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Geochemistry of a Septic-System Plume in a Coastal Barrier Bar, Point Pelee, Ontario, Canada

BY:

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NWRI Contribution No: 97-102

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MANAGEMENT PERSPECTIVE

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NWRI Publication#: 97-102

Citation: Journal of Contaminant Hydrology

EC Priority/Issue: This work was conducted as part of a larger study on the hydrogeology of the Point Pelee coastal barrier bar/wetland complex funded by Parks Canada, and by the GL2000 program. The work supports the ESD issue "Conserving Canada's Ecosystems" (nutrients and wetlands). For the business plan deliverables it supports Thrust #1 for Conserving Canada's Ecosystesm (nutrient loading, great Lakes coastal wetlands). Under EC Action Plan, the work supports the action item "Conserving Canada's Ecosystems" with the focus "Understand the impacts of human activities on ecosystems; develop and implement strategies to conserve ecosystems".

Current Status: The paper describes the results of detailed chemical analyses of groundwater samples collected in 1994 from one high capacity tile-bed located close to a large wetland. Analysis of data collected from a second tile bed is currently underway. High concentrations of nutrients are present in the groundwater below and downgradient of the tile bed. Elevated concentrations of nitrate and phosphate persist as far as 60 m from the tile bed. The study began late in 1993 and is expected to be complete in 1998. Annual reports have been provided to EP Ontario Region and to Parks Canada.

Next Steps: Complete solid phase analyses to determine spatial variation of phosphorous bound to aquifer materials. Monitor discharge of nutrient-rich groundwater into eutrophic marsh, and quantify mass of nutrients released to surface water body. Results will assist in evaluating the impact of nutrient-rich wastewater release into wetlands, and in the understanding of the dynamics of constructed wetlands as a method of wastewater treatment. Continued temporal monitoring of decommissioned tile beds will help to determine if elevated nutrient concentrations persist after decommissioning. Final report targeted for 1998.

Abstract

The major ion and trace metal geochemistry of a septic system plume in an unconfined carbonate aquifer next to a coastal wetland was characterized using a three-dimensional groundwater sampling network. At the time of sampling, the aquifer had received tile-bed discharge intermittently for 16 years from an overnight camp. The resulting plume is > 60 m long, > 40 m wide, and contains elevated concentrations of NO_3, NH_4, PO_4, dissolved organic carbon, Mn, Fe and other constituents. The groundwater pH is near neutral, with lower pH values observed near the plume core. These lower pH values are attributed to H^+ generation from oxidation of NH_4. The oxidation-reduction potential of the groundwater varies by more than 300 mV, with distinct redox zones observed. There is a shallow Mn-rich zone close to the tile bed, a deep Fe-rich zone at the base of the aquifer, and a shallow Mn-depleted zone distal from the tile bed. In the shallow Mn-rich zone, groundwater concentrations of Mn vary between 1 and 3 mg/L, Eh values are generally intermediate (> 400 mV), concentrations of dissolved oxygen (DO) are low (< 1.0 mg/L), and concentrations of nutrients are generally high (10 - 80 mg/ L NO_3-N, 1 - 15 mg/L NH_4-N, 0.1 - 1.5 mg/L PO_4-P, 6 - 13 mg/L dissolved organic carbon). In the deeper Fe-rich zone, reducing conditions (Eh < 200 mV) are encountered, corresponding to elevated concentrations of dissolved Fe (1-14 mg/L), o-PO_4 and NH_4, and negligible concentrations of NO_3 (< 0.01 mg/L N). Mineral saturation indices, calculated using MINTEQA2, along a cross-section close to the plume centerline, indicate that, in the Mn-rich zone, the groundwater is close to saturation or supersaturated with respect to hydroxyapatite, rhodochrosite, calcite and ferrihydrite. In the reduced zone, the groundwater is close to saturation or supersaturated with respect to hydroxyapatite, vivianite, calcite and siderite. Formation of these phases, or related phases, may be limiting the concentrations of Fe, Mn and PO_4 in the groundwater.

Keywords: wastewater, groundwater, geochemistry, nutrients, metals

Geochemistry of a Septic-System Plume in a Coastal Barrier Bar, Point Pelee, Ontario, Canada

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Abstract

The major ion and trace metal geochemistry of a septic system plume in an unconfined carbonate aquifer next to a coastal wetland was characterized using a three-dimensional groundwater sampling network. At the time of sampling, the aquifer had received tile-bed discharge intermittently for 16 years from an overnight camp. The resulting plume is > 60 m long, > 40 m wide, and contains elevated concentrations of NO_3, NH_4, PO_4, dissolved organic carbon, Mn, Fe and other constituents. The groundwater pH is near neutral, with lower pH values observed near the plume core. These lower pH values are attributed to H^+ generation from oxidation of NH_4. The oxidation-reduction potential of the groundwater varies by more than 300 mV, with distinct redox zones observed. There is a shallow Mn-rich zone close to the tile bed, a deep Fe-rich zone at the base of the aquifer, and a shallow Mn-depleted zone distal from the tile bed. In the shallow Mn-rich zone, groundwater concentrations of Mn vary between 1 and 3 mg/L, Eh values are generally intermediate (> 400 mV), concentrations of dissolved oxygen (DO) are low (< 1.0 mg/L), and concentrations of nutrients are generally high (10 - 80 mg/ L NO_3-N, 1 - 15 mg/L NH_4-N, 0.1 - 1.5 mg/L PO_4-P, 6 - 13 mg/L dissolved organic carbon). In the deeper Fe-rich zone, reducing conditions (Eh < 200 mV) are encountered, corresponding to elevated concentrations of dissolved Fe (1-14 mg/L), o-PO_4 and NH_4, and negligible concentrations of NO_3 (< 0.01 mg/L N). Mineral saturation indices, calculated using

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MINTEQA2, along a cross-section close to the plume centerline, indicate that, in the Mn-rich zone, the groundwater is close to saturation or supersaturated with respect to hydroxyapatite, rhodochrosite, calcite and ferrihydrite. In the reduced zone, the groundwater is close to saturation or supersaturated with respect to hydroxyapatite, vivianite, calcite and siderite. Formation of these phases, or related phases, may be limiting the concentrations of Fe, Mn and PO_4 in the groundwater.
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1. Introduction

Land-based release of septic system effluent, through conventional tile beds or other means, constitutes the single largest volumetric source of effluent discharged to the groundwater zone (Robertson et al., 1991). Groundwater plumes containing elevated concentrations of nutrients and other constituents are commonly observed downgradient of locations of wastewater discharge (LeBlanc, 1985; Robertson et al., 1991; Robertson and Cherry, 1992; Wilhelm et al., 1994; Walter et al., 1995; Harman et al., 1996). The most common method of wastewater disposal is release from a holding tank into leach fields or tile beds. This method of release encourages even distribution and enhances oxidation of the effluent in the unsaturated zone, prior to its recharge to the groundwater zone. While the use of tile bed leach fields leads to improved water quality, e.g., through oxidation of NH_4 and dissolved organic carbon (DOC) and attenuation of bacteria and phosphorous, relatively high concentrations of NO_3 and PO_4 often remain in the effluent when it enters the saturated zone. At sites where oxidation of the effluent in the unsaturated zone is incomplete, relatively high concentrations of NH_4 and DOC can also enter the groundwater zone.

Once in the groundwater zone, NO_3 can be transported long distances from the source areas,

provided aerobic conditions prevail (Robertson et al., 1991; Harman et al., 1996). If sufficiently reducing conditions are encountered, however, NO_3 can be removed from groundwater by bacterial denitrification reactions (Appelo and Postma, 1995).

Phosphorous present in wastewater, as o-PO_4, condensed phosphates or organophosphorous, often is attenuated strongly in the unsaturated zone (Reneau and Perry, 1976; Sawhney and Starr, 1977; Jones and Lee, 1979; Harman et al., 1996; Zanini, 1996). At some sites, up to 85% of the phosphorous initially contained in wastewater has been observed to accumulate as an adsorbed or precipitated phase directly below the leach fields (Harman et al., 1996; Zanini, 1996). Despite this relatively strong removal in the unsaturated zone, at some sites, large-scale plumes of groundwater containing concentrations of phosphorous sufficiently high to be of concern have been delineated at a number of sites (LeBlanc, 1985, Robertson, 1995; Harman et al., 1996; Robertson et al., 1997).

The study presented here was undertaken to assess the geochemical processes controlling the transport of septic-system derived constituents from a tile-bed in a shallow sand aquifer next to a marsh. The focus is specifically on phosphorous, because phosphorous is often the limiting nutrient in surface-water environments. At the study site, the groundwater covers a large range in oxidation-reduction potential, allowing the effect of redox zonation on the transport of septic-system derived nutrients to be evaluated. Geochemical speciation calculations were performed to determine mineral saturation indices for a number of phosphate-bearing solids along a vertical cross-section taken close to the plume centerline. The results assist in identifying geochemical processes controlling nutrient concentrations under varying Eh conditions.

2. Site description

The shallow groundwater zone downgradient of a multi-user tile bed, located at Point Pelee National

Park, was instrumented for this study. Point Pelee is a narrow triangular shaped peninsula extending southward into Lake Erie, and consists of two narrow barrier bars which surround an interior marsh system (Fig. 1). The western barrier bar at the park is developed and has more than 30 septic-system tile beds servicing the park staff and visitors. Several open water ponds in the interior marsh, in particular those adjacent to the western barrier bar, were observed to contain moderate to high concentrations of phosphorous (total P > 0.3 mg/L), and elevated concentrations of NO_3 and NH_4 (McCrea, 1993). This study was initiated to determine whether groundwater discharge of nutrients derived from the many tile beds is leading to these elevated concentrations.

The study area is located on the eastern (marsh) side of the western barrier bar (Fig. 1). Two tile beds are present at the site, an 'old' tile bed installed directly into the barrier bar sands in the late 1970's and a new raised tile bed installed more recently (Fig. 2). Both beds were installed to service the Camp Henry children's camp, which accommodates visitors on an overnight basis intermittently through the year. The plume generated from the old tile bed was monitored in this study. The old tile bed is 75 m^2 in area (9.1 m long by 8.2 m wide) and is constructed from perforated polyvinyl chloride (PVC) pipe trenched into the native dune sand. Five tile drainage lines, each 9.1 m in length, are arranged in a parallel network. The lines are installed about 30 cm below ground surface, and overlie coarse gravel packs.

The wastewater was gravity fed to the tile lines from a holding tank. The effluent is derived from toilets and showers on an irregular basis and can be classified as blackwater. A separate tile bed located approximately 100 m upgradient of the old tile bed is used for discharge of wastewater derived from food preparation. The maximum estimated day population at the site is 50, and the maximum estimated day water use is 2500 L/day (MacLaren Engineers, 1989). In September 1995,

discharge was diverted from the old tile bed to the nearby new raised tile bed (Fig. 2).

The upper sand unit at the site varies in composition and thickness across the bar, and is 7-8 m thick locally. It consists of poorly sorted sand, with occasional coarse sand and pebble layers. Mineralogical analysis, using transmitting light microscopy and x-ray diffraction, of several core samples collected near the center of the plume indicates the barrier sands contain approximately 60% quartz, 25% limestone, including shell fragments, and lesser amounts of microcline, Ca-plagioclase, magnetite, epidote, amphibole and kyanite. X-ray diffraction analysis of the limestone fraction indicates, in addition to calcite, the possible presence of ankerite and dolomite. A grain size analysis of a composite sample collected in the center of the plume, indicates the aquifer material contains 99% sand and1% silt and clay, with mean grain size of 470 μm, and is classified as a sand using the Folk classification system. Below the surficial sand unit there is very dense, low permeability clay till which is flat-lying and continuous under the barrier bar (Coakley, 1976).

3. Methods of investigation

3.1. Piezometer Installation

A network of bundle piezometers and larger diameter single-point piezometers was installed in the vicinity of the tile bed using conventional auger drilling methods (Fig. 2). The bundle piezometers are constructed of 1.9 cm (3/4 in.) PVC hard-wall tube, placed at the deepest elevation, with from four to nine 0.6 or 1.3 cm (1/4 or 1/2 in.) nylon or polyethylene sampling tubes placed at 0.5 or 1.0 m depth-intervals upward from the center PVC tube. The bottom 15 cm of each tube was slotted and covered with Nytex screen. The large diameter single-point piezometers are constructed of 5 cm (2 in.) PVC pipe with 0.3 m (1 ft.) long slotted endpoints.

Water samples were collected from both the bundle and standpipe piezometers. Hydraulic

head measurements were made using the bundle center tubes and the larger 1.3 cm diameter tubing of the bundle piezometers, in addition to the large diameter single-point piezometers. The large diameter single-point piezometers were also used for hydraulic property tests.

3.2. Groundwater Sample Collection

Samples of groundwater were collected in May and June 1994 using a peristaltic pump. Samples collected for analyses were filtered in-line using 0.45 μm mesh filters. Samples collected for cation and trace metal analyses were acidified to pH < 1.5 using metal-free HCl. Samples collected for o-PO_4 (soluble reactive phosphate) were acidified to pH < 1.5 using PO_4-free H_2SO_4. Determinations of temperature, electrical conductivity, pH, Eh and DO were made in the field on unfiltered samples. The pH, Eh and DO determinations were made in a sealed flow-through cell. The pH determinations were made using a combination Ross electrode (Orion Model 8156) calibrated with standard pH 4, 7 and 9.18 buffers. The Eh determinations were made using a combination platinum Ag/AgCl reference electrode (Orion Model 9678) standardized with ZoBell solution (Nordstrom, 1977). Concentrations of DO were measured using an Orion Model 820 dissolved oxygen meter. Determinations of alkalinity were made in the field on filtered samples, shortly after sample collection, by titration with standardized H_2SO_4 using a Hach digital titrator. Determinations of cation and trace metal concentrations were made by the National Laboratory for Environmental Testing (NLET) using inductively coupled plasma emission spectrometry. Determinations of NO_3-NO_2, NH_3, and DOC concentrations were made using automatic analysis techniques by NLET. Concentrations of Cl, Br and SO_4 were determined using ion chromatography. Concentrations of o-PO_4 were determined both in the field and in the laboratory using a phosphomolybdic acid colorimetric technique (Standard Methods, 1992) and a HACH portable spectrophotometer. A comparison of o-PO_4 concentrations

in acidified and unacidified samples determined in the field within 30 minutes of sample collection and in the laboratory within one week of sample collection indicated no statistical difference between values obtained from acidified and unacidified samples in the field, and from acidified samples later in the laboratory. Based on these results, the majority of o-PO_4 samples were acidified in the field and were analyzed within one week in the laboratory. Field duplicates and field blanks were collected routinely to check for analytical error and sample contamination.

4. Results and Discussion

4.1. Groundwater flow

The water table at the site is shallow (<1.5 m below ground surface in June 1994), and large seasonal fluctuations in the groundwater flow system have been observed in the Point Pelee barrier bar. Flow is from the marsh toward Lake Erie in the winter and early spring, and is from the Lake toward the marsh in the summer and early fall (Crowe and Ptacek, 1997). These seasonal reversals are very pronounced at locations where the barrier bar is relatively narrow (100 - 300 m). At Camp Henry, where the barrier bar is wider (400 m wide), the groundwater flow direction also varies seasonally, but less dramatically than at locations where the barrier bar is narrow. In December 1993, local flow at Camp Henry was in a north-northeast direction, whereas in May 1994 and November 1994 net flow was toward the east (Crowe and Ptacek, 1997; Ptacek and Crowe, 1997).

Groundwater velocity was calculated at the site, for November 1994, using the Darcy equation and field measured parameters. Using a mean hydraulic conductivity of 6.7×10^{-4} m/s (+/- 3.7×10^{-4}, n=9, 4 locations), an assumed porosity of 0.35, and the maximum observed hydraulic gradient (0.001), an estimate of the maximum local groundwater velocity of 60 m/a is obtained. Using the lowest observed gradient (0.0002) provides a much lower estimate of velocity (10 m/a). These

velocities are somewhat higher than estimates of velocity made elsewhere in the barrier bar (Crowe and Ptacek, 1997), probably as a result of local mounding of the water table due to the increase infiltration from the tile beds. The underlying clay unit is expected to act as a barrier to groundwater flow because of its low permeability, therefore the following discussion focuses on groundwater flow and transport in the permeable upper sand unit.

4.2. Source composition

Effluent collected from the Camp Henry holding tank in May 1996 contained high concentrations of DOC (31.8 mg/L), NH_4 (97.9 mg/L as N) and total P (11.8 mg/L) (Table 1). These concentrations are typical of effluent generated under low water use conditions (Robertson and Cherry, 1992). In addition to these constituents, the effluent contained moderate concentrations of the major ions Ca, Mg, Na, K, Cl and SO_4 and low concentrations of the metals Fe, Mn, Ca, Zn and Al. The rate of release of effluent to the tile bed was presumed to be highly variable over the 16 year operation period, both seasonally and annually. There were long periods of no loading (days to months) during the year, with sporadic periods of high loading. Transport of the effluent through the unsaturated zone was, therefore, variable depending on the effluent loading rates and on the precipitation recharge rates during periods of rest.

4.3. Groundwater plume composition

4.3.1 Bulk composition

When septic system effluent migrates through the unsaturated zone, nitrification of NH_4, release of N and P from organic compounds, and oxidation of DOC normally occur, leading to increased concentrations of NO_3, o-PO_4, CO_2, H^+ and other dissolved constituents. This oxidized effluent, together with rainfall and snowmelt, infiltrates to the groundwater zone. Once in the groundwater

zone, the effluent migrates away from the site in the direction of the flowing groundwater.

In the unsaturated zone, the principal oxidant of DOC and ammonia contained in septic system effluent is gaseous oxygen. Below the water table, transport of O_2 is in the dissolved form. The solubility of O_2 is low (8-13 mg/L at typical groundwater temperatures), therefore the rapid and extensive oxidation of septic system effluent by atmospheric O_2 is limited to the unsaturated zone. If the organic carbon and ammonia in septic system effluent is not completely oxidized in the unsaturated zone, further oxidation in the saturated zone may continue, but usually at a much lower rate. Oxidation may be by reaction with dissolved O_2, and, in the case of DOC, by reaction with other oxidant sources (e.g. Mn(IV) and Fe(III) oxides and (oxy)hydroxides). Changes in pH and alkalinity also occur along the plume flow path. Oxidation of the organic wastes by O_2 in the unsaturated zone leads to the production of CO_2 and changes in the pore-water pH; whereas oxidation of NH_4^+ leads to the production of NO_3^- and H^+. These chemical changes indirectly influence nutrient migration from the source area. Attenuation of septic-system derived NO_3, NH_4 and PO_4 along the groundwater flow path is, therefore, highly dependent on the changing geochemical conditions that result from both oxidation-reduction and pH-buffering reactions.

4.3.2. Dissolved organic carbon

Concentrations of DOC in the plume ranged between 6 and 13 mg/L, indicating removal of approximately 60 - 80% of the DOC originally released to the tile beds. The concentrations of DOC remaining in the groundwater are somewhat higher than values reported for groundwater samples collected near several other tile beds (3-6 mg/L, Robertson et al., 1991; Robertson and Cherry, 1992). These higher values suggest that removal of DOC by biodegradation during transport through the unsaturated zone and in the groundwater zone was less effective at the Camp Henry site compared

to these other sites. The highest concentrations of DOC were observed close to the tile bed, with concentrations > 12 mg/L observed up to 5 m downgradient of the tile bed. Slightly elevated concentrations of DOC (6-10 mg/L) were observed, however, throughout the complete thickness of the sand aquifer below and downgradient of the tile bed. At the time of sampling, a plume of groundwater containing high concentrations of NO_3, NH_4, PO_4, DOC and other dissolved constituents and relatively high values of electrical conductivity was below and north-northeast of the tile bed, in the same direction as the predominant flow direction measured in December 1993 (Fig. 3). This plume extends to the edge of a wetland, and probably beyond, and is at least 60 m in length and 40 m in width. Considering the 16 year loading period, a net groundwater velocity of at least 3.8 m/a would be required to generate the observed plume length, a velocity close to the lower velocity value calculated using the Darcy equation. There is a slight spreading of the plume toward the east, consistent with the observed shifting hydraulic gradient toward the east for part of the monitoring period. In cross-sectional view (section A-A', Fig. 4) elevated values of electrical conductivity (> 800 μS/cm) downgradient of the tile bed indicate a fairly uniform plume geometry consistent with that expected for flow toward the north-north east.

In September 1995 release of septic system effluent to the old tile bed was terminated. More recent groundwater sampling for electrical conductivity, NO_3, NH_4 and PO_4, conducted in Spring and Autumn of 1995 and 1996 indicate little change in the composition of the plume at that time.

4.3.3. Nitrogen species

Elevated concentrations of NO_3+NO_2, ranging between 1 mg/L to > 80 mg/L (as N), were observed throughout most of the upper 4 m of the saturated zone along cross-section A-A'. A pocket containing very high concentrations of NO_3+NO_2 (> 50 mg/L N at bundle CH5, and > 80 mg/L N at

bundle CH9) was observed 20 m downgradient of the tile bed (Fig. 4). At the base of the aquifer, there is a 1 - 2 m thick zone directly above the clay unit, where concentrations of NO_3+NO_2 were consistently very low (< 0.05 mg/L as N). Analysis of NO_2 made on several samples indicated that very low concentrations of NO_2 were present in the groundwater, therefore the concentration of NO_3+NO_2 is presumed to be represented primarily as NO_3, and is presented as such here.

Elevated concentrations of total NH_3 were observed throughout the plume, including the deeper sampling locations. At the near-neutral pH conditions of the plume, NH_3 is present predominantly as NH_4^+, and will therefore be referred to as NH_4. The concentrations of NH_4 ranged between 0.1 and > 15 mg/L (as N) along cross-section A-A' (Fig. 4). As with NO_3, a pocket of groundwater was observed 20 m downgradient of the tile bed (CH4-CH6) that contained concentrations of NH_4 that exceeded 15 mg/L (as N). At other bundle locations not on cross-section A-A', concentrations of NH_4 were > 5 mg/L during the summer of 1994 and exceeded 80 mg/L (as N) during other monitoring periods. At the base of the aquifer the groundwater contained concentrations of NH_4 that ranged between 0.1 and 1.0 mg/L (as N). The presence of NH_4 and relatively high concentrations of DOC below the water table indicate oxidation of the effluent in the unsaturated zone was incomplete prior to its recharge to the groundwater zone. The incomplete oxidation of the effluent could be due to either a short residence time in the unsaturated zone because of the permeable nature of the sands, high loading rates, and shallow water table position; or, possibly that insufficient development of active microbial populations occurred due to the sporadic nature of the wastewater discharge.

4.3.4. Phosphorous

Elevated concentrations of o-PO_4 were observed at sampling locations close to the tile bed (> 3.0

mg/L as P, November 1994, not shown) and in a separate zone confined to the lower 2 - 3 m of the sand aquifer (> 0.3 mg/L as P). The elevated concentrations near the base of the aquifer occured over the complete sampling network, to a distance > 60 m from the tile bed. Close to the tile bed, the concentrations of PO_4 are similar to those observed in other septic system plumes (Robertson et al., 1991; Harman et al., 1996). The maximum concentration of dissolved PO_4 observed in summer 1994 (1.5 mg/L P) along section A-A' was observed at location CH7, 5 m from the tile bed at a depth of approximately 2 m below ground surface. This decline from an original concentration of > 10 mg/L indicates at least 80% of the PO_4 originally present in the effluent was removed during transport between the holding tank and well location CH7. This removal is consistent with removals on the order of 50 - 80% observed at other sites receiving tile-bed effluent (Robertson, 1995; Harman et al., 1996; Zanini, 1996).

4.3.5. pH

The plume was near neutral in pH, with values ranging between pH 7.0 and 7.4 (Fig. 5). Near the inner core of the plume, the pH was depressed by about 0.4 pH units relative to the pH at the plume margins and in background groundwaters. This decrease in pH is consistent with changes expected by the release of CO_2 from organic matter oxidation (Eq. 1, Table 2) and as a result of the release of H^+ through NH_4 oxidation (Wilhelm et al., 1996):

$$NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$$

In near neutral pH systems with excess carbonate minerals present, as is the case at Camp Henry, the decrease in pH due to CO_2 evolution and H^+ release will lead to carbonate mineral dissolution, resulting in increased alkalinity, increased concentrations of Ca^{2+}, and possible increases in other

cations (e.g. Mg) contained in the carbonate minerals. Increases in alkalinity were observed to coincide closely with the decreases in pH near the plume core. Alkalinity values of approximately 200 mg/L as $CaCO_3$ were observed at locations with lower values of electrical conductivity, whereas in the plume core, alkalinity values ranged between 350 and 500 mg/L as $CaCO_3$. A decrease in pH also favours dissolution of (oxy)hydroxide minerals. The solubility of most common (oxy)hydroxide minerals, however, remains relatively low at near neutral pH, thus substantially increased concentrations of dissolved metals are not expected to occur at Camp Henry as a result of this process.

4.3.6. Eh and dissolved metals

The Eh in the plume showed greater variation than pH (Fig. 5). At the base of the aquifer there is a zone that was consistently low in Eh, ranging between 50 and 200 mV. This zone coincides with elevated concentrations of dissolved Fe (up to 14 mg/L; Fig. 5), DOC, NH_4 (0.1 to 1.0 mg/L), and PO_4 (0.01 - 0.3 mg/L as P) (Fig. 4), and negligible concentrations of NO_3 (< 0.05 mg/L) and dissolved oxygen (DO) (< 1.0 mg/L; not shown).

Above the reducing zone, there is a zone that was more variable in redox potential. Along cross-section A-A', Eh values were > 400 mV, concentrations of Mn were elevated close to the tile bed (1 - 3 mg/L in the shallow zone *versus* 0.1 - 0.5 mg/L in the deeper zone), concentrations of DO were below detection (< 1 mg/L), and concentrations of Fe were generally low (< 0.1 mg/L). At a few locations not on cross-section A-A' (CH16, CH17 and CH23), and at bundle location CH22 near the marsh edge on cross-section A-A', elevated concentrations of Fe were observed (~ 5 mg/L), indicating that at these locations the groundwater was more highly reducing.

At location CH15 upgradient of the tile bed, concentrations of DO were > 1.5 mg/L in the

upper 2 m of the saturated zone. This is the only location where elevated DO concentrations were were encountered.

4.4. Geochemical processes controlling nutrient transport

4.4.1 Development of redox zones

When partially oxidized septic-system leachate enters a soil or aquifer system, oxygen as a terminal electron acceptor is usually not available at sufficient concentrations to completely oxidize DOC and NH_4^+. Further oxidation of DOC, therefore, requires an alternative electron acceptor. In the absence of O_2, the expected sequence of terminal electron acceptors for the oxidation of organic matter, based on thermodynamic considerations and field observations, is denitrification, followed by reductive dissolution of Mn-oxides, and reductive dissolution of Fe-oxides (Table 2; Stumm and Morgan, 1981). The occurrence of these reactions is typically confirmed by a decrease in NO_3 concentrations, and an increase in concentrations of dissolved Mn^{2+} and Fe^{2+}. Additional reactions, including sulfate reduction and methanogenesis, will occur under more strongly reducing conditions.

At sites where wastewater is discharged to aquifers, the role of elevated concentrations of NO_3 and NH_4 in the development of redox zones along the groundwater flow paths needs to be considered. The septic-system effluent at Camp Henry contains higher concentrations of N species (>98 mg/L) than DOC (31.8 mg/L). Along the groundwater flow path, there will be locations where oxidation of NH_4 by molecular oxygen will be occuring concurrent to DOC oxidation by molecular oxygen. At other locations oxidation of DOC will be coupled to the reduction of nitrate and a variety of other reactants. Nitrate reduction by solid-phase organic matter and possibly sulfide minerals may also be occurring. At different locations, different redox reactions are expected to be active.

At Camp Henry elevated concentrations of Mn are observed downgradient of the tile bed in

the proximal plume zone. These elevated concentrations are likely due to reductive dissolution of Mn(IV) oxide coatings or Mn(VI)-rich grains coupled to DOC oxidation. At the base of the aquifer, elevated concentrations of Fe correspond closely to the low Eh zone, and are thus likely developed as a result of the reductive dissolution of Fe(III) (oxy)hydroxide coatings or dissolution of Fe-bearing minerals. At the locations not on cross-section A-A' where elevated concentrations of Fe were observed (CH16, CH17, CH23), reductive dissolution of Fe(III) (oxy)hydroxide solids coupled to DOC oxidation also likely is occurring. Visual observation of drill cuttings, indicate that the upper few meters of sand are stained orange-red in colour, in particular, away from the tile bed, consistent with the presence of Fe(III) (oxy)hydroxide solids. Sediment collected from locations near the base of the aquifer and from locations in the shallow zone that are close to the tile bed are notably dark gray in colour, indicating a deficiency of Fe(III) in grain coatings.

Increased concentrations of dissolved metals downgradient of sites receiving incompletely oxidized wastewater has been documented previously. Robertson and Blowes (1994) describe a similar increase in concentrations of dissolved Fe and Mn, and other metals, in the groundwater zone below a tile bed at Killarney, Ontario. In a sand and gravel aquifer at Cape Cod, Massachusetts, Walter et al. (1995) describe Mn- and Fe-rich plumes forming downgradient from infiltration lagoons receiving primary treated wastewater. At the Cape Cod site, the Fe-rich plume is confined to the zone closest to the infiltration lagoons, whereas the much larger Mn-rich plume is developed further downgradient of the lagoons. The sequence of encounter of the Fe- and Mn-rich zones at this latter site correspond closely to that expected based on thermodynamic considerations (Table 2). A similar sequence has been observed at landfills and other sites where the transport of DOC-rich water leads to a predictable migration of redox fronts (Lingkilde and Christensen, 1992; Heren and Christensen,

1994).

In the shallow zone proximal to the Camp Henry tile bed, the elevated concentrations of both Mn and Fe suggest reduction of both Mn(IV) and Fe(III) oxides is occurring. The irregular nature of the elevated Fe concentrations suggest that there is some local heterogeneity in the characteristics of the aquifer solids, either physical or mineralogical, or some variation in the wastewater release rates. The generally higher concentration of Mn relative to Fe and the generally higher Eh readings suggest, however, that the inner core of the Camp Henry plume is not as strongly reducing as the inner cores of the Cape Cod or Killarney plumes (Robertson and Blowes, 1994; Walter et al., 1995).

At the base of the aquifer the extensive reducing zone may have developed as a result of natural oxidant consuming processes that occurred prior to release of wastewater at the site, such as oxidation of solid-phase organic matter or oxidation of reduced mineral phases. This zone may also be the result of historical releases of wastewater from other tile beds located nearby, or as a result of historical changes in geochemical conditions for the current tile bed. There are elevated concentrations of Na and DOC over the complete thickness of the sand aquifer below and downgradient of the tile bed, indicating that the plume is present in this lower reducing zone, and may be contributing to the development of the reducing zone, but beecause of the extensive nature of the lower reducing zone and much higher Fe concentrations than elsewhere in the plume, factors other than the release of effluent from the old tile bed are likely contributing to its development.

4.4.2. Nitrogen

Concentrations of total inorganic N, calculated as the sum of NH_4 plus NO_3+NO_2, in the plume were consistently lower than the concentration of N present originally as NH_4 in the effluent source. While variations in source concentrations are expected, much lower values of total N in the

plume suggest loss of N in the groundwater zone has occurred. This loss is probably due to microbial denitrification of NO_3 and subsequent removal of N_2 gas. Removal of NH_4 through cation exchange reactions could also be occurring. At one location (CH9, 3 m above the clay aquitard), the concentration of total N was 85 mg/L, close to the concentration measured for the effluent of 98 mg/L. At this location, however, concentrations of Cl were also higher, suggesting the effluent was more concentrated when it originally entered the saturated zone. Assuming N/Cl ratios in the raw effluent remain approximately constant over time, a comparison of the N/Cl ratio for the present-day effluent of 1.7 with the N/Cl ratio for groundwater at CH-9 of 0.7, is consistent with a loss of N during transport from the source area. Elsewhere, similar or lower plume ratios of N/Cl are observed suggesting loss of N.

In aerobic aquifers NO_3 is usually transported conservatively (Freeze and Cherry, 1979). In anoxic aquifers, removal of NO_3 from septic system effluent by denitrification reactions, coupled to organic matter oxidation and possibly also to sulfide mineral oxidation, has been described (Robertson and Cherry, 1992). Denitrification of NO_3 can be coupled to microbial oxidation of organic matter either in a dissolved or solid form. Elevated concentrations of NO_3+NO_2 that occur near the inner core of the plume and in the upper portion of the aquifer, coincide with locations where concentrations of dissolved Fe are low. In the upper portion of the aquifer where concentrations of Fe are elevated, concentrations of NO_3+NO_2 are very low (< 0.05 mg/L), indicating nitrate reduction is occurring in these local high-Fe pockets. Near the base of the aquifer, where reducing conditions are present, concentrations of NO_3+NO_2 are also consistently low, indicating that nitrate reduction is probably occurring in this zone as well.

The principal geochemical mechanisms influencing concentrations of dissolved NH_4 in

groundwater are oxidation and cation exchange reactions. Oxidation of NH_4 by O_2, either in the dissolved or gaseous form, leads to the formation of NO_3 and no net change in the total concentrations of N. In the absence of oxygen, transport of NH_4 is expected to be controlled principally by cation exchange reactions. The highest concentrations of NH_4 coincide also with the highest concentrations of NO_3, and occur in the plume core about 20 m downgradient from the tile bed. In the upper Mn-depleted zone distal from the tile bed, concentrations of NH_4 are lower. The decline in NH_4 concentrations is either from dilution, or loss from oxidation or cation exchange reactions. Oxidation of NH_4 where anoxic water contacts oxygenated water has been documented (LeBlanc, 1985). The concentrations of dissolved O_2 downgradient of the tile bed were consistently < 0.5 mg/L. Because of the lack of high concentrations of O_2, oxidation of NH_4 is not expected to be extensive due to the high concentrations of NH_4 relative to the low concentrations of O_2. If exchange of NH_4 for other cations on mineral surfaces is occurring, the process is not very strong considering the high concentrations and long distance NH_4 has migrated from the source. The elevated concentrations of NH_4 in the reducing zone, correspond to elevated values of electrical conductivity and other effluent-derived constituents (e.g. Na), indicating that effluent has migrated to the base of the aquifer at downgradient locations. In the reducing zone, oxidation of NH_4 is not expected, and is consistent with the continued presence of NH_4.

4.4.3. Phosphate

The geochemical mechanisms controlling the movement of PO_4 in septic-system environments include adsorption/desorption and precipitation/dissolution reactions. Phosphate potentially can be adsorbed by a number of mineral and amorphous phases present in aquifer solids. Phosphate is a protolytic acid with PO_4^{3-} protonating to form HPO_4^{2-}, $H_2PO_4^-$, and $H_3PO_4^0$. Under normal

groundwater pH conditions, the dominant forms of PO_4 are HPO_4^{2-} and $H_2PO_4^-$, both of which are anions. The adsorption of these anions requires the presence of positively-charged mineral surfaces. Studies on the adsorption of PO_4 onto mineral surfaces indicate that the adsorption process is pH-dependent and that PO_4 is strongly adsorbed. Conversion to a solid phase precipitate is also possible (Stumm and Morgan, 1981).

The principal solids present in aquifers that are positively charged under near neutral pH conditions are Al-, Mn(IV)- and Fe(III)-containing oxides and (oxy)hydroxides and some clay minerals. As reductive dissolution reactions occur, some of the natural PO_4 adsorption capacity of the soil or aquifer solids may be depleted. Other solids, including Al-containing solids and clays are expected to be more stable under reducing conditions. If present, these latter solids can contribute to the PO_4 adsorption capacity, even if the system is highly reducing.

The second major process influencing the migration of PO_4 in natural systems is the precipitation and dissolution of PO_4-containing solid phases. There are numerous PO_4 phases that occur in nature, the most common being Al, Fe, and Ca solids (Nriagu and Dell, 1974). Solids commonly proposed to be major controls on dissolved PO_4 concentrations under low-temperature conditions, include hydroxyapatite, variscite, strengite and vivianite, or closely related amorphous and hydrated solid phases (Stumm and Morgan, 1981). The latter two phases strengite and vivianite, contain Fe in the Fe(III) and Fe(II) forms, respectively.

In the upper portion of the sand aquifer at Camp Henry, there appears to be some retardation of PO_4 relative to other wastewater derived constituents. The highest concentrations of PO_4 were observed close to the tile bed, whereas the highest concentrations of NO_3 and NH_4 were observed between 10 and 40 m downgradient of the tile bed. Considering the current overall plume size and

the calculated groundwater velocities at the site, the rate of PO_4 migration is likely on the order of 1/5 to 1/20 of the rate of migration of conservative plume constituents (e.g. Na, Fig. 5). This retardation of PO_4 is consistent with observations at other tile bed sites (Robertson, 1995; Harman et al., 1996).

In the lower reducing zone, the elevated concentrations of PO_4 persist over the complete sampling network and correspond closely to elevated concentrations of dissolved Fe. At the few shallower locations (CH16, CH17, CH22, CH23) where dissolved Fe concentrations were elevated, concentrations of dissolved PO_4 were also elevated, suggesting different geochemical mechanisms are active in controlling the concentrations of PO_4 in the different Eh zones.

Mineral saturation indices were calculated using MINTEQA2 (Allison et al., 1990) for groundwater samples collected along cross-section A-A' (Fig. 6). The groundwater is near saturation with respect to calcite at all sampling locations along cross-section A-A', with the exception of one sample of intermediate depth at bundle location CH4. The aquifer material at Camp Henry contains > 25% carbonate minerals, thus calcite saturated conditions are consistent with the presence of excess carbonate phases. In the high Mn zone close to the tile-bed, the groundwater is near saturation with respect to rhodochrosite. The formation of rhodochrosite is expected under conditions of reductive dissolution of Mn(VI) phases in the presence of excess carbonate.

At most sampling locations along cross-section A-A', the groundwater is near saturation or supersaturated with respect to hydroxyapatite ($Ca_5(PO_4)_3OH$). Groundwaters and pore waters that contain phosphate in contact with carbonate bearing solids frequently are near saturated or are supersaturated with respect to hydroxyapatite, and a number of studies suggest precipitation of a Ca-PO_4 phase may be a potential control on dissolved phosphate concentrations. For example, Wilhelm

et al. (1994) suggest removal of PO_4 by reaction with $CaCO_3$ as a potential control on PO_4 concentrations in a septic-system plume in a carbonate aquifer. Baker (1996) suggests β-tricalciumphosphate ($\beta Ca_3(PO_4)_2$), a more soluble precursor of hydroxyapatite, best describes PO_4 concentrations in calcium carbonate-rich aquifer materials. In lake sediments, supersaturated conditions with respect to hydroxyapatite have also been documented (e.g., Emerson, 1976; Wersin et al., 1991). In the proximal core of the plume, where highest concentrations of phosphate occur (0.1 - 1.5 mg/L), a high degree of supersaturation with respect to hydroxyapatite is indicated, suggesting that the formation of hydroxyapatite is probably kinetically limited.

Near the base of the aquifer, where concentrations of Fe ranged between 1 and 14 mg/L, the groundwater is near saturation or slightly supersaturated with respect to siderite ($FeCO_3$) suggesting this carbonate phase is controlling the concentration of dissolved Fe in the lower reduced zone. In the shallow portion of the aquifer, where concentrations of Fe were low, the groundwater is undersaturated with respect to siderite. Where the groundwater is near saturated with respect to siderite, the groundwater is also near saturation or supersaturated with respect to vivianite ($Fe_3(PO_4)_2 \cdot 8H_2O$), suggesting this phase may be a potential control on the concentrations of dissolved PO_4 in the lower reduced zone. Formation of vivianite was also suggested by Gschwend and Reynoldson (1987) for the sand and gravel aquifer at Cape Cod, Massachussets, which was receiving PO_4 from incompletely oxidized wastewater.

The formation of vivianite has also been proposed as an important control on PO_4 concentrations in other types of reducing sediments, including lake sediments receiving excess PO_4 loadings (Nriagu and Dell, 1974; Emerson, 1976; Wersin et al., 1991) and including some bog sediments (Postma, 1981). At several of the sites described, supersaturation with respect to both

siderite and vivianite was observed, consistent with this study. Both siderite and vivianite were identified mineralogically by Postma (1981) at locations where bog pore waters were observed to be supersaturated with respect to these phases. At all locations sampled along cross-section A-A', the groundwater is slightly supersaturated with respect to ferrihydrite, with saturation indices ranging between +0.2 and +3.0. These values suggest that ferrihydrite or another Fe(III) (oxy)hydroxide phase may be present in the sediments, and that the Eh in the lower reduced zone is controlled by near equilibrium conditions with respect to both siderite and a ferrihydrite. If a Fe(III) (oxy)hydroxide phase is present in the deeper reduced zone, it is likely present at very trace concentrations that were not visually identifiable.

At Camp Henry a variety of geochemical processes are likely leading to the observed attenuation of phosphate. Below the tile bed, removal of a large portion of the phosphate originally contained in the effluent has occurred prior to the effluent reaching the water table, as indicated by the much lower concentrations of phosphate observed in the groundwater at the closest sampling location relative to the effluent concentrations (1.5 vs. 11.8 mg/L P). Once in the groundwater zone, a combination of adsorption reactions and precipitation reactions is likely occurring. In the intermediate Eh zone, adsorption reactions and formation of a Ca-phosphate solid may be leading to the attenuation of PO_4. In the reduced zones encountered at the deeper sampling points and at several shallow sampling points close to the tile bed, PO_4 may have migrated from the old tile bed or from even earlier discharges. Alternatively, there is a possibility that the PO_4 in the reduced zone is derived naturally from the decay of organic matter. If the elevated concentrations of PO_4 in the reduced zone are derived from the old tile bed, its mobility is relatively high considering the long distance that it is observed away from the tile bed (> 60 m). Increased PO_4 mobility under strongly reducing conditions

is expected because of a deficiency of ferric (oxy)hydroxide coatings as potential adsorbent sites. In the reducing zone, the maximum concentrations of phosphate do not, however, exceed 0.9 mg/L, probably as a result of a mineral solubility control such as vivianite and/or hydroxyapatite formation. Mineralogical analyses, using a variety of near-surface and bulk analysis techniques, have been conducted in an attempt to identify the form of PO_4 present in the reduced zone, however, these attempts have been unsuccessful to date, possibly due to the small mass of PO_4 likely present in this zone.

5. Conclusions

A groundwater study was conducted to delineate the mechanisms controlling the transport of nutrients derived from a septic-system tile-bed installed in the barrier bar sands of Point Pelee, Ontario. Septic-system derived constituents have migrated > 60 m from the tile bed over a 16 year period, representing a minimum migration rate of 3.8 m/a. In the inner core of the plume, concentrations of NO_3, NH_4 and PO_4 are high. Further away from the tile bed, elevated concentrations of NO_3 are limited to an upper zone that is Mn-rich and of intermediate Eh. Deeper in the aquifer, there is an Fe-rich reduced zone; here the absence of NO_3 is likely due to denitrification reactions. Elevated concentrations of NH_4 are present in both the intermediate Eh and lower reduced zone. Relatively high concentrations of dissolved PO_4 are observed close to the tile bed, up to distances of 20 m. The PO_4 zone is diminished in size compared to other more mobile plume constituents indicating a retardation factor on the order of 5-20 in this zone. In the reduced zone, elevated concentrations of PO_4 are ubiquitous. This PO_4 may be derived from the Camp Herny tile bed, from other nearby tile beds or wastewater releases or it may be derived from natural processes. Geochemical equilibrium calculations indicate that the groundwater is close to saturation or is

undersaturated with respect to hydroxyapatite in the upper intermediate-Eh zone, and is close to saturation or is supersaturated with respect to hydroxyapatite and vivianite in the lower reduced zone. In the plume zone proximal to the tile bed, the groundwater is highly supersaturated with respect to hydroxyapatite. A combination of adsorption and precipitation reactions likely control the attenuation of phosphate. Whereas there appears to be a solubility control on phosphate in the lower reduced zone, the concentration of phosphate in this zone typically exceeds 0.2 mg/L and occasionally exceeds 0.8 mg/L. In the zone close to the tile bed, concentrations of PO_4 > 3 mg/L were observed during other sampling sessions. There are over 30 tile-beds in the Park, many of which are positioned close to open-water ponds. Release of groundwater with such elevated phosphate concentrations to nearby open water bodies may be sufficient to contribute locally to the development of eutrophic conditions.

Acknowledgements

This paper benefitted from discussions with D. Blowes, A. Crowe, R. McCrae, and W. Robertson, and from the assistance of L. Durham, J. Voralek, C. Talbot, S. Bruce, J. FitzGerald, K. Devos, K. Waybrant, and L. Hinch. Mineralogical analyses were provided by A. Pratt. Funding was provided by Parks and Heritage Canada and Environment Canada. We thank G. Mouland, B. Horan and D. Rieve who kindly facilitated the field aspects of this study.

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Table 1. Composition of septic-system effluent obtained from Camp Henry holding tank, May, 1996.

Parameter	Concentration (mg/L)
NO_2 (as N) and NO_3 (as N)	0.05*
NH_4 (as N)	97.9
P, total	11.8
DOC	31.8
Ca	83.6
Mg	12.9
Na	42.8
K	20.6
Cl	57.0
SO_4	34.1
SiO_2	9.65
Fe	0.599
Mn	0.480
Cu	0.029
Zn	0.069
Al	0.10

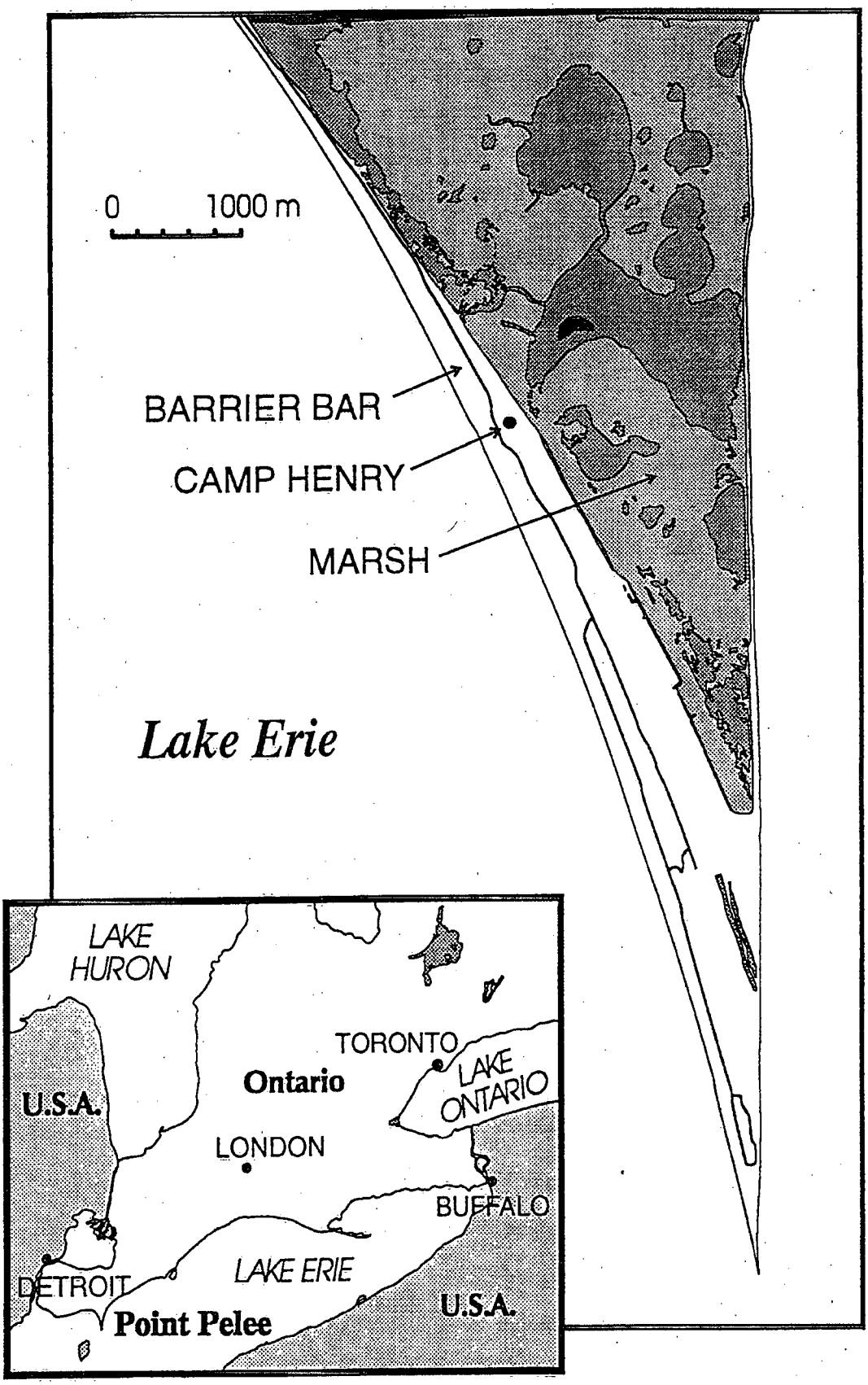
* Concentration equal to analytical detection limit

Table 2. Free-energy for organic matter oxidation using different electron-acceptors.

Process	Reaction[a]	Free energy[b] (kcal mol^{-1})
O_2 reduction	$CH_2O + 1/2\ O_2 = HCO_3^- + H^+$	-118.8
Denitrification	$CH_2O + 4/5NO_3^- = 2/5N_2(g) + HCO_3^- + 1/5H^+ + 2/5H_2O$	-112.7
Manganese(IV) reduction	$CH_2O + 2MnO_2(s) + 3H^+ = 2Mn^{2+} + HCO_3^- + 2H_2O$	-84.9
Iron(III) reduction	$CH_2O + 4Fe(OH)_3(s) + 7H^+ = 4Fe^{2+} + HCO_3^- + 10H_2O$	-26.8
Sulphate reduction	$CH_2O + 1/2SO_4^{2-} = 1/2HS^- + HCO_3^- + 1/2H^+$	-23.9
Methane fermentation	$CH_2O + 1/2H_2O = 1/2CH_4 + 1/2HCO_3^- + 1/2H^+$	-21.6

[a] Reactions from Freeze and Cherry (1979)
[b] Free energy data from Garrels and Christ (1965); Brock et al. (1984); calculated for pH = 7.0

List of Figures


0 1000 m
BARRIER BAR
CAMP HENRY
MARSH
Lake Erie
LAKE HURON
U.S.A.
Ontario
TORONTO
LAKE ONTARIO
LONDON
BUFFALO
DETROIT
LAKE ERIE
Point Pelee
U.S.A.

Ptacek Fig. 1

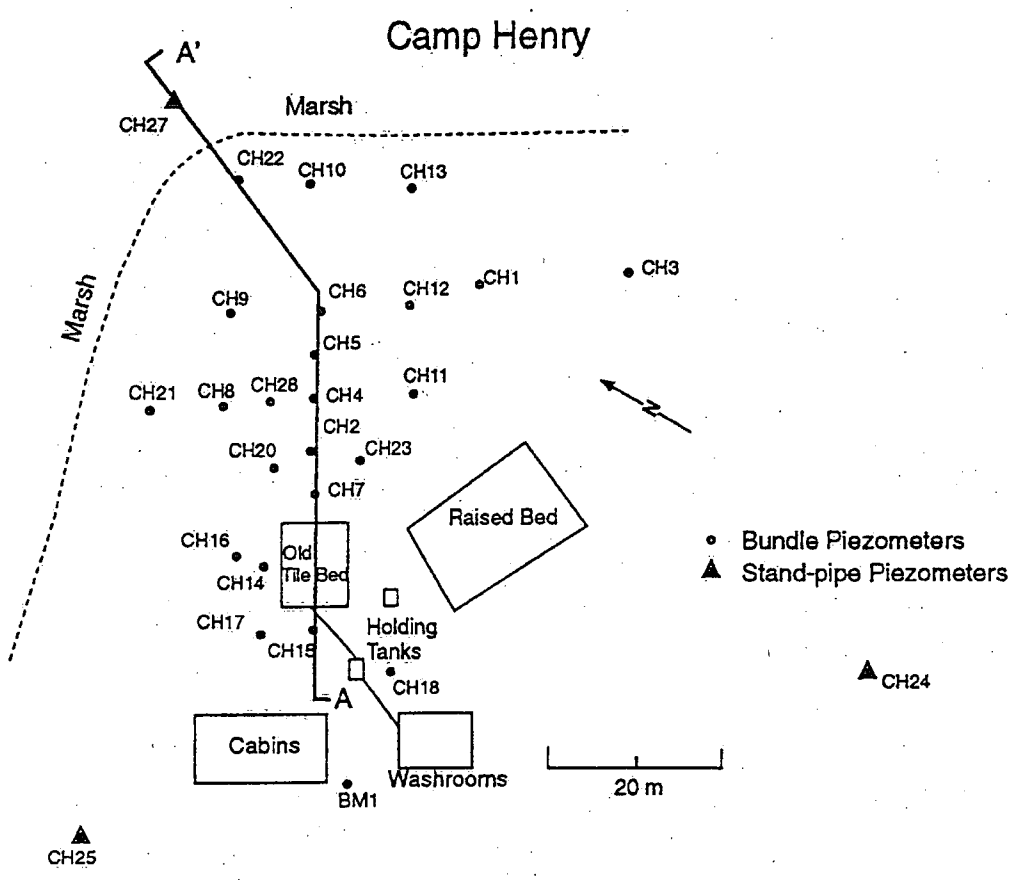


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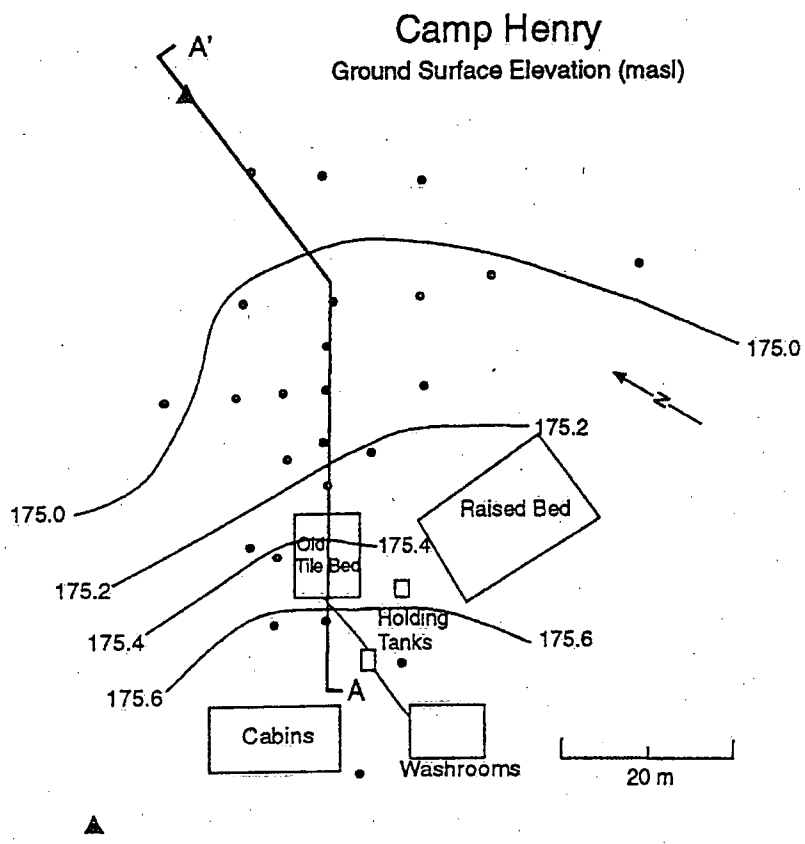
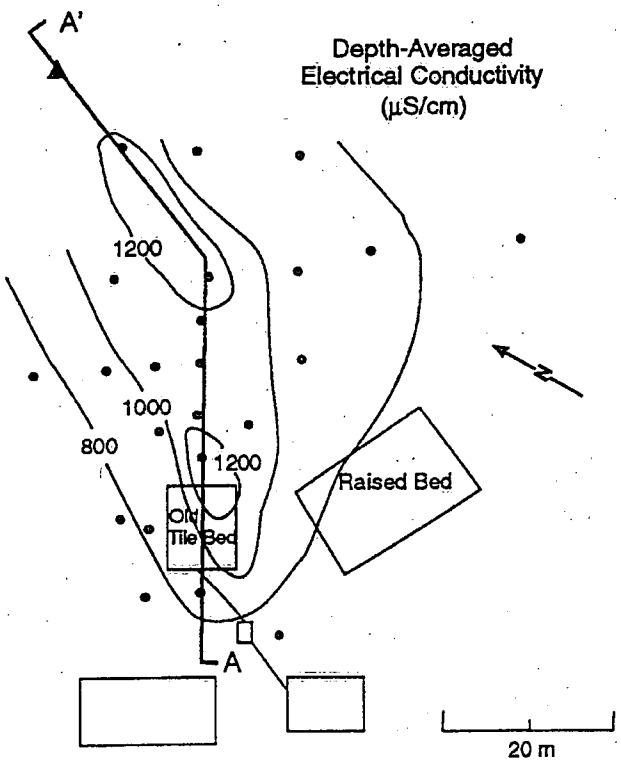
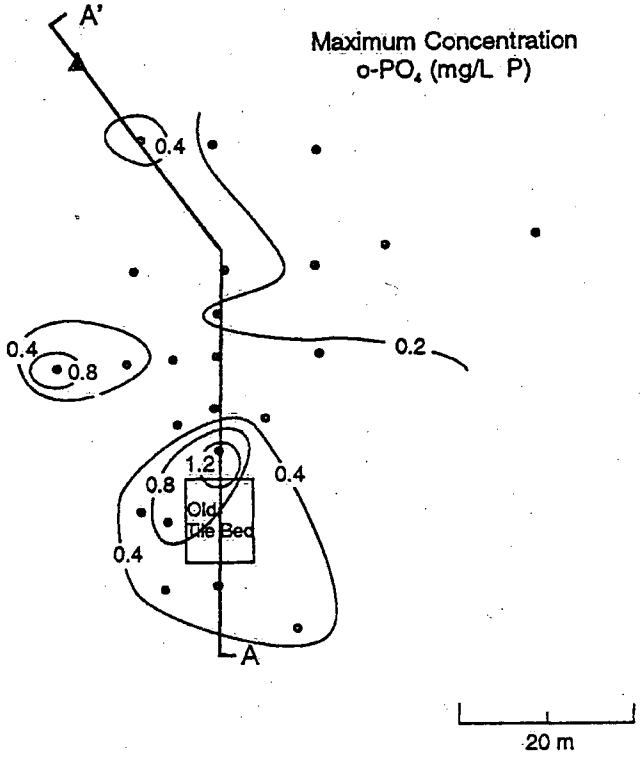
Fig. 2a

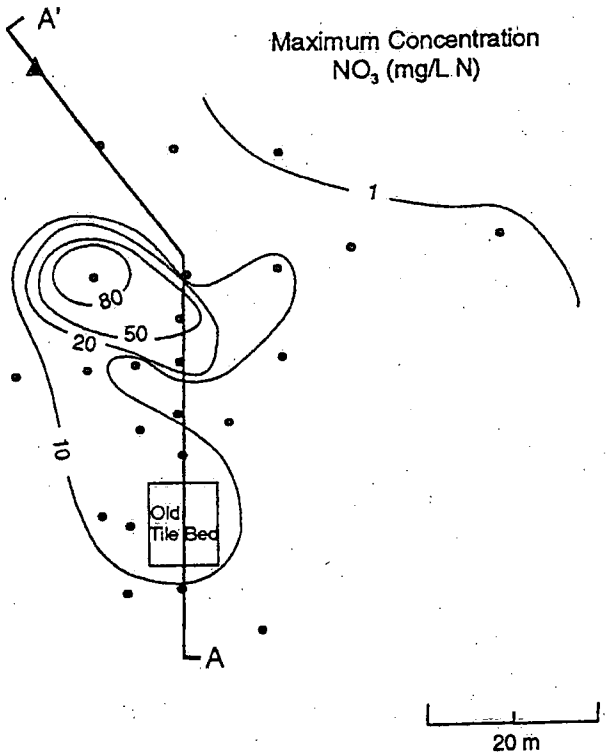


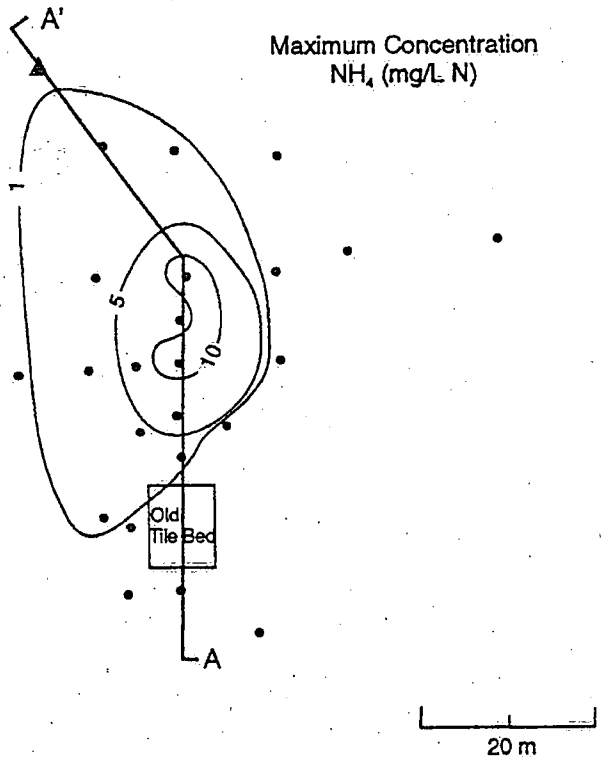
P Jacek

Fig 25

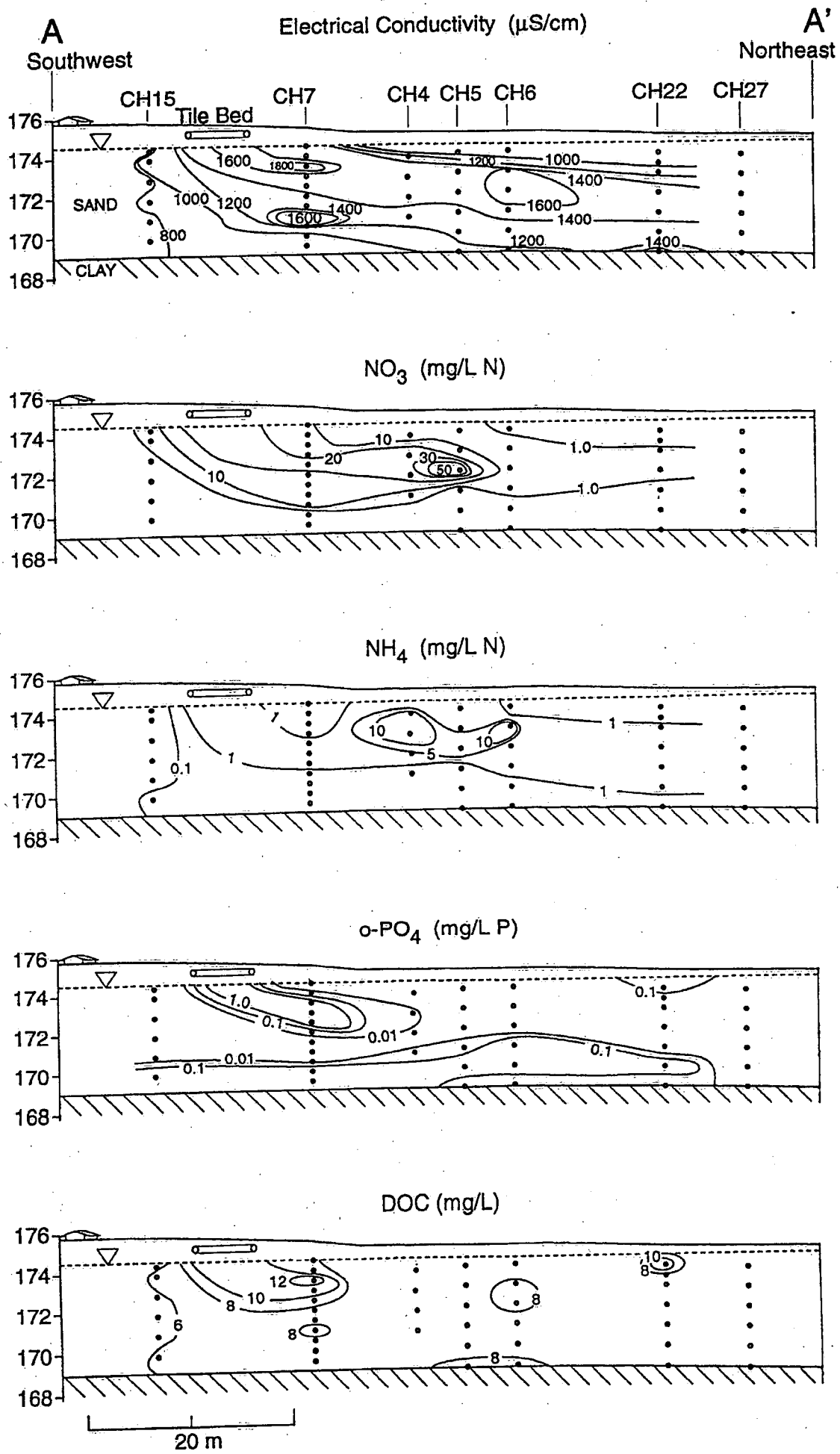

A'
Depth-Averaged
Electrical Conductivity
(µS/cm)
1200
1000
800
1200
Raised Bed
Old
Tile Bed
A
20 m


A'
Maximum Concentration
o-PO4 (mg/L P)
0.4
0.4
0.8
0.2
1.2
0.8
0.4
0.4
Old
Tile Bed
A
20 m

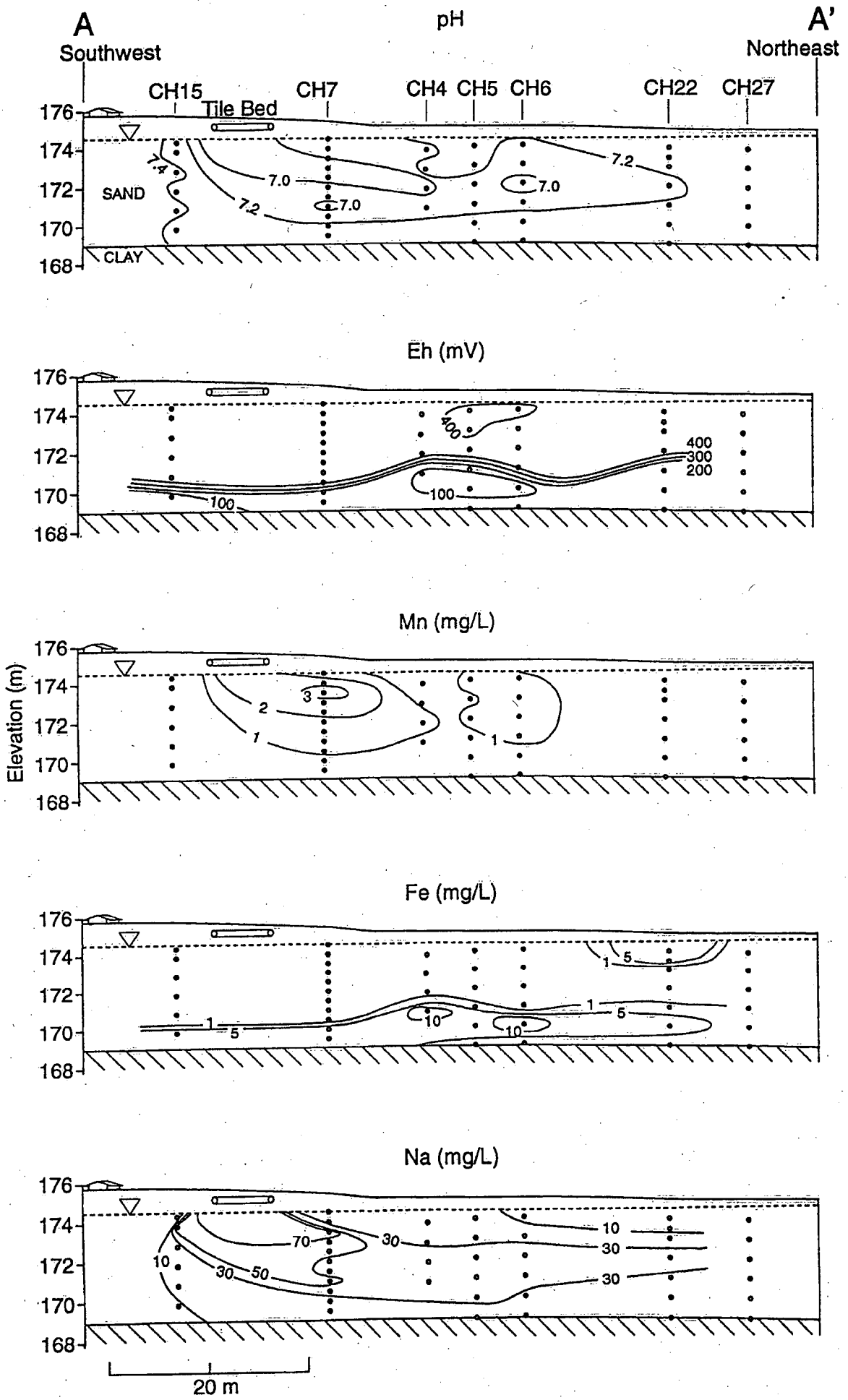

A'
Maximum Concentration
NO3 (mg/L N)
1
80
50
20
10
Old
Tile Bed
A
20 m


A'
Maximum Concentration
NH4 (mg/L N)
1
5
10
Old
Tile Bed
A
20 m

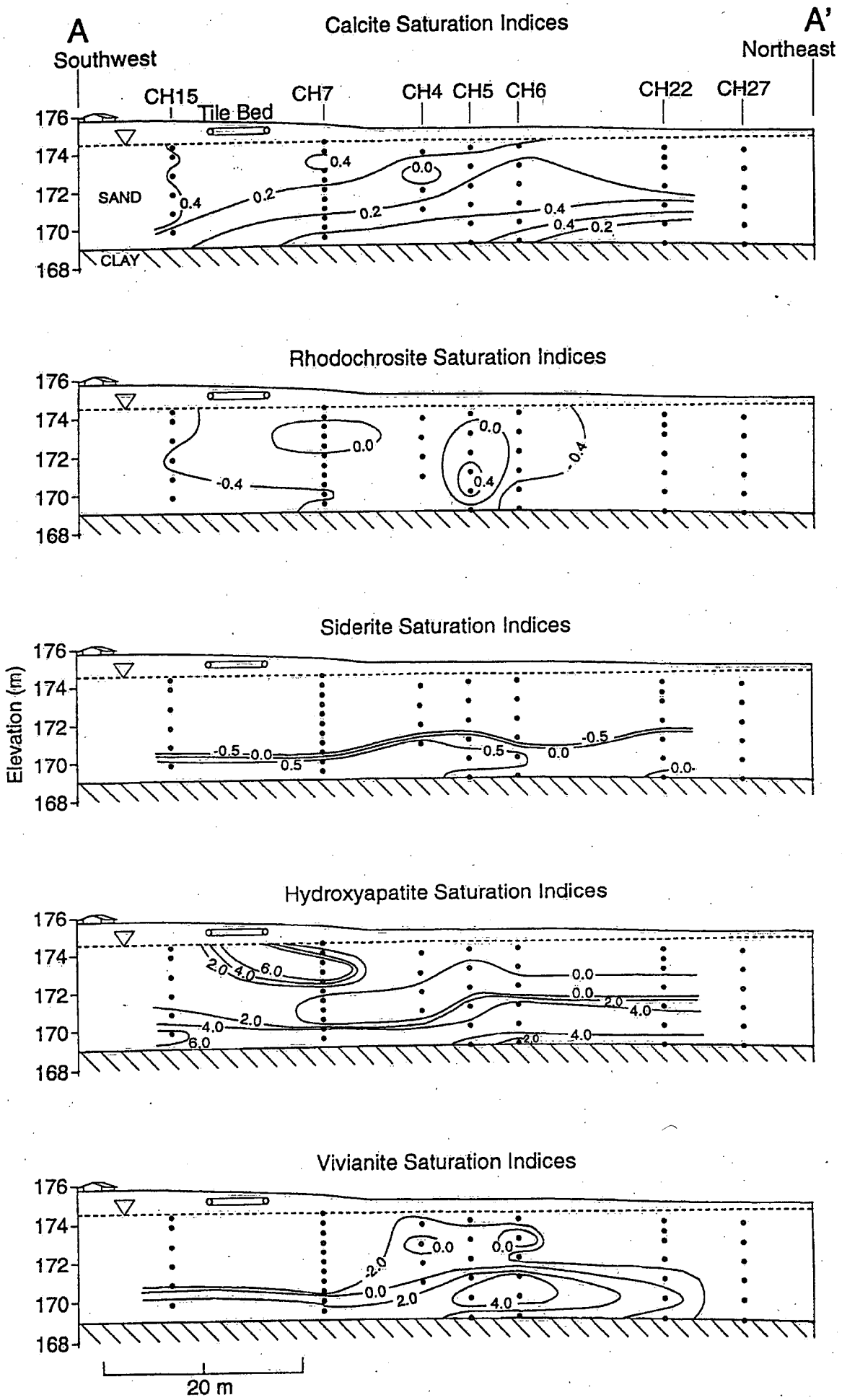
Ptacek
Fig 3


A
Southwest
Electrical Conductivity (µS/cm)
A'
Northeast
CH15
Tile Bed
CH7
CH4
CH5
CH6
CH22
CH27
176
174
172
170
168
SAND
CLAY
1600
1800
1200
1000
1400
1600
1000
1200
1400
1600
1400
800
1200
1400
NO3 (mg/L N)
10
20
30
50
1.0
10
1.0
NH4 (mg/L N)
1
10
10
5
1
0.1
1
1
o-PO4 (mg/L P)
1.0
0.1
0.01
0.1
0.01
0.1
0.1
DOC (mg/L)
12
10
8
6
8
8
10
8
8
20 m

Ptacek
Fig 4


A
Southwest
pH
A'
Northeast
CH15
Tile Bed
CH7
CH4
CH5
CH6
CH22
CH27
176
174
172
170
168
SAND
CLAY
7.4
7.0
7.2
7.0
7.0
7.2
Eh (mV)
400
100
100
400
300
200
Mn (mg/L)
Elevation (m)
3
2
1
1
Fe (mg/L)
1
5
10
10
1
5
1
5
Na (mg/L)
70
30
50
10
30
10
30
30
20 m

Ptacek
Fig 5


A
Southwest
Calcite Saturation Indices
A'
Northeast
CH15
Tile Bed
CH7
CH4
CH5
CH6
CH22
CH27
176
174
172
170
168
SAND
CLAY
0.4
0.0
0.2
0.4
0.2
0.4
0.4
0.2
Rhodochrosite Saturation Indices
0.0
0.0
0.4
-0.4
0.4
Siderite Saturation Indices
Elevation (m)
-0.5
0.0
0.5
0.5
0.0
-0.5
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PRINTED IN CANADA
IMPRIMÉ AU CANADA
ON RECYCLED PAPER
SUR DU PAPIER RECYCLÉ

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