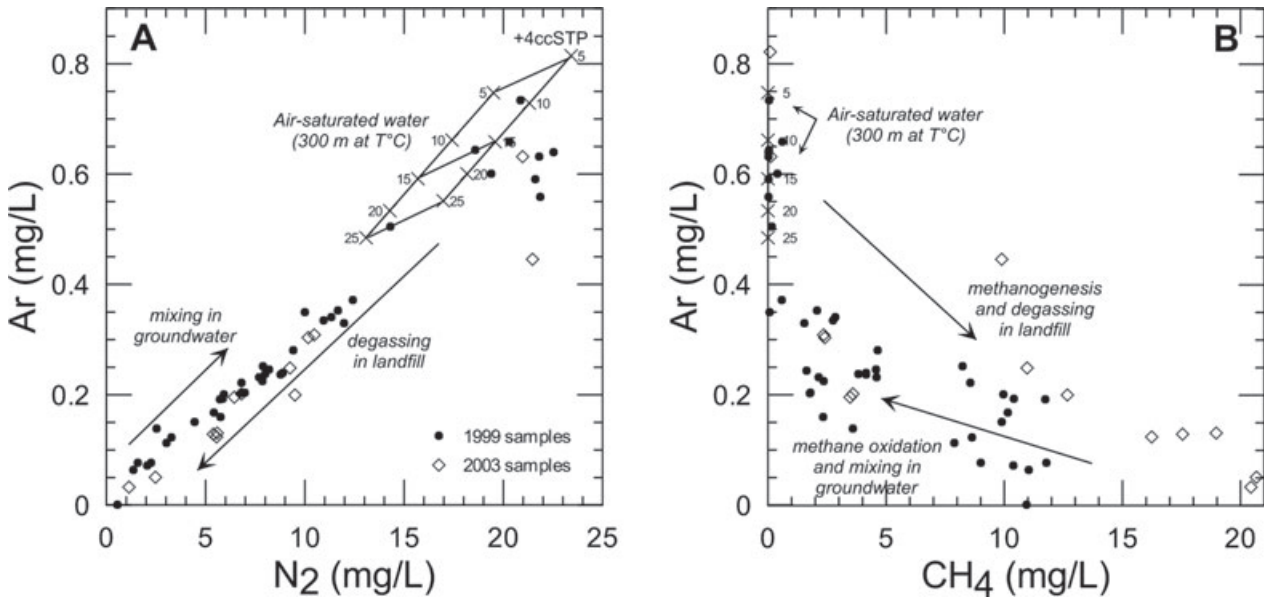

Figure 11. Concentrations of Ar, N_2, and CH_4 in selected groundwater samples collected in 1999 and 2003, compared to estimated normal recharge values (boxed area includes a range of equilibrium temperatures and excess air from 0 to 4 ccSTP/L). Arrows indicate qualitatively some of the major processes thought to be responsible for the variations.

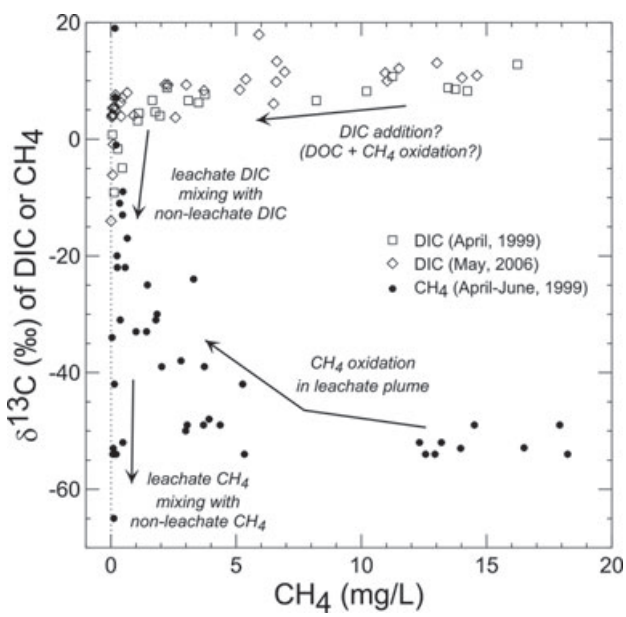

Figure 12. Variation of $\delta^{13}C$ values (‰) of CH_4 and DIC with CH_4 concentration in groundwater. Arrows indicate qualitatively some of the major processes thought to be responsible for the variations. $\delta^{13}C$ values of CH_4 are from Grossman et al. (2002), who report an isotope fractionation parameter ($\varepsilon = \alpha - 1$) of −13‰ for CH_4 oxidation, after adjustment of these data for mixing.

incompletely reduced as well as the regeneration of Fe(III) phases near the water table.

Dissolved Fe^{2+} concentrations are irregular, spatially and temporally (Figure 6B), and, although the shape of the Fe plume largely corresponds to the high NVDOC plume, high Fe^{2+} concentrations do not correspond directly to concentrations of CH_4, HCO_3^-, or the depletion of SO_4^{2-}. The variation may reflect precipitation of secondary mineral phases or the heterogeneous availability of reactive-iron phases along variable flow paths. Precipitation of Fe(II)-carbonate and Fe(II)-sulfide minerals are expected in the plume, as a result of mixing of water masses with high Fe^{2+} concentrations with water containing measurable H_2S and high HCO_3^- concentrations. Báez-Cazull et al. (2007) found shallow groundwater beneath the slough was greatly oversaturated with respect to siderite, and Tuttle et al. (2009) describe the abundance of FeS and pyrite in the alluvium. With increased exposure to the plume over time, the remaining Fe(III) oxides are expected to become less accessible, such that solution transport will eventually exceed the rate of Fe(III) oxide reduction and dissolved Fe^{2+} concentrations will decline. This probably occurred to a variable extent, in portions of the alluvium, even though extractable Fe(III) concentrations in the sediment do not demonstrate substantial total Fe losses overall in alluvium affected by the leachate plume. In summary, the distribution of dissolved Fe^{2+} in the plume is a complex product of Fe supplied directly the landfill, spatially and temporally variable contributions from reduction of Fe(III) oxides in the sediment, and the precipitation of secondary Fe(II) phases.

Plume-Scale Sulfur Transport and Reaction

The dominant dissolved S species in the leachate plume and background groundwater was SO_4^{2-}. Dissolved sulfide (H_2S) concentrations rarely exceeded 0.05 mg/L. Low H_2S concentrations are consistent with the abundance of dissolved Fe^{2+} and solid FeS and FeS_2 within the sediment. Sulfate concentrations ranged from less than 1 mg/L in the center of the contaminant plume, to near 1000 mg/L at the water table. Near the lower

boundary of the plume SO_4^{2-} ranges from 10 to 60 mg/L, consistent with mixing of background groundwater with SO_4^{2-}-depleted plume water. The plume-scale distribution of SO_4^{2-} concentrations changed substantially over the 9 years of sampling (Figure 7B). Between 1997 and 2001, the extent of the SO_4^{2-} depletion zone had more than doubled.

The Norman Landfill leachate plume was used by numerous investigators as a model system to study the progress of SO_4^{2-} reduction in an anaerobic aquifer (Ulrich et al. 2003; Harris et al. 2006; Scholl et al. 2006; Kneeshaw et al. 2007; Tuttle et al. 2009). Quantitative analyses of the different sources of SO_4^{2-} in the aquifer show that SO_4^{2-} plays a major role in supporting biodegradation processes. Detailed investigations of sulfur isotope geochemistry have shown that the variable sources and sinks for sulfur in this aquifer reflect the effect of the leachate superimposed on natural sulfur cycling within the alluvium. Tuttle et al. (2009) used values of $\delta^{34}S_{SO_4}$ and $\delta^{18}O_{SO_4}$ to distinguish dissolved SO_4^{2-} originating from mineral weathering, oxidation of iron sulfide minerals, and decomposition of organosulfur, in both groundwater and surface water.

Bacterial SO_4^{2-} reduction lowered SO_4^{2-} concentrations resulting in residual dissolved SO_4^{2-} having $\delta^{34}S$ values much greater than the recognized sulfate sources (Figure 13). The extent of SO_4^{2-} reduction varied temporally and spatially because of changing hydrologic conditions and variations in carbon quality (Harris et al. 2006; Tuttle et al. 2009). Reduction was evident in shallow background sediment by the presence of black FeS phases in the slough sediment, bars in the active river channel, and near the water table. The extent of reduction is near completion within the leachate plume. This favored dissolution of detrital barite (Ulrich et al. 2003; Tuttle et al. 2009). Dissolution of barite may already be near completion in some portions of the aquifer as indicated by locally lower sediment barium concentrations, undersaturation of barite in some portions of the leachate plume, delicate dissolution textures on detrital grains, and the relative lack of barite in plume-affected sediment as determined by examination with a scanning electron microscope.

Another source of SO_4^{2-} is from S assimilated by plants and released during vegetative decay. Within the soil zone, fungal and bacterial activities are expected to form organic SO_4^{2-} compounds (ester sulfates) that represent an interim SO_4^{2-} storage. Sulfate derived from organosulfur in the soils and landfill trash was identified by relatively low $\delta^{18}O_{SO_4}$.

Despite the substantially lower dissolved SO_4^{2-} concentrations, sediment within the core of the leachate plume does not contain significantly greater amounts of Fe-S phases (Breit et al. 2005, 2008). This apparent inconsistency is best explained by much of the SO_4^{2-} reduction and Fe-S formation occurring within and beneath the landfill upgradient from the sediment sampling sites, similar to the location proposed for methanogenesis and iron reduction. In contrast to the pervasive reduction, Tuttle et al.

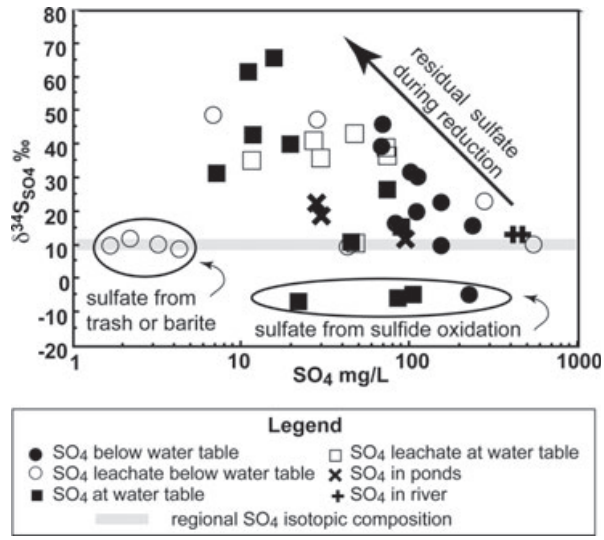

Figure 13. $\delta^{34}S$ of SO_4 relative to SO_4 concentration (modified from Tuttle et al. 2009). Three sources of SO_4 are represented: (1) SO_4 derived from landfill trash or dissolution of barite in the aquifer (low concentration, $\delta^{34}S$ of regional SO_4, (2) SO_4 derived from oxidation of sulfide (higher concentrations and $\delta^{34}S$ of SO_4 more representative of sulfide composition in the aquifer), and (3) residual SO_4 in a reservoir of regional SO_4 undergoing various degrees of reduction (variable concentrations and a trend of increasing $\delta^{34}S$ of SO_4 with decreasing SO_4 concentration). Arrows indicate qualitatively some of the major processes thought to be responsible for the variations. Symbols represent environment from which the water was sampled.

(2009) and Scholl et al. (2006) proposed that oxidation of iron sulfides explained the relatively low $\delta^{34}S_{SO_4}$ values of sulfate in some wells. These wells are typically screened near the unsaturated/saturated zone interface where atmospheric oxygen would be available to react with FeS phases.

In their study of the Banisveld landfill, the Netherlands, van Breukelen et al. (2003) investigated redox processes coupled to the oxidation of NVDOC in a landfill leachate plume flowing through unconsolidated clayey sands with anoxic background groundwater. In contrast to the results obtained for the Norman Landfill, SO_4^{2-} concentrations are not reduced in groundwater downgradient from the Banisveld landfill and SO_4^{2-} mineral dissolution does not occur. van Breukelen et al. (2003) attribute this lack of sulfate reduction to the dominance of Fe(III) reduction in the Banisveld plume.

Plume-Scale Nitrogen Transport and Reaction

Ammonium was the dominant N species in the landfill leachate plume. Ammonium concentrations in the center of the plume had a median value around 151 mg/L (concentrations expressed as mg/L of N), compared with approximately 1 to 2 mg/L in upgradient groundwater. Dissolved organic nitrogen was 0.2 mg/L in the background groundwater and averaged 19 mg/L in the center of the leachate plume. Dissolved atmospheric N_2 gas was low in the leachate plume as a result of

CH_4 production in the landfill (see section on *Plume-Scale Carbon Transport and Reaction*). Nitrate was not a component of the leachate plume, but was detected sporadically near the upper boundary of the plume near the water table (see section on *Monitoring Seasonal and Inter-Annual Variation of Selected Constituents* and Scholl et al. 2006).

Although leachate-derived Cl^- and NVDOC appear to have moved downgradient relatively conservatively, the extent of high NH_4^+ concentrations was initially smaller and increased during the study (Figure 8). The front of the NH_4^+-rich region, as defined by the 75 mg/L contour, moved downgradient 35 m in the 7 years between 1999 and 2006 (average of 5 m/year), substantially slower than the estimated median groundwater flow velocity (15 m/year) and apparent flushing rate of high Cl^-. This pattern of slow front migration could be consistent with a sustained leachate NH_4^+ supply that was attenuated by sorption and/or biodegradation/oxidation within the main body of the leachate plume. As shown at other landfill sites, K^+ and NH_4^+ have high affinities for cation exchange sites in sediments, consistent with the lyotropic series, and are the most attenuated major cations in leachate plumes (Christensen et al. 2001; van Breukelen and Griffioen 2004; van Breukelen et al. 2004). At the Norman Landfill site, several types of evidence indicate NH_4^+ was attenuated largely by ion exchange: (1) the progress of high K^+ concentrations in the leachate plume was retarded in much the same way as NH_4^+ at the plume-scale (not shown) and locally beneath the slough (Lorah et al. 2009), consistent with ion exchange of K^+ and NH_4^+ into clay minerals; (2) fine sediments from the site contained large amounts of smectite and smectite-illite (Table S2), which typically have high cation exchange capacities; (3) experiments with less than 10 μm sediment size fraction from the Canadian River alluvium at the site indicated NH_4^+ uptake was reversible and was saturated at levels consistent with estimated cation exchange capacities of around 250 μequiv/g (Table S3).

Consistent with the sediment characteristics, the NH_4^+ isotopic data indicate cation exchange was the more important NH_4^+ attenuation process, except in a limited region along the upper boundary of the plume where oxidation occurred. Figure 14 shows two different patterns of variation between NH_4^+ concentrations and $\delta^{15}N$ values, compared to those of concentrated leachate plume water with $\delta^{15}N \approx 6$ to 7‰: (1) increasing $\delta^{15}N$ with decreasing concentration is consistent with NH_4^+ oxidation (e.g., nitrification), and (2) constant or decreasing $\delta^{15}N$ with decreasing concentration is consistent with ion exchange and/or mixing with background NH_4^+. Elevated $\delta^{15}N$ values (greater than 7‰) occur only in shallow groundwater where the upper boundary of the leachate plume is near the water table (Figure 9C). In this zone, aerobic NH_4^+ oxidation can occur when oxygen is introduced by recharge events and water-table fluctuations. $\delta^{15}N$ values between 7‰ and 30‰ are qualitatively consistent with documented effects of nitrification (Delwiche and Steyn 1970; Mariotti et al. 1981; Hübner 1986; Casciotti et al. 2003), although it is difficult to quantify these effects at the plume margin because of heterogeneity, mixing, and sorption. Furthermore, it is possible that aerobic NH_4^+ oxidation could be associated with anaerobic NH_4^+ oxidation (anammox) at this dynamic interface.

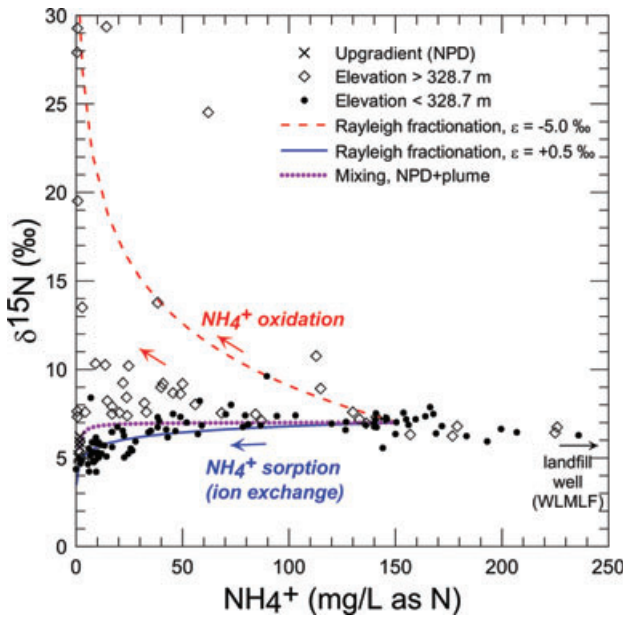

Figure 14. Variation of $\delta^{15}N$ values with NH_4^+ concentrations in groundwater, highlighting contrasting isotope effects near the upper boundary of the leachate plume (elevation greater than 328.7 m) vs. deeper in the contaminated aquifer. Hypothetical mixing and isotope fractionation (Rayleigh) curves originate at values typical of the middle of the leachate plume just downgradient from the landfill, with $NH_4^+ = 151$ mg/L and $\delta^{15}N = +7$‰. Plotted isotope fractionation parameters ($\varepsilon = \alpha - 1$) are for comparison only, and may not represent intrinsic parameters because of mixing, dilution, sorption (ion exchange), and chromatographic separation along flow paths.

There is no isotopic evidence for NH_4^+ oxidation within the main body of the leachate plume or around the downgradient margins of the plume. Instead, relatively low $\delta^{15}N$ values around the downgradient margins of the plume (commonly less than 5‰) can be attributed to a small isotope fractionation effect of ion exchange, and possibly a minor amount of mixing with background NH_4^+, which had relatively low $\delta^{15}N$ (≈5 to 6‰) but was much less abundant. Ion exchange can cause $\delta^{15}N$ of aqueous NH_4^+ to be lower than that of sorbed NH_4^+, although this effect is small and may be undetectable in some environmental settings (Delwiche and Steyn 1970; Böhlke et al. 2006). Equilibrium exchange experiments with Canadian River alluvium from the Norman Landfill site indicated large sorption coefficients with almost negligible isotope effects of sorption (Tables S2 and S3). The mean apparent equilibrium N isotope fractionation parameter ($\varepsilon = \alpha - 1$) between solid (sorbed) and aqueous NH_4^+ in four batch experiments was +0.12 ± 0.15‰. In the middle and lower parts of the leachate plume, where NH_4^+ concentrations ranged over 3 orders of magnitude from the center outward, a small decrease

in $\delta^{15}N$ with decreasing NH_4^+ concentration could be consistent with an apparent ε value slightly greater than 0 (Figure 14), although a direct comparison with the experiments may not be appropriate because of possible cumulative chromatographic isotope effects in the aquifer.

Similarly divergent spatial patterns of NH_4^+ sorption, oxidation, and isotope fractionation were observed in a domestic waste water plume with relatively low dispersion and nonreactive aquifer framework (Böhlke et al. 2006). Ammonium oxidation was limited to thin zones of lateral mixing with oxygenated groundwater at plume boundaries, such that the main mass of NH_4^+ moved conservatively but more slowly than more mobile contaminants. Somewhat broader NH_4^+ oxidation zones may be present near the leading edge of plumes in cases where aquifers are oxic and ion exchange is more limited (Christensen et al. 2001). In general, it can be expected that NH_4^+ contamination will persist within contaminated suboxic aquifers and discharge to surface waters long after more mobile contaminants have been flushed out. In addition to slowing the rate of NH_4^+ movement, clay-bearing sediment constitutes an important reservoir of NH_4^+ that can support sustained release of this contaminant.

The fate of NH_4^+ in the vicinity of the slough was investigated in some detail (Lorah et al. 2009). Ion exchange was indicated as a dominant attenuation mechanism for NH_4^+ in slough sediment pore water and the underlying aquifer by a concomitant decrease in $\delta^{15}N$ values and NH_4^+ concentrations and by similar attenuation rate constants for NH_4^+ and K^+. Although retardation of NH_4^+ and K^+ was observed beneath the slough at the Norman site, this retardation was not sufficient to prevent leachate-derived NH_4^+ from being transported laterally beneath the slough to the shallow aquifer downgradient (Lorah et al. 2009). Some leachate NH_4^+ must have discharged to the slough, but its effect on the wetland apparently was limited by rapid sub-slough transport, downward movement of slough recharge in some hydraulic conditions, and the major shift in the plume discharge area from the vicinity of the slough to the new location of the river in 1987.

Monitoring Seasonal and Inter-Annual Variation of Selected Constituents

Relatively frequent monitoring was done for selected constituents in the landfill well (WLMLF) and the upgradient multilevel well (MLS35) to assess changes in the leachate source and effects of climate on redox reactions near the water table (Figure 15). Chloride concentrations ranged from 700 mg/L to greater than 1200 mg/L in WLMLF. Although the concentration of Cl^- in the center of the plume (MLS35-5, Figure 15A) and the 2D plume patterns (Figure 4A) appear to show a long-term decrease in Cl^-, this trend was not apparent in the landfill well itself. Changes in Cl^- concentrations between 1998 and 2004 in MLS35 appear to indicate a decrease in the vertical chemical heterogeneity, as concentrations of Cl^- from levels 2 through 5 converged at a value of approximately 500 mg/L. Between 2004 and 2008, however, this trend appears to have reversed, resulting in substantial vertical chemical heterogeneity. A higher degree of vertical heterogeneity in the plume appears to be related to the wettest conditions, when the water table was the highest. For NH_4^+, repeat sampling at MLS35-3 between 1999 and 2007 ($n = 17$) indicated relatively constant concentrations and $\delta^{15}N$ values entering the core of the plume: mean concentration = 152 ± 17 mg N/L and mean $\delta^{15}N = +7.1 \pm 0.4‰$. At MLS35-5 (approximately 3 m below MLS35-3), mean values were 13 ± 12 mg N/L and +5.5 ± 0.4‰, indicating a relatively stable vertical pattern of NH_4^+ retardation by ion exchange with minor isotope fractionation over the same time period.

Temporal variability of water chemistry and redox cycling was especially pronounced in shallow wells affected by changing water-table elevations. Monthly water-level data from the first 5 years of the study followed a fairly regular seasonal pattern, whereas in the last 4 years of the study the variations were less systematic (Figure 15F). Although higher water levels typically occurred in April and lower levels in August through October, there were exceptions to this pattern. In 2004 and 2007, the summers were unusually wet and the water levels stayed near the annual maximum until August when they started to decline. In 2005 through 2006 there was an unusually dry winter and the water table did not start to rise until April 2006. Scholl et al. (2006) demonstrated that the interface between leachate and overlying recharge water moved vertically over a depth interval of 1.2 m between 1998 and 2000. Differences in the magnitude of seasonal variations in water levels and degree of mixing affect rates of biogeochemical reactions at this interface and illustrate the importance of seasonal and inter-annual climate variations in forecasting short-term effects of natural attenuation.

Recharge water diluted the plume near the water table (e.g., MLS35-2, Figure 15A and 15B); this is clearly illustrated by the Cl^- and NVDOC dilution during the sustained period of high recharge in early 2001 and again in early 2007. Electron acceptors such as dissolved O_2, NO_3^-, and SO_4^{2-}, derived from the atmosphere and processes in the unsaturated sediment, entered the shallow aquifer with infiltrating recharge water. Some oxidation of sediment-bound reduced species is expected as infiltrating water that contains oxidants reacts with the sediment. Sulfate entering with recharge water (Figure 15D) generally was reduced below the water table; nonetheless, during periods of high recharge, SO_4^{2-} was detected 2 m below the water table at MLS35-3. Nitrate was also detected sporadically in some of the shallow wells (Figure 15E). Concentrations greater than 70 mg/L (as N) were observed, with the maximum occurring during the period of highest recharge in spring 2007, when the water table was less than 0.5 m below land surface. Nitrate production is consistent with N isotope fractionation of NH_4^+ at the upper plume boundary (Figures 9C and 14). Although the highest NO_3^- concentrations probably could not have been produced entirely within the saturated zone by mixing

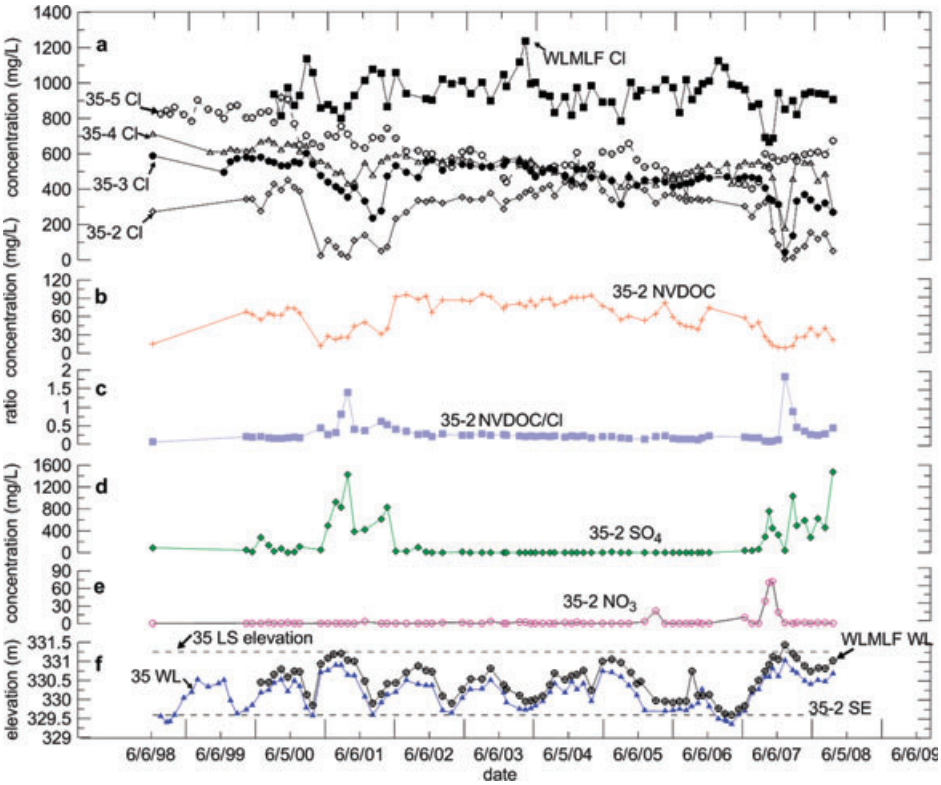

Figure 15. Temporal variability between 1998 and 2008 of (A) chloride concentrations in mg/L in the Landfill well (WLMLF) and at selected depths in the well at the toe of the landfill (MLS35, levels 2 through 5, elevations 329.6 to 325.7 m), (B) NVDOC concentrations in mg/L in the shallow well at MLS35 (level 2, elevation 329.6 m), (C) ratio of DOC to Cl concentrations in the shallow well at MLS35 (level 2), (D) SO_4^{2-} concentrations in mg/L in the shallow well at MLS35 (level 2), (E) NO_3^- concentrations in mg/L in the shallow well at MLS35 (level 2), and (F) Water-level changes at WLMLF and MLS35 and the position of the land surface (LS) elevation at MLS35 and the screened interval elevation (SE) at MLS35-2 (level 2).

oxic groundwater with plume NH_4^+ (not enough O_2 in air-saturated water), the NO_3^- could be a result of more complex interactions among aqueous and sorbed NH_4^+ in partially to completely saturated conditions as water levels changed. Furthermore, high and variable $\delta^{15}N$ values (+15 to +40‰) and $\delta^{18}O$ values (+2 to +22‰) were measured in NO_3^- (MLS35 at 329.6 m elevation in 2005 and 2007) and provide evidence for NO_3^- reduction as part of the active redox cycling in this zone of transient hydrologic conditions near the water table. Episodic NO_3^- production and reduction near the upper boundary of the plume could potentially provide a favorable environment for anaerobic NH_4^+ oxidation by NO_2^- to produce N_2 (anammox; Engström et al. 2005), but the importance of this process was not demonstrated in the current study.

The abundance of solid forms of Fe and S in the sediment within the upper 2.8 m of aquifer was quantified to assess whether water-table fluctuations affected the availability of solid-phase electron acceptors necessary for natural attenuation processes at this plume boundary (Breit et al. 2008). Reducing conditions were indicated a few tens of centimeters below the water table by high dissolved Fe^{2+} concentrations and increased concentrations of extractable Fe(II) in the sediment (Breit et al. 2008). Nonetheless, oxidation of FeS minerals during dry periods and decomposition of particulate organic material containing ester sulfates increased the available Fe(III) iron and sulfate pools at this interface (Tuttle et al. 2009). Iron reduction in sediment samples collected near the water table progressed at a rate of 6.5 nmol Fe/g-sed/d (Cozzarelli et al. 2000). These results are consistent with microbially reducible Fe(III) near the water table that formed from aeration of the sediment during low water tables and from infiltration of oxygenated water during recharge events. During times of rising water tables, these Fe(III) oxyhydroxides were important electron acceptors that were more reactive than disseminated hematite.

Greater availability of electron acceptors and enhanced rates of reactions at the saturated/unsaturated zone mixing interface did not cause a substantial decrease in NVDOC concentrations beyond what can be explained by dilution. Instead, the NVDOC/Cl^- ratios increased during recharge events when Cl^- concentrations decreased (Figure 15C), possibly indicating another source of C entering the aquifer during recharge events. The additional C likely originated from decaying biomass in overlying soils on the alluvium.

Lessons Learned for Evaluating Leachate Attenuation Processes

Few studies of landfill leachate plumes have examined the relative importance of center vs. fringe processes,

which depend not only on the composition of aquifer solids and background groundwater, but also on physical properties related to dispersion and mixing. Commonly, much of the natural attenuation occurs at the boundaries of a plume where electron acceptors are available. Bjerg et al. (2009) and van Breukelen et al. (2004) note the importance of quantifying fringe processes, requiring detailed sampling on the scale of tens of centimeters. Moreover, van Breukelen and Griffioen (2004) note that reactions at plume fringes can be limited by the absence of electron acceptors in background water that mixes with the contaminant plume at these interfaces. At the Norman landfill site, variations in water-table elevation shifted the position of the steep redox gradients, causing reversal in sediment-water redox reactions near the unsaturated/saturated zone interface. The effect of the recharge water and surface water interactions was clearly evident near the upper boundary of the plume and illustrates the importance of accounting for reactions at the fringes. In evaluating the effectiveness of natural attenuation, plume-scale chemical and isotopic patterns indicated long-term interactions between leachate and aquifer water and sediments, whereas monthly monitoring data indicated especially active transient processes along the upper plume boundary including a small wetland area (slough). Temporal variability in chemical and isotopic gradients were effective tools for identifying biogeochemical reactions at the plume boundaries and within the center of the plume.

Biogeochemical attenuation of leachate contaminants in the main body of the Norman landfill plume depended largely on the combined effects of leachate chemistry and aquifer lithology. Background groundwater was reducing except near the water table, where oxygenated recharge mixed with anoxic groundwater and the plume during recharge events. Evidence of aerobic reactions affecting leachate contaminants was limited to this boundary and did not have a major effect on mass fluxes of contaminants through the aquifer. Methane and NH_4^+ exhibited similar distribution patterns indicating substantial natural attenuation, but for different reasons. Although CH_4 was being oxidized anaerobically and may be prevented from discharging farther downgradient, NH_4^+ was retarded by ion exchange but was not oxidized substantially, and therefore this "stored" NH_4^+ may cause a long-term contamination problem at this site. In general, where aquifers are naturally oxic, such as is the case for several landfills studied in Denmark (Bjerg et al. 2009), reactions around the fringe of the plume may be sufficient to keep the anoxic plume from migrating, hence creating a steady state and making natural attenuation an effective remedial option. However, even in oxic aquifers, availability of dissolved electron acceptors from outside the plume for natural attenuation of electron donors in the plume will be limited by rates of mixing around plume margins (Böhlke et al. 2006).

Investigations of the natural attenuation of contaminants commonly involve assessment of groundwater concentrations and rarely involve analyses of sediment (Anneser et al. 2010). At the Norman Landfill site, a key lesson learned was that although anaerobic oxidation was supported in part by aqueous SO_4^{2-} from background groundwater in mixing zones, aquifer solids were more important as sources of electron acceptors in the core of the plume. Furthermore slow dissolution of solid-phase electron acceptors, such as barite, and the isolation of Fe(III) oxides largely within clay particles may limit rates of oxidation-reduction reactions. Investigation of the sediment fraction not only provided insight into the sources and sinks of important elements such as Fe and S, but the sediments also recorded the cumulative history of reactions, whereas the groundwater moved and thus gave only a snapshot in time. In addition, predicting the eventual recovery of the groundwater ecosystem would require consideration of the changes that have occurred in the aquifer solids, which have taken a long time to develop and would likely take a substantial time to recover.

Complex transient flow patterns are common in landfill leachate plumes and may be especially important at landfills located near rivers with shifting channels. Changes in groundwater flow rate and direction at seasonal and other time scales can cause fixed sampling networks to be parallel or oblique to flow paths at different times, complicating identification of discrete flow paths and underscoring the importance of taking a process-understanding approach to interpreting plume behavior. Bjerg et al. (2009) note the importance of in situ contaminant biodegradation indicators, such as presence of metabolites or fractionation of stable isotopes, for documenting natural attenuation processes in landfill leachate plumes, due to the difficulties in following mass removal of critical compounds along a flow path. Although rarely assessed in detail, groundwater/surface water interactions and temporal variations in hydrologic flow need to be considered when evaluating both the effect of landfill leachate on local ecosystems and the potential for natural attenuation of leachate components. The slough (wetland) at the Norman Landfill site is an important hydrologic feature that serves as a source and sink for dissolved constituents transported in the aquifer, influencing the geochemical processes occurring in the leachate plume. Discharge of waste plumes into surface water, such as the slough, can have greater consequences than contaminated groundwater because some contaminants are nontoxic to humans but may degrade aquatic ecosystems. At the Norman Landfill, the shape of the plume and distribution of various contaminants were complicated by disruption of the groundwater flow system. Riverbed migration in 1987 caused a sudden shift in the principal location of groundwater discharge, such that the leading edge of the leachate plume entered sediment previously unexposed to leachate. The distributions of mobile constituents like Cl^- and ^2H enriched H_2O seem to reflect the current discharge configuration, but the distributions of attenuated constituents, such as NH_4^+, may still be adjusting to this hydrologic shift.

The detection of numerous VOCs and other organic compounds of emerging concern in old municipal landfills (Baun et al. 2003; Buszka et al. 2009), underscores the

importance of analyzing for a broad suite of compounds when assessing the potential for leaching of trace organics into aquifer systems or sensitive ecosystems. At the Norman Landfill, low concentrations of VOCs and waste water compounds appear to have persisted in the leachate plume for decades. Furthermore, concentrations of NVDOC persisted in the Norman Landfill leachate source and in the aquifer plume. The persistence of high concentrations of NVDOC has important implications because NVDOC can serve to facilitate the transport of other organic compounds and metals (Larsen et al. 1992; Guggenberger et al. 1994). The persistence of NVDOC at the Norman Landfill is in contrast to the substantial degradation of NVDOC reported by Christensen et al. (2001) for landfills where iron reduction was the dominant redox process.

Reaction-rate measurements using in situ experiments and laboratory incubations were useful for quantifying the important microbial reactions that affect aquifer geochemistry at the Norman Landfill site. Bioassays indicated that the overall reactivity of the organic carbon in this system was poor and were consistent with the persistently high NVDOC concentrations observed in the plume. Nonetheless, the large flux and slow reactivity of organic carbon were sufficient to substantially reduce the oxidation capacity of the aquifer over time and this has implications for the long-term fate of redox-sensitive organic and inorganic components of the leachate plume.

Results at the Norman Landfill and a small number of other landfill research sites indicate that leachate plumes evolve through reactions of dissolved constituents with each other and with dissolved and solid phases in the aquifer. Elucidating these processes, their rates, and impact, in order to assess natural attenuation potential, requires observations at the appropriate spatial and temporal scales. The distribution of reactions can be divided into several different regimes with different reaction controls: (1) plume-scale reactions within the main mass of the plume, requiring reactants from the leachate and(or) residual solid aquifer materials; (2) reactions around the plume boundary including the leading edge that may include reactants in the aquifer sediment as well as downgradient or lateral groundwater that mix with the plume gradually; (3) local and (or) transient reactions along the upper boundary of the plume that may include readily reactive solids that respond to the shift in geochemical conditions and additional dissolved reactants infiltrating from above related to precipitation events; and (4) interactions with surface water near discharge areas. Throughout the system, and particularly in regime 1, major attenuation controls include solid-phase aquifer geochemistry and anaerobic reactivity of plume contaminants. In regime 2, additional controls include ambient groundwater composition and hydraulic features promoting mixing between groundwater masses. In regime 3, additional controls include climate, vegetation, recharge rate, and proximity to the water table. Hydrological, geochemical, and microbiological processes link these interactions, and ultimately control the long-term outcome of MNA. Because local properties of leachates, aquifers, and climate can differ substantially between sites, the potential effectiveness of MNA as a remediation strategy needs to be evaluated using a combination of general principles and local targeted approaches.

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Supporting Information

Additional Supporting Information may be found in the online version of this article:

Supporting information includes details on the design of the sampling network, including figures showing the elevations of each sampling port (Figures S1 and S2), sample collection procedures, analytical procedures, and a table of groundwater velocity estimates (Table S1). Sediment particle-size data and estimated cation exchange capacities are included in Table S2 and the results of sorption experiments documenting isotopic fraction of NH_4^+ are in Table S3. Figure S3 shows tritium data for a selected group of samples from the leachate plume.

Table S1. Range of groundwater velocities (m/year) calculated using minimum, median, and maximum hydraulic conductivities (k, m/s) and gradients (dh/dl).

Table S2. Sediment particle-size data and estimated cation exchange capacities (CEC).

Table S3. Results from NH_4^+ exchange experiments.

Figure S1. Location of MLS, IC, and SI well screens along the MLS 35-80 transect and water levels measured during sampling of the well transect (1997 through 2006). The MLS well clusters, which contained 7 separate wells screened at different depths are labeled −1 through −7.

Figure S2. Groundwater flow direction and slope of water table along the MLS 35-80 transect at different sampling times, corresponding to the same dates that the geochemical data were collected, May 1987, March through April 1999, June through August 2001, September 2003, and May 2006.

Figure S3. Tritium concentrations versus d-excess values for a selected group of samples from the leachate plume and slough.

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