Biogeochemical Evolution of Domestic Waste Water in Septic Systems: 2. Application of Conceptual Model in Sandy Aquifers

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Abstract

Aqueous geochemical data from unconfined sand aquifers beneath two operating domestic septic systems are used to illustrate and evaluate a conceptual model of septic-system geochemistry. This model emphasizes the changing redox and alkalinity conditions in the septic system and the subsurface. The septic-tank effluents flow as distinct plumes downward through the unsaturated zones and then primarily laterally in the ground-water zones. The composition of the effluent was measured at several points in each system. At each site, the septic-tank effluent underwent aerobic oxidation in the unsaturated zone, which caused conversion of NH_4^+ to NO_3^-, organic C to CO_2 and organic S to SO_4^{2-}. At the first site, calcium carbonate dissolution in the unsaturated zone buffered the acidity released by the redox reactions. In contrast, the second system was poorly buffered and the pH dropped from 6.7 to 4.9 as aerobic oxidation occurred. Below the water table a small amount of aerobic oxidation occurred at each site. Nitrate-N concentrations in the cores of both plumes were above 25 mg/l as the plumes traveled from the septic systems. At the second site, the ground-water plume discharges to a river at the edge of the property. As the effluent flowed through the organic C-rich sediments of the river bed, NO_3^- disappeared and alkalinity increased, presumably due to denitrification. Differences in sediment composition at the two sites also led to different behaviors of Fe, Al, and possibly PO_4^{3-}. The conceptual model offers an organized approach to interpreting the major geochemical trends observed in the two systems, which are determined mostly by the well-aerated unsaturated zones below the drain fields and the amount of buffering material present in the sediments.

Introduction

Domestic septic systems receive many different waste-water constituents and treat them to various extents before releasing them to ground water. Despite the variety of constituents, the reactions of a few constituents dominate the geochemistry of the treated waste water. The conceptual model presented in Wilhelm et al. (1994a) concentrates on these major reactions in order to provide a framework for the interpretation of overall septic-system geochemistry. According to this model, the main geochemical changes in septic systems result from the microbially mediated oxidation of the organic matter in waste water. The most important reactions in septic systems are the anaerobic digestion of organic matter in the septic tank and the aerobic oxidation of organic C to CO_2 and reduced N to NO_3^- in the unsaturated zone. In typical systems these reactions result in the removal of organic C and the production of NO_3^- and acidity. Poorly functioning systems remain anaerobic throughout their reaction zones, usually degrading less organic C, producing

NH_4^+, and maintaining high alkalinity. Since these reactions affect both the redox and pH conditions of the effluent, they also influence the behavior of many other constituents of the effluent.

Septic systems are a cause for public health and environmental concern in all settings, but sand aquifers and sand-and-gravel aquifers deserve special attention. The hydrogeologic characteristics of such aquifers provide both advantages and disadvantages for waste-water disposal via septic systems. Typically, sands have a higher hydraulic conductivity than silty or clay-rich materials and thus provide the high percolation rates desired for septic-system operation. High areal densities of septic systems are often situated in extensive sand deposits, such as the sand plains of Florida, Michigan, and western Australia (Geraghty and Miller, 1978; Troyan et al., 1985). However, high permeability and weak dispersion in these aquifers results in concentrated plumes from contaminant sources. These plumes may travel rapidly in the horizontal plane and mix only slightly with background ground water (Sudicky and Huyakorn, 1991). In addition, these aquifers are often used for water supply by the same households that use septic systems for waste-water disposal. This combination of factors gives sand aquifers and sand-and-gravel aquifers a high potential for contamination from septic systems and for human exposure to such contamination.

The preceding paper in this series (Wilhelm et al., 1994a) illustrated the conceptual model with examples from various studies. This paper focuses on detailed geochemical studies of
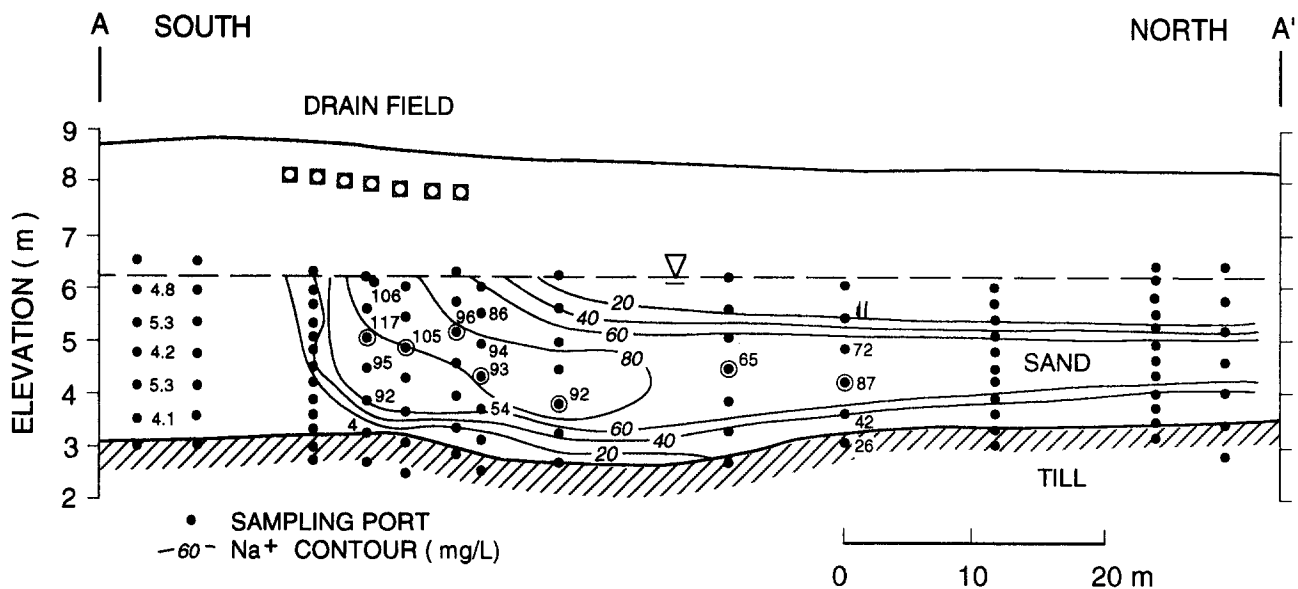
Fig. 1. Cross section of Cambridge septic system and effluent ground-water plume as shown by Na⁺ concentrations (mg/1). Contours constructed from measurements in September 1987; numerical values from measurements in October 1989. Water table measured in November 1987. Locations sampled for centerline chemistry and used in later profiles are circled.

waste-water evolution at two single-family septic systems. The two sites are located on sandy aquifers and provide useful contrasts in sediment composition and waste-water treatment. In order to record the long-term operating conditions of the systems, geochemical conditions were monitored at several points along the effluent flowpaths over a three-year period. The conceptual model is used to interpret the observed geochemical patterns by first defining the major redox zones in the systems and then looking for the expected impacts on alkalinity and pH. Where appropriate, simple calculations are used to determine order-of-magnitude estimates of biogeochemical properties.

The monitoring network, ground-water flow, and plume behavior at the two sites are described in detail in an earlier paper (Robertson et al., 1991). At each site the effluent spends one to two weeks traveling through an unsaturated zone of 1.5 to 3 m thickness in the septic-system drain field (Figures 1 and 2). In the saturated zone, the effluent forms a distinct plume. The Cambridge site is located amidst agricultural lands in southern Ontario. The septic system has served a family of four since 1977 and is situated on a sand aquifer in which sands contain 20% by weight (w/w) calcium carbonate ($CaCO_3$) (Figure 1). Due to high background values of Cl⁻, Na⁺ was used to determine the
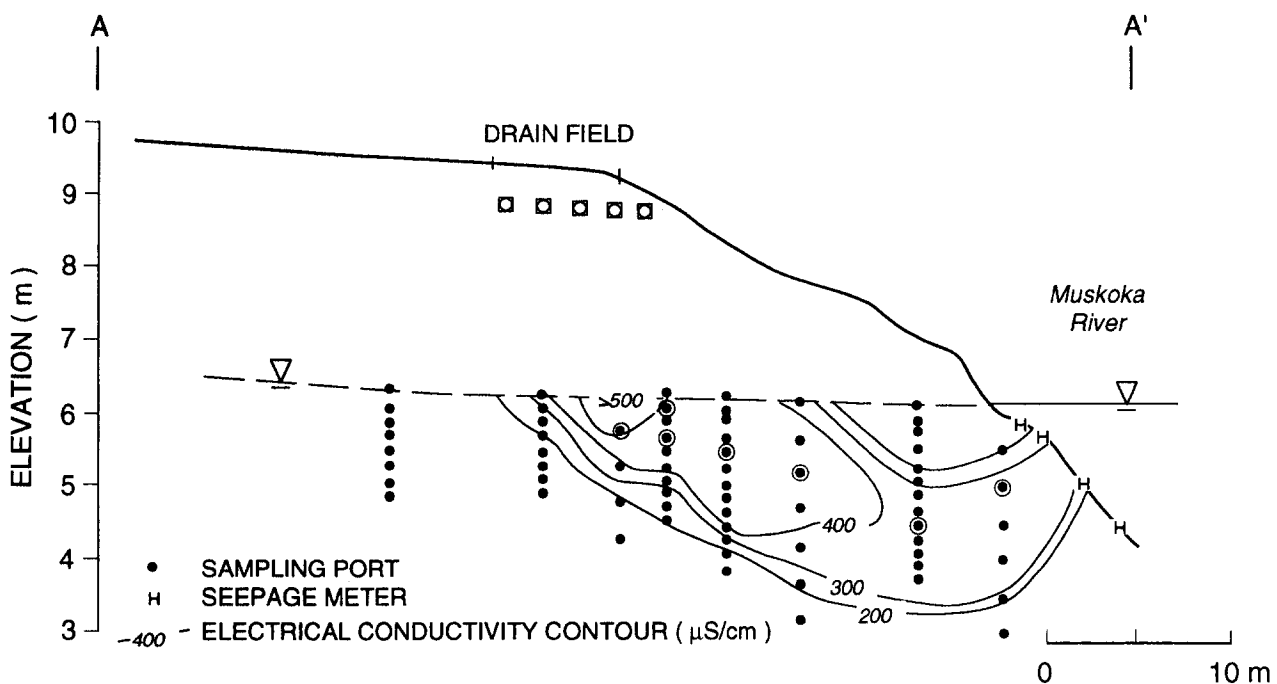

Fig. 2. Cross section of Muskoka septic system and effluent ground-water plume as shown by electrical conductivity contours (μS/cm). Background conductivity averages 70 μS/cm. Electrical conductivity measured in October 1989. Water table measured in September 1988. Locations sampled for centerline chemistry and used in later profiles are circled.

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extent of the ground-water plume in the aquifer, as explained in Robertson et al. (1991). The ground-water plume moves laterally at an average of 20 to 25 m/yr laterally. The Muskoka septic system began operation in 1987 and serves two adults in Ontario's cottage country (Figure 2). This septic system discharges to an aquifer of noncalcareous (0.6% $CaCO_3$ w/w) sands in a forested area of the Canadian shield. Chloride content and electrical conductivity were used to determine the extent of the ground-water plume. The plume travels horizontally at a rate of approximately 20 m/yr and discharges to the Muskoka River at the edge of the property.

Methods

During the period 1987 to 1990, the treatment of waste water was traced by sampling at different points along the waste water's flowpath at each site. The septic-tank effluent was sampled via a plastic tube inserted into a distribution pipe. At Muskoka aqueous samples were also collected from three plastic-pan lysimeters, which were installed 0.1 m below the gravel pack surrounding the distribution pipes. These lysimeters had a horizontal surface area of approximately 200 cm^2 and funneled the sample into 1-liter containers which were accessed via tubes from the ground surface. The lysimeters were first

pumped dry and then sampled within 24 hours. The lysimeters were sampled during two sampling rounds.

The impacted ground water was sampled beneath the drain field and throughout the saturated zone by a network of multi-level piezometers (Robertson et al., 1991). "Water-table" samples were collected from saturated-zone sampling points located less than 0.6 m below the water table. In the saturated zone, geochemical sampling concentrated on the cores of the ground-water plumes, as defined by the highest electrical conductivity measurement at the time of sampling. The Cambridge plume was sampled twice. The Muskoka plume was sampled completely five times, with additional sampling at a subset of points at other times. The plume at Muskoka was sampled once with mini-piezometers (Lee and Cherry, 1978) where it flows through the river bed. In addition, tap water and background ground water were sampled at each site as was the Muskoka River. Aqueous samples were collected by peristaltic pump and kept cold until analysis. Major ion, dissolved organic carbon (DOC), and trace metal samples were filtered immediately with a 0.45 μm cellulose nitrate filter.

Samples from all locations were analyzed for the following components: DOC, NH_4^+, NO_3^-, Cl^-, PO_4^{3-}, SO_4^{2-}, major cations, alkalinity, pH, and Cu, Fe, Mn, and Zn. Effluent from

Table 1. Comparison of Various Waters Related to Cambridge Septic System

Constituent	Tap water (N = 1)	Septic tank effluent (N = 6)	Water-table samples[a] (N = 8)	Background samples (N = 7)
Alkalinity (as $CaCO_3$)	170.	374. (35.0)	280. (32.1)	168. (40.4)
Calcium	40.0	41.2 (3.2)	92.5 (25.4)	106.6 (25.2)
Chloride	2.3	40.0 (15.3)	26.9 (3.4)	20.0 (7.8)
DIC[b]	46.	102.	79.	44.
DOC	3.0	38.2[c] (29.2)	3.3 (1.4)	3.3 (1.5)
Iron	<0.02	0.067 (0.071)	0.163 (0.168)	0.247 (0.248)
Magnesium	13.0	14.0 (0.9)	15.1 (5.0)	15.7 (2.1)
Ammonia-N	0.15	32.0[d] (5.1)	0.09 (0.07)	<0.05 —
Nitrate-N	<0.05	1.3[c] (1.5)	26.7 (9.3)	28.1 (7.1)
Phosphate-P	<0.01	8.9 (3.0)	5.6 (1.5)	≤0.01 —
Potassium	1.9	11.7 (1.9)	10.8 (2.1)	1.4 (0.9)
Sodium	15.6	89.7 (15.6)	90.9 (12.5)	4.4 (1.2)
Sulphate-S	4.7	6.9 (7.1)	20.4 (7.1)	15.4 (5.9)
pH	7.3	7.2	7.1	7.4

Average concentration of constituent followed by standard deviation in parentheses. All concentrations, except pH, reported in mg/l.
[a]"Water-table" samples collected from sampling points in the upper 0.6 m of the saturated zone directly beneath the drain field.
[b]DIC calculated from alkalinity and pH (Parkhurst et al., 1985).
[c]N = 4.
[d]N =5.

Table 2. Comparison of Various Waters Related to Muskoka Septic System

Constituent	Tap water (N = 2)	Septic-tank effluent (N = 6)	Water-table samples[a] (N = 11)	Effluent concentration at W.T.[b]	Background samples (N = 9 to 12)
Alkalinity (as $CaCO_3$)	10.5	316.4 (40.2)	23.2 (24.4)	28.	13.1 (9.8)
Calcium	5.7	14.3 (2.9)	47.2 (10.3)	65.	9.8 (2.7)
Chloride	1.0	54.8 (6.7)	38.2 (7.1)	55.	3.6 (2.0)
DIC[c]		90.3 (3.5)	47.9 (11.6)	65.	12.4 (3.0)
DOC	1.0	71.3 (38.2)	2.9 (0.8)	3.8	1.1 (0.3)
Iron	0.09	0.248 (0.060)	0.042 (0.019)	0.053	0.019 (0.013)
Magnesium	1.3	3.4 (0.7)	4.3 (1.0)	5.8	1.2 (0.7)
Ammonia-N	<0.05	57.6 (7.5)	0.48 (0.81)	0.6	0.18 (0.45)
Nitrate-N	0.47	0.083 (0.037)	40.4 (5.9)	58.	3.9 (2.2)
Phosphate-P	<0.01	13.1 (3.0)	0.014 (0.005)	~0.02	<0.01 (0.0)
Potassium	0.5	21.8 (3.5)	13.9 (2.5)	20.0	1.1 (0.5)
Sodium	1.5	84.9 (20.5)	45.5 (4.6)	66.2	2.3 (1.0)
Sulphate-S	4.2	11.8 (8.6)	11.4 (4.1)	15.7	2.4 (0.8)
pH	5.8	6.7	4.9	—	5.9

Average concentration of constituent followed by standard deviation in parentheses. All concentrations, except pH, reported in mg/l.
[a]"Water-table" samples collected from sampling points in the upper 0.6 m of the saturated zone directly beneath the drain field.
[b]Calculated by assuming conservative mixing of Cl⁻ in septic-tank effluent and background to form water-table concentration. Under this assumption, septic-tank effluent makes up 67.6% of the water-table samples and background water makes up 32.4% of the water-table samples:

$$0.676 \times 54.8 \ mg/l + 0.324 \times 3.6 \ mg/l = 38.2 \ mg/l$$

The concentration of other constituents in the undiluted effluent at the water table is calculated using these mixing percentages:

$$\text{Undiluted effluent concentration at water table} = \frac{[C_{water\ table}] - (0.324 \times [C_{background}])}{0.676}$$

[c]DIC: Effluent N = 2, water table N = 4, background N = 5.

the distribution pipes and samples from the lysimeters were characterized for chemical oxygen demand (COD) and total Kjeldahl N (TKN). Dissolved oxygen (DO) measurements were made once at each site. In 1990 selected samples from the saturated zone at Muskoka were analyzed for dissolved inorganic carbon (DIC) and aluminum, and two effluent samples were analyzed for SO_4^{2-} and total S simultaneously.

Electrical conductivity, pH, alkalinity, and DO measurements were conducted immediately after sample collection. Inorganic ion analyses, waste-water analyses, and DOC measurements were made at Fenwick Laboratories and Victoria General Hospital, Halifax, Nova Scotia. DIC was analyzed at the University of Waterloo. All analyses were performed using standard laboratory methods (Wilhelm, 1991). Partial pressure of CO_2 and $CaCO_3$ saturation indices, as well as DIC at Cambridge, were calculated by PHREEQE (Parkhurst et al., 1985).

In order to estimate waste-water flow rates, a known and constant amount of KBr tracer was added daily to the septic tank at each site via a household drain. Once the Br⁻ concentration in the septic-tank effluent reached a steady level, the flow rate was calculated from the dilution of the Br⁻.

Data from the aqueous samples were supplemented by information about the soil material and soil gas at each site. Four soil samples from the biological mat at each site were analyzed for organic C content. Simple percolation tests were performed at each site according to Ontario Ministry of Environment guidelines (Ontario Ministry of Environment, 1982). Soil gas sampling for O_2 was conducted at both sites in the Fall of 1990 with a Neutronics Pb-PbO_2 portable O_2 meter. Oxygen profiles were measured in the drain field at Muskoka and in both the drain field and background locations at Cambridge. Two hand auger borings were dug in the vicinity of the river at Muskoka,

and four sediment samples from these borings were analyzed for organic C content.

Results and Discussion

Redox Zones in the Septic Systems

As described in the conceptual model a typical septic system consists of an anaerobic septic tank followed by an aerobic unsaturated zone. The changes in concentrations and speciation of C, N, and S, as well as the changes in O_2 concentration, provide evidence of the redox zones in these two systems.

According to the analyses of the septic-tank effluent (Tables 1 and 2), the septic tanks represent primarily anaerobic environments at both sites. The effluents contained large amounts of NH_4^+-N and organic C and very little NO_3^--N. Assuming a molar COD:TOC ratio of 3:1 (Tchobanoglous et al., 1991), the effluent at Cambridge contained roughly 90 mg/l organic C and the Muskoka effluent contained 150 to 290 mg/l organic C. Both effluents contained oxidized S as SO_4^{2-}, indicating that SO_4^{2-} reduction in the septic tanks was incomplete or did not occur. At Muskoka the total S content of two effluent samples was approximately 60% higher than the SO_4^{2-}-S measured at the same time, indicating the presence of other forms of S.

Biological mats were observed below the gravel packs surrounding the distribution pipes at both sites. The mats were 2 to 10 cm thick, and their dark, moist appearance indicates an accumulation of organic matter and possibly metal sulfides. At Cambridge, the solid organic C content of the biological mat averaged 0.2% (w/w), compared to 0.05% (w/w) in the surrounding sands. At Muskoka, organic C comprised 0.74% (w/w) of the biological mat sediments, compared to 0.03% (w/w) in the background sands.

According to the results of the lysimeter samples from the Muskoka site (Table 3), the transition from anaerobic to aerobic conditions occurred in the depth interval directly below the biological mat. Gaseous O_2 diffusion probably occurs more easily in the unsaturated sands below the mat than in the moist, clogged sediments of the mat itself. All lysimeter samples contained measurable amounts of NO_3^-, indicating significant oxi-

Table 3. Comparison of Septic-Tank Effluent and Lysimeter Samples at Muskoka

Constituent	Septic-tank effluent (N = 2)	Lysimeters (N = 6)
Alkalinity (as $CaCO_3$)	320, 271	167 (65)
Calcium	15, 15	47 (11)
Chloride	60, 40	48 (8.2)
COD	838, 438	272[a] (101)
DOC	120, 62	28.8 (12)
Ammonium-N	44, 59	16.7 (6.8)
Nitrate-N	0.15, 0.06	15.5 (13)
TKN	68, 73	41.5[b] (4.9)
Phosphate-P	18, 9.1	6.9 (2.8)
Sulphate-S	26, 40	15.6 (13)

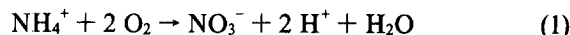Samples collected June and October 1990.
All concentrations in mg/l.
Standard deviations given in parentheses.
[a]N = 3.
[b]N = 2.

dation of NH_4^+ in a short distance below the distribution pipes. Aerobic oxidation of NH_4^+ occurs via:

$$NH_4^+ + 2 O_2 \rightarrow NO_3^- + 2 H^+ + H_2O \qquad (1)$$

Higher concentrations of NO_3^- were observed in those lysimeters that collected less effluent, suggesting that more O_2 was available for nitrification in areas that experienced lighter flow. (As discussed below, N did not behave conservatively relative to Cl^- in these samples or the unsaturated zone overall.) Organic C oxidation to CO_2 was suggested by the roughly 50% decrease in COD and DOC concentrations between the distribution pipe and the lysimeters. In that same interval increases in SO_4^{2-} concentrations relative to the effluent may have occurred by oxidation of reduced S via:

$$2 O_2 + H_2S \text{ (or organic S)} \rightarrow SO_4^{2-} + 2 H^+ \qquad (2)$$
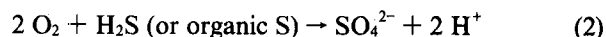
The effluent in these samples was possibly exposed to a smaller amount of O_2 than the effluent traveling normally through the unsaturated zone for two reasons: (1) the lysimeters probably accumulate fluid only during periods of local saturated flow, and (2) the samples in the lysimeters are collected in flasks as aqueous samples and are therefore held in saturated conditions. Thus these samples represent the worst case of treatment that may occur near the biological mat over the period of a day.

At both sites, most of the aerobic oxidation occurs in the unsaturated zone below the biological mat. The evidence for aerobic oxidation is derived from the analyses of O_2 and the reduced species in this region. According to soil gas measurements, O_2 was available throughout the unsaturated zone at both sites (Figure 3). The zones of lowest O_2 concentrations, assumed
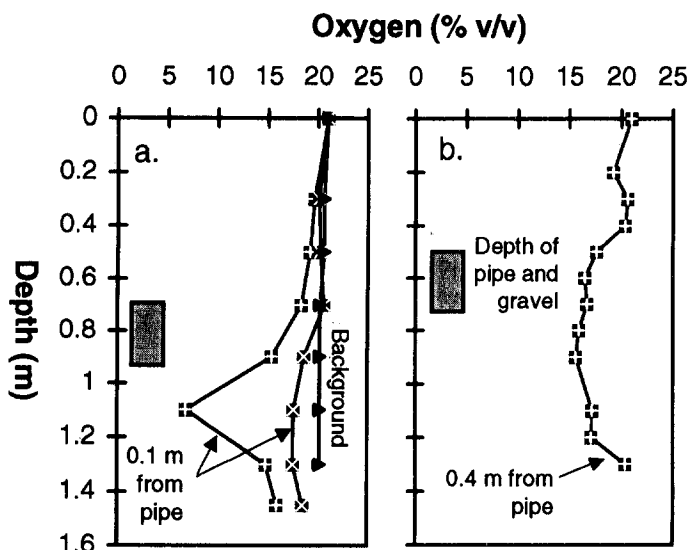
Oxygen (% v/v)

Fig. 3. Oxygen profiles in unsaturated zone, reported as percentage of oxygen in soil atmosphere, at (a) Cambridge, and (b) Muskoka. Depth of distribution pipes and gravel pack shown for reference. Depth to ground water at each site is 2.5 to 3.0 m below ground surface.
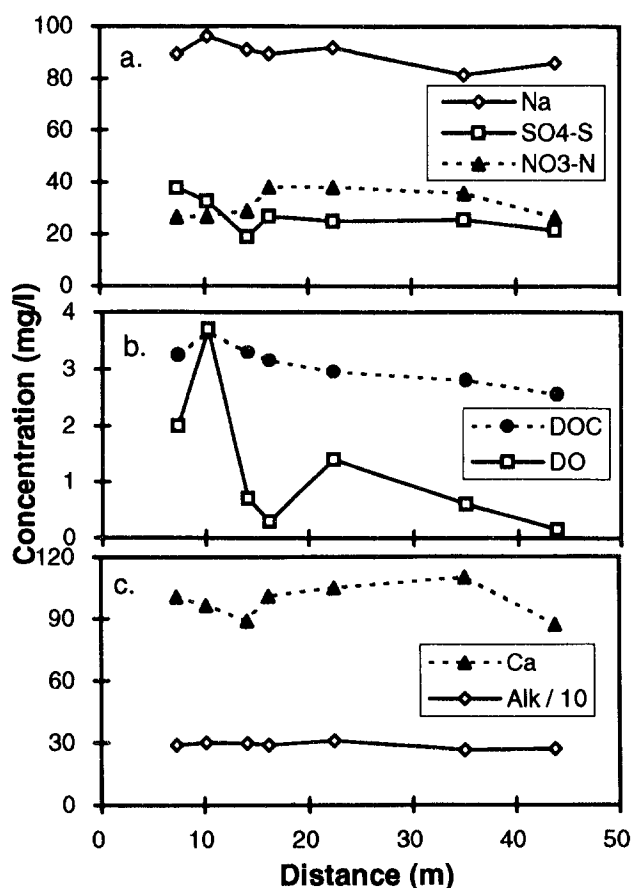
Fig. 4. Chemical profiles along centerline of Cambridge plume from samples collected in 1988 and 1989. Each point represents an average of two to three samples. Distance measured horizontally from upgradient edge of drain field, which extends for approximately 14 m. Alkalinity is reported as mg/l $CaCO_3$ and plotted at one-tenth its actual value.

to correspond roughly to the zones of highest O_2 consumption, were found directly below the biological mats. No significant decreases in O_2 concentrations were found at any depth in background locations. A previous study at Cambridge found favorable conditions for subsurface O_2 diffusion in the drain field, specifically a porosity of roughly 40% and a moisture content less than 20% in the soils between the tiles (Shutter et al., 1994).

As the septic-tank effluent traveled from the distribution pipe to the water table, the concentrations of reduced species decreased while the concentrations of oxidized species increased. The changes in this interval are shown by comparing the composition of the septic-tank effluent with that of ground water sampled at the water table directly below the drain field. Since the Na^+ concentrations changed very little over this interval at Cambridge, the composition of the effluent in the distribution pipe and at the water table can be compared directly (Table 1). At Muskoka, the Cl^- concentrations indicate that the effluent was diluted to approximately 68% of its original strength in the most concentrated samples. Thus the water-table concentrations are corrected for dilution with the background waters before comparison to the septic-tank effluent (Table 2). In the core of each ground-water plume, the concentrations of the chosen tracers remained close to those measured at the water table directly below the drain fields (Figures 4a and 5a).

The N species most clearly indicate the aerobic nature of the unsaturated zone. The majority of the N in the effluent existed in

reduced form (NH_4^+) in the distribution pipe, whereas almost all of the N in the impacted ground water at the water table existed as NO_3^- at both sites. A comparison of the total inorganic N concentrations over this interval indicates a loss of 20% at Cambridge and of 29% at Muskoka (Tables 1 and 2). Possible removal mechanisms include denitrification at anaerobic microsites (Sexstone et al., 1985) and NH_4^+ retention on solid surfaces by cation exchange and fixation (Nommik and Vahtras, 1982).

Reduced C and S were also oxidized in the unsaturated zone, based on the decreases in DOC and the increases in SO_4^{2-} in the effluents (Tables 1 and 2). The exact amount of organic C oxidation is difficult to determine, since CO_2, the product of oxidation, is probably degassed into the soil atmosphere. The concentrations of SO_4^{2-}-S increased at each site, apparently due to oxidation of reduced S [Tables 1 and 2; equation (2)]; the increase measured at Muskoka roughly matches the amount of nonsulphate S measured in the septic-tank effluent.

The Br^- dilution tests indicate that per-capita water use at Muskoka was approximately 240 l/day or 120 l/person/day whereas water use at Cambridge was 1100 l/day or 275 l/person/ day (calculation 1). (All calculations are shown in Table 4.) Assuming that all the COD is removed by aerobic oxidation and summing this oxygen demand with the amount of NO_3^- and SO_4^{2-} created in the unsaturated zones, the Cambridge and Muskoka unsaturated zones treated approximately 2.4 to 4.6 g O_2 demand/day/meter of distribution pipe (calculations 2 and 3).
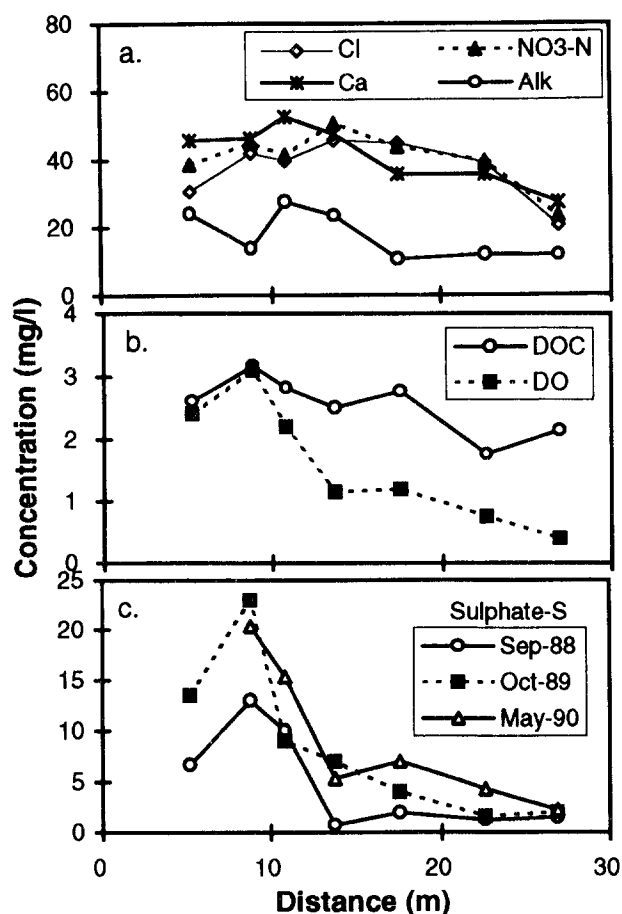

Fig. 5. Chemical profiles along centerline of Muskoka plume from samples collected in 1987 through 1990. Each point represents an average of two to eight samples. Distance measured horizontally from upgradient edge of drain field, which extends for approximately 11 m. Alkalinity is reported as mg/l $CaCO_3$.

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Table 4. Simple Calculations

Description and formula	Cambridge	Muskoka
A. Calculations		
1. Estimated daily flowrate of waste water $F_{ww} = M_{Br}/C_{Br}$	1100 l/day	238 l/day
2. Oxygen demand of waste water $OD_{ww} = OD_{Org\ C} + (2 \times C_{NH4}) + (2 \times C_S)$	13.7 mmol/l O_2 or 428 mg/l O_2	29.3 mmol/l O_2 or 916 mg/l O_2
3. Oxygen demand per length of distribution pipe $OD_{pipe} = (OD_{ww} \times F_{ww})/L_{pipe}$	5.5 g O_2/m/day	2.8 g O_2/m/day
4. Organic carbon demand of denitrification [eq. (3)] $CD_{denitr} = C_{NO3} \times F_{ww} \times 0.8 \times 365$ day/yr	—	2.9 kmol/yr or 35 kg/yr
5. Organic carbon content of river sediments $C_{Sed\ Org\ C} = Fr_{Org\ C} \times \rho_{sed}$	—	57 kg/m^3
6. Calcium carbonate dissolved in unsaturated zone $D_{CaCO3} = (\Delta Ca_{effl}/Fr_{Ca:CaCO3}) \times F_{ww} \times 365$ day/yr	47 kg/yr	—
7. Calcium carbonate content of drain field $C_{CaCO3} = Fr_{CaCO3} \times \rho_{soil}$	320 kg/m^3	—
8. Alkalinity balance in river bed $B = \Delta Alk_{RB-obs} - \Delta Alk_{RB-denitr}$	—	−1.6 meq/l
9. Alkalinity changes from septic tank to river $\Delta Alk_{total} = Alk_{STE} + \Delta Alk_{nitr} + \Delta Alk_{denitr}$	—	+2.1 meq/l

| Abbr.	Description	Cambridge	Muskoka
B. Parameters			
Alk_{STE}	Alkalinity in septic-tank effluent	—	6.3 meq/l
ΔAlk_{RB-obs}	Observed change in alkalinity in river bed	—	1.3 meq/l
ΔAlk_{nitr}	Theoretical change in alkalinity due to production of nitrate observed at water table by nitrification [equation (1)]	—	−8.4 meq/l
ΔAlk_{denitr}	Theoretical change in alkalinity due to denitrification of nitrate observed at water table [equation (3)]	—	4.2 meq/l
$\Delta Alk_{RB-denitr}$	Expected change in alkalinity due to denitrification of nitrate observed to be lost in river bed [equation (3)]	—	2.9 meq/l
C_{Br}	Concentration of bromide in effluent	90.9 mg/l	281 mg/l
C_{NH4}	Concentration of ammonium in original effluent	2.3 mmol/l	4.1 mmol/l
C_{NO3}	Concentration of nitrate in effluent, as measured at water table	—	4.2 mmol/l
C_S	Concentration of sulphate gained by effluent in unsaturated zone	0.4 mmol/l	0.1 mmol/l
ΔCa_{effl}	Change in calcium concentration in effluent in unsaturated zone	5.13×10^{-5} kg/l	—
F_{ww}	See Calculation 1	—	—
Fr_{CaCO3}	Fraction of calcium carbonate in drain field soils	20%	—
$Fr_{Ca:CaCO3}$	Fraction of calcium in calcium carbonate by mass	40%	—
$Fr_{Org\ C}$	Fraction of organic carbon in river sediments	—	4.1%
L_{pipe}	Length of pipe in drain field	80 m	80 m
M_{Br}	Mass of bromide added daily to septic system	100,000 mg/day	67,000 mg/day
$OD_{Org\ C}$	Oxygen demand of organic carbon in effluent (from COD test)	8.3 mmol/l O_2	20.9 mmol/l O_2
OD_{ww}	See Calculation 2	—	—
ρ_{sed}	Assumed density of river-bed sediments	—	1400 kg/m^3
ρ_{soil}	Assumed density of soil in drain field	1600 mg/m^3	—

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Redox Zones in Ground Water

According to the conceptual model, very little aerobic oxidation is expected in the saturated zone due to the low diffusivity and solubility of O_2 in water. Anaerobic conditions may develop if the native sediments contain a significant amount of labile organic carbon, whose oxidation could deplete O_2 in the ground water and then possibly NO_3^- via denitrification. At the two study sites, both DOC and DO concentrations decreased downgradient in the effluent plumes (Figure 4b and 5b), but the amount of aerobic oxidation implied by these declines is much smaller than that which occurred in the unsaturated zone. Apparently some DOC travels through the unsaturated zone only to be consumed in the saturated zone. The nature of this DOC is not known, but it may be relatively recalcitrant organic C from the effluent or organic products from microbial activity in the unsaturated zone.

Although the DO concentrations were low in the cores of the plumes, there was no evidence of reduction of NO_3^-. Below the water table the NO_3^- concentrations (relative to the tracer) did not significantly decrease along the core of the plume at either site (Figures 4a and 5a). In addition the content of ^{15}N and ^{18}O in NO_3^- were found to be constant along the Cambridge plume centerline (Aravena et al., 1993). If denitrification were occurring, the aqueous NO_3^- would become enriched with respect to these heavier isotopes (Mariotti et al., 1988).

Similarly the reduction of SO_4^{2-} is an unlikely possibility, since SO_4^{2-} is a less favorable electron-acceptor than NO_3^-. Sulphate-S concentrations did decrease initially in the ground-water plume at Cambridge (Figure 4a), but O_2 and NO_3^- were still present in this region. The apparent decrease is believed to be due to the large variability of SO_4^{2-} in the effluent. At Muskoka, SO_4^{2-} seems to be retained in the saturated zone. After reaching the water table, SO_4^{2-}-S concentations in the plume dropped by roughly 80% within 5 m of the drain field (Figure 5c). Iron and aluminum hydroxides are known to adsorb SO_4^{2-} (Mitchell et al., 1992), which may be an important mechanism in this acidic environment. Downgradient concentrations of SO_4^{2-}-S have increased slowly over time, which can be interpreted as saturation of the adsorption sites (Figure 5c).

Unlike the Cambridge plume, the effluent plume at Muskoka flows through a third redox zone in the sediments of the river bed. This layer is approximately 1 m thick and contains an average of 4.1% (w/w) solid organic C, compared to 0.03% (w/w) in the aquifer sands. Most of the organic matter in the river bed appears to be from terrestrial sources and includes tree trunks from clearing of the site. In this region, dissolved oxygen and then NO_3^- were apparently depleted in the oxidation of organic C (Figure 6). The NO_3^--N concentrations dropped from 40 mg/l to less than 0.05 mg/l over a flowpath of less than 2 m. An estimated 35 kg of organic C is consumed from the river bed each year if NO_3^- is removed completely from the plume via denitrification with organic C (calculation 4):

$$5\ CH_2O + 4\ NO_3^- + 4\ H^+ \rightarrow 2\ N_2 + 5\ CO_2 + 7\ H_2O \qquad (3)$$
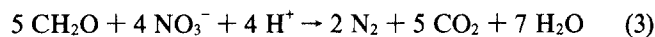
In comparison, the river bed sediments contain approximately 60 kg/m^3 of organic C [calculation (5)].

Alkalinity and pH Conditions

As described in the conceptual model, the redox reactions which occur in septic systems alter the alkalinity and pH of the waste water. Aerobic oxidation of reduced N and S can decrease

both the alkalinity and pH of the effluent [equations (1) and (2)], while denitrification in a subsequent anaerobic zone can cause alkalinity and pH increases [equation (3)]. In this study large changes in alkalinity and pH occurred in the unsaturated zones in both systems and in the river bed at the Muskoka site. In contrast only minor changes in pH or alkalinity were observed in the ground-water plumes in the aquifers at either site (Figures 4c and 5a). The different responses to the redox changes in the two systems are primarily due to their different soil compositions.

At Cambridge the septic-tank effluent had a near-neutral pH and almost 400 mg/l of alkalinity, 50% of which is contributed by the water supply (Table 1). As N and S oxidation produced H^+ in the unsaturated zone, the alkalinity in the effluent decreased. Increased Ca^{2+} concentrations at the water table relative to the effluent (Table 1) indicate that calcium carbonate from the sediments dissolved to buffer the acidity added by the oxidation reactions:

$$H^+ + CaCO_3 \rightarrow HCO_3^- + Ca^{2+} \qquad (4)$$
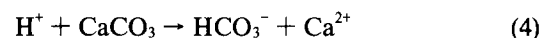
Only a small decrease in pH occurred (Table 1). Both background ground water and the effluent at the water table are calculated to be close to saturation with respect to calcite (log saturation index [SI] +0.06 and −0.11, respectively). Using the stoichiometric relationships in equations (1), (2), and (4), the observed and expected alkalinity decreases in the unsaturated zone are very similar (Table 5A). Based on the observed increase in Ca^{2+} concentrations, the effluent dissolves about 47 kg $CaCO_3$/yr (calculation 6). In comparison, 1 m^3 of Cambridge sands contains approximately 320 kg $CaCO_3$ (calculation 7), and the unsaturated zone below the distribution pipes contains approximately 150 m^3.

The Muskoka system is much poorer in buffering ability, and the progress of the effluent in the drain field was marked by significant decreases in pH and alkalinity (Table 2). The best supply of buffering materials is the layer of imported limestone gravel below the distribution pipes, and thus the largest Ca^{2+} increase occurred near the biological mat, as shown by the lysimeter samples (Table 3). The effluent in the lysimeters was close to saturation with respect to calcite (log SI −0.8), but the alkalinity of the effluent had decreased since the effluent left the distribution pipes.
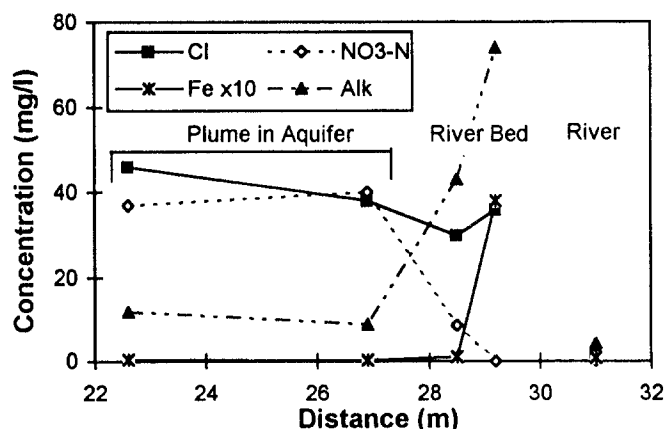

Fig. 6. Chemical profiles in plume in river bed at Muskoka, October 1989. Alkalinity shown as mg/l $CaCO_3$. Iron plotted at 10 times its actual value. Distance measured horizontally from upgradient edge of drain field.

Table 5. Alkalinity Changes in the Unsaturated Zones

	Septic-tank effluent (mM)	Effluent at water table (mM)	Net change (mM)	Alkalinity added (meq/l)
A. CAMBRIDGE				
Expected change in alkalinity:				
Nitrate-N	0.1	1.9	+1.8	−3.6
Sulphate-S	0.2	0.6	+0.4	−0.4 to −0.8
Calcium	1.0	2.3	+1.3	+2.6
			TOTAL	−1.4 to −1.8
Observed change in alkalinity:				
Alkalinity (as CaCO₃)	3.7	2.8	−0.9	−1.8
B. MUSKOKA				
Expected change in alkalinity:				
Nitrate-N	0.0	4.2	+4.2	−8.4
Sulphate-S	0.3	0.5	+0.2	−≤0.4
Calcium	0.3	1.6	+1.3	+2.6
			TOTAL	−≤6.2
Observed change in alkalinity:				
Alkalinity (as CaCO₃)	3.2	0.3	−2.9	−5.8

This simplified alkalinity balance calculates the change in alkalinity as follows, based on the stoichiometry of equations (1), (2), and (4):

$$\text{DAlkalinity} = (2 \times \text{DCa}^{2+}) - (2 \times \text{DNO}_3^-) - ([1 \text{ to } 2] \times \text{DSO}_4^{2-})$$

Alkalinity of the effluent continued to decrease in the remainder of the unsaturated zone, as did the pH (Table 2). Alkalinity at the water table was occasionally 0.0 mg/l (titration to pH 4.5), and the pH has been measured to be as low as 4.4. At the water table, the calcite saturation of the impacted ground water (log SI −3.6) was similar to that of the background ground water (log SI −3.9). The alkalinity balance over the entire unsaturated zone is close to that expected (Table 5b).

At Muskoka, alkalinity increased as NO_3^- was removed from the plume within the river bed (Figure 6). pH was not measured in these samples, but pH values as high as 5.9 were measured in this region at a later time (Wilhelm, 1991). The observed increase in alkalinity is lower than that expected from the observed loss of NO_3^- (calculation 8), perhaps because denitrification may not be complete in this region or because the additional alkalinity may be consumed by metal hydroxides or organic acids adsorbed on solid matter (Stumm and Morgan, 1981). Assuming that denitrification is complete and carried out via equation (3), the overall alkalinity "balance" for the waste water in this system is positive and results in a net addition of alkalinity to this setting by the septic system (calculation 9).

Other Constituents

The redox and alkalinity-related reactions described in the preceding sections cause the largest changes in geochemical conditions observed in these systems. As discussed below, other constituents in the waste water undergo changes which are influenced to various extents by the major reactions.

The concentrations of major cations (Na^+, K^+, Ca^{2+}, and Mg^{2+}) in these systems are expected to be affected primarily by cation exchange and mineral dissolution. The only known mineral dissolution occurring in these two systems is calcite dissolution, which increased the dissolved Ca^{2+} concentrations as de-

scribed above. Possible cation exchange effects are seen in the behavior of K^+ at Cambridge and K^+ and Na^+ at Muskoka. At Cambridge K^+ concentrations decreased by 50% relative to the Na^+ concentrations in the ground-water plume within 25 m of the drain field (Wilhelm et al., 1994b). At Muskoka Na^+ concentrations dropped by roughly 25% over the unsaturated zone but were steady in the ground-water plume, while K^+ concentration was steady in the unsaturated zone but decreased by up to 50% along the plume centerline (Table 2; Wilhelm, 1991). In the regions in which little or no change in concentrations of specific cations was observed, as was the case for Mg^{2+}, the cation exchange sites are apparently close to equilibrium with the concentrations and proportions of those cations found in the effluent and impacted ground water.

The trace metals monitored in this study have two possible sources: the original waste water and the soils through which the effluent plume passes. At Cambridge the concentrations throughout the drain field and ground-water plume were 10 to 300 μg/l for Fe and below 100 μg/l for Cu, Mn, and Zn. Apparently the waste water contained very low concentrations of these metals, and the consistently aerobic, basic setting in the subsurface did not favor mobilization from the soils.

At Muskoka, Fe and Al illustrate the range of trace-metal behavior in septic systems. The changes in Fe correspond primarily to changing redox conditions: Fe was present in the septic-tank effluent but was lost when it entered the oxic unsaturated zone (Table 2), presumably as reduced Fe^{2+} was oxidized to less soluble Fe^{3+}. In the reducing conditions of the organic-rich river bed, Fe concentrations increased, probably due to the release of Fe^{2+} from the sediments (Figure 6). On the other hand, Al concentrations were more affected by the changing pH conditions, since Al solubility increases steeply below pH 4.5 to 5.0 (Nordstrom and Ball, 1986). Aluminum was not detected in the

original septic-tank effluent (detection limit 0.05 mg/l), but its concentration was found to be 5.5 mg/l directly below the drain field and 0.1 mg/l and 0.5 mg/l in the two other plume samples; concentrations of 0.08 mg/l were obtained in the two background samples.

Phosphate was strongly retarded in both systems: Muskoka PO_4^{3-} from the effluent was not detected at the water table, while at Cambridge detectable PO_4^{3-} existed only in ground-water samples collected directly below or within 3 m of the drain field (Wilhelm et al., 1994b). More recent sampling of the Cambridge plume (Robertson, 1995) has shown that PO_4^{3-} has now migrated beyond the area of the drain field and is advancing at a slow but detectable rate of about one meter per year. In calcareous settings such as Cambridge, PO_4^{3-} may be retained by interactions with $CaCO_3$ (Bohn et al., 1985). In more acidic settings such as Muskoka, PO_4^{3-} behavior is probably dominated by interactions with Fe and Al oxides (Doner and Lynn, 1989).

A separate study at the Cambridge site investigated the potential removal of a volatile organic compound by the septic system (Robertson, 1994). A known amount of drain cleaner containing dichlorobenzene (DCB) was added to pre-tank waste water together with Br^- as a conservative tracer. DCB transport was retarded relative to Br^-, and the DCB concentrations decreased significantly relative to Br^- as the effluent flowed through the unsaturated zone. Biodegradation was considered to be the main removal mechanism, since DCB is known to biodegrade under aerobic conditions (Bouwer and McCarty, 1984). Other possible removal mechanisms included volatilization and sorption.

Site Comparison

As in many states and provinces, the Ontario regulations prescribe septic-system design parameters on the basis of a few site characteristics, especially the percolation time of the soil and, as a measure of expected waste-water flow rate, the number of bedrooms in the house. In addition these regulations set a minumum depth-to-water below distribution pipes and a minimum setback distance from wells and property boundaries. According to Ontario regulations, the Cambridge and Muskoka sites are almost identical. They both have high percolation times (measured as 0.6 cm/min and 10 cm/min respectively in this study), unsaturated zones approximately three times deeper than the minimum required, and the same number of bedrooms in the houses. As interpreted by the conceptual model, however, these two systems have different patterns of redox zones and different abilities to buffer additions of acidity, leading to different degrees of waste-water treatment and different compositions of ground-water plumes.

Both of these systems contain the two redox zones described as typical in the conceptual model: a septic tank where anaerobic digestion and physical treatment occur and an unsaturated zone where aerobic oxidation and downward flow of the effluent occur. The similarities of these systems result mostly from the similar characteristics of their drain fields and unsaturated zones, which allow for an adequate supply of O_2. Waste-water treatment is more complete at Muskoka than at Cambridge because the third redox zone at Muskoka, the river bed, removes NO_3^- from the ground-water plume. The sediments of the river bed provide an external reservoir of organic C to the plume after the effluent has undergone nitrification.

In addition to treating nitrogen differently, the two sites provide a contrast in terms of the relative impact of NO_3^- from the septic systems. At the Muskoka site the background concentrations of NO_3^- are below 4 mg/l, making the effluent a relatively large contributor of NO_3^- to the ground water. At the Cambridge site the plume concentrations of NO_3^- are similar to those found in the background, which are apparently caused by NO_3^- inputs from agricultural activities.

The acidity created by aerobic oxidation affects the two systems differently, mostly due to the different composition of the natural sediments. At the time of sampling, the acidity additions had no major impact on the functioning of the two systems. However, the differences do affect the mobility of species such as Al and probably the controls on PO_4^{3-} behavior. At Cambridge, the $CaCO_3$ content of the sediments is very high, and the combination of original alkalinity in the effluent and $CaCO_3$ dissolution results in higher alkalinity concentrations in the effluent plume than in the background ground water. The Muskoka site is located on the granitic bedrock of the Canadian shield and is sensitive to acidification, either by acid rain or by septic systems. During the monitoring period, aerobic oxidation in the drain field caused the effluent pH to drop by more than 1 unit below background, and only denitrification in the river bed keeps the system from adding significant amounts of acid to the environment overall.

The Cambridge system has operated since 1977, and its geochemical conditions were stable over the time of the monitoring activity. Its well-drained sands and abundant $CaCO_3$ seem to provide a stable geochemical environment for waste-water oxidation over the long term. In this setting, the most likely perturbations to the system will come from physical changes, such as breakage of the distribution lines or the gradual clogging of the drain field with recalcitrant organic matter. Without major changes the system will be a steady source of NO_3^- to the ground water.

The Muskoka system is younger and its geochemical conditions, such as the pH and SO_4^{2-} distributions, were changing during the monitoring period. Although abundant O_2 assures continued aerobic oxidation at the Muskoka site, the low buffering capacity of the soils is already resulting in lower pH and alkalinity in the ground-water plume. Over time these decreases may lead to further mobilization of aluminum and changes in the composition of the microbiological community. The long-term capacity for denitrification in the river bed is unclear; this reaction depends upon a continued supply of labile organic C, which may change if river levels or flowpaths change.

Applicability of Conceptual Model

The conceptual model's focus on the major redox and pH-affecting reactions accounts for the large-scale geochemical changes observed at these two septic systems. In particular the observed sequence of N transformations fits the conceptual model's expectations, as does the loss of organic C in the unsaturated zone. The pH and alkalinity changes occur almost wholly in response to the major redox reactions. Observations of changes in four elements (N, C, O, and Ca) and pH lead to a good overall description of geochemical conditions along the flowpath of the waste water.

Within this framework of large-scale redox and alkalinity changes, however, smaller changes occur that are not integral to the conceptual model. The conceptual model emphasizes reac-

tions which occur in the aqueous solution, along with the dissolution of gaseous O_2 and solid $CaCO_3$ and the loss of gaseous CO_2. Many waste-water constituents interact with the solid matrix in more site-specific ways than those described by the model. In particular, P dynamics in septic systems result mostly from solubility relationships and the interactions of PO_4^{3-} with adsorbing surfaces. Other ion exchange reactions may also occur, such as SO_4^{2-} adsorption in the plume at Muskoka. In some cases cation exchange may interfere with the use of Ca^{2+} as an indicator of $CaCO_3$ dissolution. Fortunately the effect of these reactions on redox and alkalinity conditions is small in the two systems studied. The conceptual model is most easily applied in sand aquifers, where the solid matrix is relatively nonreactive and the O_2 supply is relatively steady. In settings with a higher content of reactive clay particles or organic matter, the solid-solution interactions may play a larger role in determining waste-water chemistry and evolution. In addition the subsurface supply of O_2 is often lower in such settings and may show more daily and seasonal variability.

Application of the conceptual model in the detailed interpretation of waste-water evolution is limited by the variability inherent in operating septic systems. The waste water received at an individual system can vary considerably in both quantity and quality, which makes calculation of loading rates and observation of subsurface changes very difficult. For instance the high number of laundry loads on Saturdays at Cambridge may cause variability, such as a temporary increase in the concentration of SO_4^{2-}, an ingredient in the laundry detergent (Wilhelm, 1991). In addition, different components of waste water are contributed by different sources, so the concentrations of many constituents may vary inversely rather than proportionately. Thus an increase in the amount of laundry water may increase SO_4^{2-} concentrations, while diluting the N from human wastes. This phenomenon makes it difficult to detect minor geochemical changes based on a component's variation relative to some nonreactive component.

Model Predictability

The ability to predict the degree of treatment that a septic system will provide is especially important in protecting groundwater resources. Although this conceptual model is not capable of predicting, for instance, the exact concentration of NO_3^- expected from a proposed septic system, it does identify important questions to ask in order to evaluate the possible impacts. Whereas the traditional design process asks primarily "Can these soils accept this waste water and provide a certain depth of unsaturated flow?", the conceptual model also prompts questions about the O_2 supply, the redox settings, the availability of organic C in the soils, and the soil's buffering capacity.

The O_2 supply in the unsaturated zone is crucial to the long-term functioning of septic systems. Oxygen is made available at these two sites by a combination of sandy sediments, a trench layout for the drain fields and thick unsaturated zones. In fact, the depth-to-water below the distribution pipes at these two sites is 1.5 to 2.0 m, compared to minimum depth requirements of 0.5 to 1.2 m in most provinces and states (Canter and Knox, 1985; Ontario Ministry of Environment, 1982). Unfortunately our ability to quantitatively estimate the adequacy of O_2 supply is limited by the large numbers of variables involved, such as the effluent loading rate and oxygen demand, the moisture content of the soils, the subsurface distribution of waste water, and the

potential metabolic rates of the subsurface microorganisms. At this time we can only generally predict an increased likelihood of failed septic systems where the O_2 supply is inadequate, such as sites with shallow unsaturated zones, poor distribution of effluent, and poorly drained soils.

Prediction of the behavior of N in septic systems requires knowledge of the expected redox conditions at a site. Specifically, full removal of N from waste water requires an aerobic zone followed by an anaerobic one. The existence of an aerobic zone depends on the availability of O_2, as discussed above. Septic systems themselves are unlikely to create the proper conditions for a succeeding anaerobic zone, so pre-existing anaerobic conditions are probably required for denitrification. The persistence of agricultural NO_3^- in the ground water at Cambridge suggests that pervasive anaerobic conditions do not develop in this setting and that NO_3^- from waste-water treatment would likewise persist. The high DO in the Muskoka aquifer also suggests NO_3^- persistence. On the other hand, the existence of reducing conditions along the waste-water flowpath provides a more favorable setting for denitrification, such as in the river-bed sediments at Muskoka. Such settings, however, may not be able to provide enough organic C for long-term denitrification of waste water.

Soil composition is the main factor controlling the resulting pH and alkalinity of the waste water after treatment, which will likewise control metal solubility and PO_4^{3-} behavior. The amount of $CaCO_3$ present is the best indicator of the sediment's ability to buffer acidity additions, but other buffers can also play a role. The sites studied here almost represent end-member conditions in sediment buffering capacity, with the Cambridge site possessing more than enough $CaCO_3$ to buffer the septic system over its lifetime and the Muskoka site possibly already depleting $CaCO_3$ in the natural sediments near its distribution pipes.

Conclusions

The Cambridge and Muskoka sites provide examples of the geochemical changes which occur beneath septic systems and the impacts of septic systems in sand aquifers. As predicted by the conceptual model, redox reactions trigger many of the other geochemical changes which occur in septic systems. In these two properly functioning septic systems, the main impacts are the creation of high concentrations of NO_3^- in the ground water and the dissolution of $CaCO_3$ from the sediments. The two sites are most similar in their ability to supply adequate O_2 in the unsaturated zone. An adequate supply of O_2 is very important for septic-system functioning, but currently the dynamics of O_2 supply in drain fields cannot be rigorously described. The two sites differ in the ultimate fate of N in the effluent and the pH conditions created by the effluent. At Muskoka the natural anaerobic setting in the river bed removes the NO_3^- from the plume at the edge of the property, whereas the NO_3^- released from the Cambridge septic system travels at least 100 m with the effluent plume (Robertson et al., 1991). As for pH, the lower content of $CaCO_3$ in the Muskoka sediments causes decreases of more than 1 pH unit after the effluent is aerobically oxidized, compared to decreases of less than 0.1 pH units at Cambridge.

The differences in waste-water treatment at these two sites result from differences in the natural buffering capacities and natural redox settings rather than from differences in the design of the septic system or the patterns of waste-water production. This observation underscores the importance of natural geo-

chemical conditions in determining septic-system impacts and the importance of considering such conditions when trying to predict these impacts. Just as the percolation test attempts to measure the ability of the subsurface to accept waste water, so could analyses of the dissolved oxygen and NO_3^- content of ground water and the organic carbon content of aquifer materials indicate the potential for NO_3^- persistence. Likewise measurement of the calcite content of soils could signal the susceptibility of a setting to pH drops following aerobic oxidation.

Acknowledgments

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