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Canada

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PHOSPHOROUS CHARACTERIZATION IN SEDIMENTS IMPACTED BY SEPTIC EFFLUENT AT FOUR SITES IN CENTRAL CANADA

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MANAGEMENT PERSPECTIVE

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EC Priority/Issue:	This work was conducted at four septic system sites in Ontario to assess the potential of nutrient release into groundwater and eventually into surface water bodies. The work was funded by an industrial research grant awarded by NSERC, and by the GL2000 program. It supports the ESD issue "Conserving Canada's Ecosystems" (nutrients), and the business plan deliverable Thrust #1 under Conserving Canada's Ecosystems (nutrient loading). 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:	This paper summarizes a geochemical study conducted to assess the processes leading to the attenuation of phosphate below septic systems. At the sites studied there was a removal of between 25 and 99% of phosphate contained in wastewater prior to its recharge to the groundwater zone. Recharge of the remaining phosphorous to the groundwater zone leads to the development of plumes of phosphate-rich groundwater which have the potential to discharge to surface water bodies. These plumes, however, contain lower concentrations of phosphorous than would occur in the absence of the strong attenuation observed in the upper unsaturated zone.
Next Steps:	Evaluate phosphorous removal processes at additional septic system sites to develop a conceptual model applicable to a broader set of conditions.

ABSTRACT

Characterization of phosphorous (P) enriched solids was undertaken in the sediments below four mature septic system infiltration beds, where previous monitoring of water table phosphate (PO_4) concentrations had indicated that substantial retention of P was occurring in the vadose zone. At each site, zones of P enrichment were identified by acid extraction of the sediments. Acid extractable sediment P concentrations were found to be 2-5 times higher than background values, within narrow discrete zones generally 10-30 cm in thickness, located within one meter of the infiltration pipes. Back scattered electron images of the P enriched zones indicated that the P solids occurred as distinct authigenic grains (up to 300 µm diameter) and as grain coatings. Microprobe analyses indicated predominantly Fe-P at the calcareous sites (Cambridge and Langton) and Al-Fe-P at the non-calcareous sites (Muskoka and Harp Lake). Porewater analyses indicated that the zones of P accumulation were closely associated with zones of redox change characterized by the conversion of effluent NH_4^+ to NO_3^-. The data suggests that a substantial amount of the septic derived P is being attenuated by mineral precipitation reactions that occur rapidly after the effluent encounters subsurface sediments. Reductive dissolution of ferric (oxy)hydroxide minerals as a consequence of reducing environments near the infiltration pipes, the release of Fe^{2+} in solution and subsequent conversion of Fe^{2+} to Fe^{3+} may promote the precipitation of ferric or ferrosoferric PO_4 minerals. In sediments with limited buffering capacity (calcite poor), the decrease in pH resulting from effluent oxidation may cause Al (oxy)hydroxide dissolution and subsequent precipitation of Al-P rich phases. These precipitation reactions appear to have the capacity to immobilize a substantial amount of septic derived P (25-99% at these sites) for a considerable period of time.

INTRODUCTION

Recognition that phosphorus (P) is generally the limiting nutrient for algal growth in many aquatic ecosystems (e.g. Dillon and Rigler, 1974; Schindler, 1977) has focused attention on P loading from septic systems in cases where these systems are located close to sensitive surface water bodies. It has long been recognized that phosphate (PO_4) has reduced mobility in soil systems due to sorption onto positively charged mineral surfaces (Parfitt et al., 1978; Rajan, 1975; Stumm and Morgan, 1981; Syers and Iskandar, 1981; Goldberg and Sposito, 1985). Moreover, PO_4 has the ability to combine with a variety of metal cations, particularly Ca, Fe, Al and Mn, to form a number of sparingly soluble secondary PO_4 minerals (Nriagu and Dell, 1974; Stumm and Morgan, 1981; Boyle and Lindsay, 1986). However, in some cases, regulators have preferred to adopt a conservative approach and assume that all P loaded to septic systems will eventually migrate downgradient and impact adjacent surface water bodies (e.g. Province of Ontario; Revised Regulations, Ontario, 1990). Such a conservative approach recognizes the often limited setback distance (15m) of septic systems from lake shorelines and their generally long periods of usage (decades) which raises the likelihood that sediment sorption capacity will eventually be exceeded along the potentially short flow path between the infiltration bed and the lake shore. Indeed, researchers have identified PO_4 zones in a number of mature septic system groundwater plumes in excess of the normal 15m setback distance (Walter et al., 1995; Harman et al. 1996; Robertson et al., 1997). In these zones, PO_4 concentrations (0.5-5 mg/L) can be up to two orders of magnitude higher than the P concentrations considered capable of stimulating algal growth (Schindler, 1977). However, in a review of PO_4 behaviour at 10 highly monitored septic system sites in central Canada, Robertson et al. (1997) noted that PO_4 concentrations reaching the water table below the infiltration beds were consistently lower than effluent concentrations and remained low during long term monitoring. This evidence suggests that a significant amount of the sewage P is being immobilized in the vadose zone sediments.

This study was undertaken to provide a more detailed assessment of the vadose zone P immobilization. It involves further field investigations at four of the sites described by Robertson et al.

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(1997). Two of the sites are located on calcareous sands (Cambridge and Langton) and two on non-calcareous sands (Muskoka and Harp Lake). Previous monitoring at these sites had indicated that approximately 25-99% of the P mass was retained in the vadose zone even after long periods of sewage loading (e.g. 44 years at Langton).

Objectives of this study were threefold: 1) to establish if identifiable zones of P enrichment were present in the vadose zones at these sites, 2) determine if the forms and composition of the attenuated P were indicative of mineral precipitation based reactions and 3) to establish the geochemical conditions controlling the accumulation of P.

The investigation was undertaken by first determining P distribution in vadose zone sediments retrieved from below the infiltration beds. When zones of P enrichment were identified, electron imaging and microprobe compositional analyses of the P solids were undertaken to establish the morphology and chemical composition of the solids. In addition, porewater samples were retrieved in order to enable characterization of the geochemical conditions in the zones of P accumulation.

STUDY SITES

All of the study sites are conventional gravity fed septic systems located in the Province of Ontario, Canada. Three (Cambridge, Langton and Muskoka) are located on unconfined sandy aquifers in which well defined sewage plumes have developed (Fig. 1). The plumes have been described in detail in previous publications. The fourth site (Harp Lake) is located on thin soil in the Precambrian Shield terrain in central Ontario "Cottage Country". Although the groundwater zone here has not been investigated in detail, due to monitoring difficulties, the site is included in this study because it represents a site typical of many lake shore environments where the thin soils make P migration from septic systems

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of great concern. The field sites were selected to represent a variety of calcareous and non-calcareous sediment types.

The Cambridge septic system has serviced a family of four since 1977 and is located on a fine to medium grained homogeneous calcareous sand. The water table lies 2 m below ground surface. A distinct PO_4 zone exists in the sewage plume. The PO_4 zone extends 20 m downgradient from the tile bed (Fig. 1., Robertson, 1995; Wilhelm et al., 1996). Long term monitoring between 1987 and 1994 established that PO_4 concentrations in the shallow water table zone below the tile bed were consistent, but remained about 25% lower than the effluent concentrations (4.6 mg/L in the groundwater versus 6.3 mg/L as P in the effluent; Robertson, 1995).

The Langton septic system serviced a school with about 200 pupils for a 44 year period prior to decommissioning in 1994. The tile bed is located on fine to medium grained calcareous sand. The water table is located at 3 m depth. Although the aquifer is calcareous at this site (28 wt% carbonate content) extensive leaching of carbonate minerals has occurred to about 2 m depth (Harman et al., 1996). A distinct PO_4 zone is present in the sewage plume and extends approximately 70 m downgradient from the tile field (Fig. 1; Harman et al., 1996). Monitoring during 1991-1994 established that PO_4 concentrations in the shallow water table zone below the tile bed remained constant at values averaging 85% lower than effluent concentrations (1.2 mg/L in the groundwater versus 8.0 mg/L P in the effluent, Robertson, 1995) even though the tile bed had been used for a long time.

The Muskoka septic system is located 20 m from a river shoreline and has serviced a two person household since 1987. The aquifer consists of a fine to coarse sand and the water table varies seasonally from 2-3 m depth. Concentration of PO_4 in the effluent averages 9.7 mg/L (Robertson et al., 1997). Currently, no distinct PO_4 plume exists in the groundwater zone, however, recent sampling has consistently shown slightly above background PO_4 levels (0.02 - 0.1 mg/L P) at several of the shallowest

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monitoring points located in the seasonal high water table zone immediately below the infiltration bed (Fig. 1; Wilhelm et al.,1996; Robertson et al., 1997).

The Harp Lake septic system is located 20 m from a lake shoreline and has serviced a seasonal use residence of an average of four persons since 1968 (Wood, 1993). Effluent is discharged into a layer of glacial till overburden, generally <1 m thick, consisting of heterogeneous silty to clean non-calcareous sand. Effluent PO_4-P concentrations average 7.0 mg/L (Wood, 1993).

METHODS OF INVESTIGATION

In 1994 continuous, undisturbed sediment cores from below the infiltration beds were collected in 5.1cm diameter aluminum tubes advanced to 0.8-2.3 m depth using a portable percussion hammer. Three cores were extracted at each of the Cambridge (UG33, UG70, UG71), Langton (LAM300, LAM310, LAM320) and Muskoka sites (MM400, MM410, MM420) and two from the Harp site (HLC, HSC). After collection, cores were split in two and stored in the dark at room temperature. Core halves were then subsampled at 5 cm intervals (2 cm for core HLC) and oven dried overnight at 50°C. Samples were kept in sealed containers prior to analyses.

Acid extractable P concentrations in the sediment were determined by igniting 0.5 g of dry sediment for 2 hours at 550°C to combust all organic matter. Acid (50 mL of 1 N HCl) was added and the sample agitated for 16 hours on an end-over-end shaker. Samples were subsequently centrifuged at 2500 rpm for 15 minutes. Extracts of the supernatant solution were analyzed for P content colorimetrically using the molybdenum blue method of Harwood et al., (1969). Mayer (1991) demonstrated that sediment P concentrations determined using this method agreed to within 5% of values determined by other methods (e.g. perchloric acid leach), and may subsequently be referred to as the total sediment P concentration. Repeat samples were analyzed on separate days to assess method precision and were found to agree within 5 - 10%.

Based on the measured total P concentrations, one core from each site was selected for more detailed characterization. Cores selected were: UG33, Cambridge; LAM300, Langton; MM410, Muskoka; and HLC, Harp Lake.

Total organic carbon content of the detailed cores was determined at the University of Waterloo by first pre-treating the sediment samples in warm HCl (50% v/v) to eliminate inorganic carbon and then heating to 800°C to provide rapid and complete combustion of the organic carbon in the sample. The amount of CO_2 evolved during combustion was then measured using a Beckman non-dispersive infrared analyzer to determine the amount of organic carbon present (Churcher and Dickhout, 1987).

Grain size analyses were completed using a Sedigraph analyzer at the Aquatic Ecosystem Restoration Branch of the National Water Research Institute, Burlington, Ontario. Sediment carbonate content was determined by quantifying the evolution of CO_2 upon sample acidification, using the Chittick apparatus (Dreimanis, 1962).

Determinations of soil paste pH values were made using the method of Welcher (1962) by allowing 5 g of sediment to equilibrate with 5 mL of distilled water while stirring continuously for 10 minutes. A combination pH electrode (Ag/AgCl), calibrated against buffers of pH 4 and 7 was immersed in the slurry and pH was recorded after a steady value was obtained, usually within 1 to 2 minutes.

To enable physical and chemical characterization of the P rich solids, core subsamples concentrated in P were analyzed using an electron microprobe. Back Scattered Electron (BSE) images and quantitative Wavelength Dispersive Spectroscopy (WDS) combined with quantitative and semi-quantitative Electron Dispersive Spectroscopy (EDS) detection systems were used to obtain elemental concentrations of the P solids. Analyses were performed using a Joel JXA-800 Superprobe at the University of Western Ontario. The samples were prepared in an epoxy matrix and were analyzed using a

15 Kv, 50 nanoamp electron beam. Samples were randomly scanned to locate P-rich solids which were observed to occur as both discrete grains and grain coatings. Several of these were then probed within each sample to determine average elemental concentrations. Occasionally, targets analyzed were smaller than the diameter required for quantitative microprobe analysis (3-5 μm) and thus may sample other minerals surrounding the target areas. In these cases analyses were deemed qualitative. Qualitative analyses use internal instrument standards rather than calibration standards and as a result total elemental concentrations are normalized to 100 wt%. Thus, the qualitative analyses may overestimate the absolute amount of elements present. However, relative elemental proportions are considered to be accurately represented due to consistency of two or more analyses of the same samples.

Samples of vadose zone porewater at the Cambridge, Langton and Muskoka sites were collected in the spring of 1995. New 7.5 cm diameter sediment cores were obtained at locations within 1-2 m of the original cores and sectioned into 40-50 cm long intervals. Porewater samples were then obtained by displacing core porewater with distilled water spiked with a tracer (NaBr). Displaced porewater was filtered (0.45 μm cellulose acetate) and analyzed for pH and alkalinity within 10 minutes of collection. The pH was measured using a combination Ag/AgCl electrode calibrated against the buffers of 4 and 7. Alkalinity was determined by titrating a filtered (0.45 μm) sample with 0.16 N H_2SO_4 using a HACH digital titrator.

Small volumes (30-40 mL) for laboratory major ion analyses were collected from the core sections to minimize dilution from the displacement water. All but a single sample at Cambridge and Langton had less than 1% breakthrough of the Br tracer. Assuming an average moisture content for the vadose zones sands of 15% (Shutter et al., 1994) the volumes collected represented only about 20% of the porewater contained within the core subsections. At the Muskoka site, collection of vadose zone porewater was more difficult due to the coarser grained sand and lower water content which resulted in approximately 20-40% dilution by the displacement water. Nonetheless, the Muskoka samples remained useful in establishing the basic geochemical characteristics of the *in situ* porewater, including Eh

conditions as indicated by examination of the redox pair NH^+_4/NO^-_3. Half of the porewater sample was acidified (pH<1) with ultrapure HCl for cation and PO_4 analyses while the second half was left untreated for anion analyses. Samples were analyzed for major ions (Ca, Mg, K, Na, Cl, SO_4, Br), nutrients (NH_4, NO_3, PO_4), trace metals (Cu, Mn, Fe, Al) and dissolved organic carbon (DOC) within two weeks of collection. Anion concentrations (including PO_4 and NH_4) were determined colorimetrically using infrared spectrometry; major cations and trace metals were determined using inductively coupled plasma emission spectrometry. DOC was determined using UV oxidation.

The geochemical speciation model PHREEQE (Parkhurst et al., 1990) was used to determine the degree of porewater saturation with respect to several PO_4 minerals that have been suggested as possible controls on PO_4 concentrations in aqueous environments and for which published thermodynamic data are available (e.g. hydroxyapatite, $Ca_5(PO_4)3 \cdot OH$; strengite, $FePO_4 \cdot 2H_2O$; variscite, $AlPO_4 \cdot 2H_2O$; and vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O$.

RESULTS

Sediment Characteristics

The Cambridge vadose zone (core UG33) is comprised of relatively homogeneous fine to medium grained sand (average median d50 ~0.4 mm; Fig. 2). Organic carbon content of the sediment is significantly higher in the 30 cm interval immediately below the infiltration pipe (0.65 wt %) compared to background values (0.06 wt%) at greater depths. Elevated solid-phase P concentrations (~1500 $\mu g/g$), up to five times higher than in underlying zones, occur in a narrow depth (~30 cm) interval, located immediately below the tile bed infiltration pipes. Cores UG70 and UG71 exhibit less pronounced P enrichment, however P concentrations of up to 783 $\mu g/g$ (twice background) are observed in core UG70 at the same depth interval (Fig. 2). Thus, the zone of P enrichment is variable under the tile bed and may be dependent on distance from the infiltration pipe perforations. The pH of the sediment varies from 7.0 just

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below the infiltration pipes to 8.3 at greater depths. Sediment carbonate content ranges from 20 to 37% in the unsaturated zone (Fig. 2).

The vadose zone at Langton is comprised of a medium grained homogeneous sand (average median d50 ~ 0.30 mm; Fig. 2). Organic carbon content is higher immediately below the infiltration pipe (0.12 - 0.29 wt %) compared to values at greater depths (~0.03 wt%). High total P concentrations of up to 1218 μg/g are observed within a 25 cm interval immediately below the infiltration pipes in core LAM300. These values are approximately three times higher than in overlying and underlying zones (Fig. 2). Core LAM310 retrieved 2 m away from core LAM300, has similarly high total P concentrations (up to 1837 μg/g) in the same depth interval, whereas the third core (LAM320) has no zones of P enrichment. The sands are generally depleted in carbonate minerals (< 1 wt%, $CaCO_3$ equiv.). However, carbonate contents of 4-7 wt% ($CaCo_3$ equiv.) are observed where limestone gravel is installed as part of the tile bed. Soil pH values range from 7.3 above the tile lines to values as low as 4.3 at greater depths (Fig. 2).

The Muskoka septic system is located on poorly sorted coarse sand (average median d50 ~ 0.7 mm) overlying a finer sand unit (d50 ~ 0.15 mm) at 1.38 m depth (Fig. 2). Average organic carbon content in the vadose zone sediment is 0.04 wt%. At the tile line depth of 0.6 - 0.8 m, total P concentrations in core MM410 increase slightly to about 750 μg/g compared to average background values of approximately 500 μg/g. Highest total P concentrations (up to 1180 μg/g) are observed in the 15 cm depth interval occurring at, and above, the interface between the overlying coarse and underlying fine sand layers. These concentrations are more than twice background values. In core MM420, located 2 m from core MM410, elevated total P concentrations (up to 918 μg/g) are observed near the tile line depth (0.6 - 0.7 m; Fig. 2). The vadose zone sediments at Muskoka are non-calcareous (< 1 wt%, $CaCO_3$ equiv.) and soil pH values are acidic (pH 4.9 - 6.4).

The sediment at Harp Lake consists of poorly sorted gravely sand (average median d50 ~ 0.5 mm) to 0.57 m depth (0.20 m below the tile lines) in core HLC. At greater depths a poorly sorted silty

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fine grained (average median d50 ~ 0.05 mm) sand is present. The organic carbon content of the sediments is relatively high (0.14 - 0.37 wt%) with the highest value (0.37 wt%) occurring in the finer sediment. The highest total P concentration (2186 μg/g), approximately four times higher than background concentrations, occurs in the fine sand material (0.57 to 0.66 m depth) very close to the stratigraphic contact. However, in a second core (HSC), high total P concentrations (up to 1250 μg/g) occur within a narrow horizon (5 cm) directly below the tile lines within the coarse sand unit (Fig. 2). Background total P concentrations average 500-600 μg/g at this site. The sediments are non-calcareous (<1wt%, $CaCo_3$ equiv.) and soil pH values are acidic (pH 3.4 to 4.1, Fig. 2).

Morphology and Geochemistry of Phosphorous Solids

BSE images combined with microprobe analyses indicate that distinct solid phases rich in P are present at all of the sites (Fig. 3 and 4, table 1). The P-rich solids, occur either as fibrous and irregular coatings, often of substantial size (tens of microns), surrounding other sediment grains or as discrete P-rich grains either unattached or extending outward from other grains. The discrete grains are also fibrous or have irregular boundaries and are tens to hundreds of microns in diameter. Microprobe analyses indicate that at all the sites P-coatings are not associated with any particular primary mineral and form on quartz, plagioclase and K-feldspar grains with equal frequency. Background sediments also contain grain coatings of similar morphology, however, these have significantly lower P contents.

The total elemental percentages of the P-solids are relatively high at Cambridge and Langton (75-80 wt%) but are somewhat lower at Muskoka and Harp Lake (average of 65 and 30 wt% respectively). Possible explanations for the missing P mass are: 1) the solids contain water or hydroxide components, 2) the solids are thin or fragile such that the electron beam passes through the P-solids and contacts the epoxy resin matrix material, or 3) the P-solids are associated with organic matter that cannot be distinguished using the microprobe. The results may reflect a combination of these factors.

A) Cambridge

The P-grains observed at the Cambridge site occur as growths extending outward from other sediment grains or as radial aggregates and are typical of low temperature precipitation (Klein and Hurlbut, 1985). The P-grains have an average P content of 14 wt% and Fe is the dominant cation (31 wt%). Minor concentrations of Ca (1.9 wt%), Mn (0.6 wt%) and Al (0.1 wt%) are also present (Fig. 3, Table 1). Elemental analyses of six separate P-grains vary little with standard deviations of <0.7 wt% (Table 1). Average Fe:P cation proportion for the P-grains is 1.2:1. However, Fe may exchange with other cations such as Mg, Mn or Ca causing impurities in P-precipitates (Moore, 1970). When the amounts of Mn, Mg and Ca are included in the ratio, a cation (Fe, Ca, Mg, Mn):P atomic ratio of 1.5:1 is obtained. Only qualitative elemental analyses were obtained on the P-coatings because of their smaller size. The coatings contain Si, Fe, Al, Ca and P (in order of decreasing abundance). The P-coatings do not normally cover the entire host grain but rather, form in crevices within the grain, or on isolated areas of the surface.

B) Langton

Both P-grains and P-coatings are observed at the Langton site and are similar in form and composition to that of the Cambridge site (Fig. 3, Table 1). P-grains averaged 13 wt% P and contain Fe as the dominant cation (30 wt%) with lesser amounts of Ca (3.0 wt%), and Al (0.2 wt%). Elemental compositions of the grains analyzed deviate only slightly (s.d. <1.3 wt%). The average Fe:P cation proportion is 1.3:1, however the total cation (Fe, Mg, Mn, Ca):P proportion is again 1.5:1, similar to the Cambridge site. Qualitative microprobe analyses of the P coatings indicate that their average composition (in order of decreasing abundance) is Si, Fe, Al, P, Ca and Mn (Table 1). The background sediment at the Langton site (LAM310 0.35-0.450 m depth), contained no P-grains but did contain similar textured Al-, Fe-, Ca-coatings, with slightly lower P content (<3wt%). A detrital fluor-apatite grain (39 wt% Ca and 18 wt% P) is also observed in core LAM300 at 1.46 - 1.51 m depth. This grain is spherical with rounded

edges and is considered representative of detrital apatite that occurs in these sediments. It provides an example of the background, non-sewage derived P minerals that are also present at these sites.

C) Muskoka

The P-solids at Muskoka occur predominantly as coatings (Fig. 4), with an average qualitative composition (in order of decreasing abundance) of Al, Fe, Si, P, Ca and Mn (Table 1). Coatings of similar texture and composition are also observed in the background sediment (Core MM440, 0.65-0.72 m depth but are relatively depleted in P (<1.5 wt%). A fluor-apatite grain of presumed detrital origin, similar to that found at the Langton site, is also observed (Core MM420, 0.65 -0.71 m depth). Several Al-P grains are also observed at Muskoka and have average composition of 18.2 wt% Al, 6.2 wt% Si, 3.4 wt% Fe and 3.3 wt% P (standard deviation <1.1 wt%; Table 1). The variable composition and texture of these grains (similar to those of the coatings) suggest that they may be of secondary origin. However, as they are observed only in the fine sand unit below 1.37 m depth even though two-thirds of the excess sediment P mass in core MM410 is located within the 10 cm interval above the fine grained unit, it is uncertain if these are sewage-derived. Only 65 wt% of the composition of these grains can be accounted for by microprobe analyses and disintegration (i.e. creating holes in the grains) was not observed during probing. This suggests that these grains may have a substantial organic matter or water content.

D) Harp Lake

At the Harp Lake site, solids containing P (2.8 wt%) and Al (10 wt%) are abundant in the samples enriched in sediment extractable P (Table 1). These solids occur as distinct grains, averaging 10-30 μm in diameter accumulated in aggregated masses (Fig. 4). These grains tended to disintegrate under the application of the microprobe electron beam and thus the microprobe results are considered qualitative. The solids appear concentrated in several areas of the sample and exist primarily as discrete

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P-grains rather than as P-coatings. Background samples taken from a core retrieved upgradient of the tile bed also contain similar aggregated grain masses enriched in Al and Si, but these are depleted in P.

Porewater Geochemistry

Over 95% of the inorganic nitrogen in the effluent at these sites occurs as NH_4 (Robertson et al., 1997). However, at each of the sites where vadose porewater was obtained (Cambridge, Langton and Muskoka) more than 90% of the inorganic N occurs as NO_3^- at all depths sampled (Fig. 5). Thus, a redox boundary occurs within approximately 0.5 m of the infiltration pipes where NH_4^+ in the effluent is converted to NO_3^-. The porewater cores were obtained from locations up to 1 m away from the infiltration pipes and were subsectioned into intervals of 40 to 50 cm in order to obtain enough water for analyses. Thus, the precise locations of the redox boundaries were not identified. However, the zones of P accumulation in the sediments underneath the tile beds are clearly in close association with the inferred locations of the redox boundaries (Fig. 5).

The pH profiles (Fig. 5) suggest that oxidation of the effluent at Cambridge and Langton has caused the pH to decline from values between 7 and 8 to between 6 and 7. As a consequence of buffering provided by the dissolution of carbonate minerals present in the sediments, the pH then increases at greater depths (Fig. 2). In contrast, at the Muskoka site where sediments are carbonate deficient, the pH continues to decline so that very acidic conditions (pH 4.3) develop near water table.

Porewater chemistry at the Cambridge site (Fig. 6) suggests that the vadose zone porewater contains lower concentrations of PO_4 (4.0 vs 7.7 mg/L as P), DOC (1.0 vs. 40 mg/L), and NH_4^+ (<0.1 vs. 19 mg/L as N), compared to the effluent. The vadose zone porewater also has lower pH (7.0 vs. 7.9) but higher NO_3^- (15 vs. 0.2 mg/L as N) and Ca (80 vs. 33 mg/L) concentrations. These changes can be readily explained as a normal consequence of oxidation of sewage effluent in calcareous sediments. Once septic effluent enters the vadose zone the biodegredation of the organic load commences. Oxidation of the

effluent causes the conversion of NH_4^+ to NO_3^- and the decomposition of DOC. These reactions generate acidity which is buffered by the carbonate minerals in the sediments (Wilhelm et al., 1995).

Mineral saturation indices in the Cambridge vadose zone were determined using the chemical equilibrium model PHREEQE (Fig. 7). For the model simulations, pe values were estimated based on previously measured pore gas O_2 values (~18 vol. %) and on groundwater dissolved oxygen levels (3 - 5 mg/L; Wilhelm, 1991). For samples where Fe or Al concentrations were below detection limits, concentrations were determined from gibbsite and $Fe(OH)_3$ equilibrium constants at measured pH values. Saturation indices (SI) are presented for the commonly suggested secondary PO_4 minerals, hydroxyapatite, strengite and variscite that are considered stable in oxidizing environments. These minerals were assessed because published thermodynamic data is available(Table 2).

All three minerals approach or exceed SI values of zero in the zone of P enrichment and at greater depths (Fig. 7). Thus, all minerals may potentially be forming in the vadose zone at Cambridge. Hydroxyapatite maintains a high degree of supersaturation (SI = 1-6) throughout the vadose zone and into the water table zone. Assuming a pe value of zero, strengite and variscite are undersaturated within the effluent. However, both vivianite and hydroxyapatite are supersaturated (SI values: 0.71 and 5.3 respectively).

DISCUSSION

The results suggest that at all four sites mineral precipitation reactions play an important part in limiting P concentrations and that these reactions persist in narrow sediment horizons (5-30 cm) immediately below the tile drains. Phosphorus accumulation within narrow sediment zones in close proximity to the infiltration pipes appears to be a common occurrence at septic system sites. Whelan (1988) reported enriched sediment P levels within 20 cm of the infiltration pipes at two ~10 year old septic systems located on calcareous sands in Australia. Enriched P concentrations were observed to occur

within 14 cm of the infiltration pipes at a 29 year old septic system located near the Harp Lake site discussed here (Wood, 1993). Walter et al., (1995) observed enriched sediment P values within a 5 m depth interval immediately below the bottom of a sewage lagoon at a military reserve in Cape Cod, Massachusetts.

The occurrence of P solids preferentially within these depth intervals, their presence as distinct grains or as relatively thick (10-50 μm) grain coatings on non-specific host grains and their general texture, all suggest that the solids formed by precipitation reactions. Moreover, because the zones of P accumulation occur in such close proximity to the infiltration lines, the reactions occur relatively rapidly and are likely completed within a few days of the effluent entering the subsurface. For example, the zone of P accumulation at Cambridge is situated within the first 30 cm below the tile drains. Assuming a 15% moisture content for the unsaturated zone and a sewage loading rate of 1 cm/day (Shutter et al., 1994) the infiltration velocity is calculated to be approximately 7 cm/day. Thus, complete effluent oxidation likely occurs within four days.

The change in redox condition that occurs upon oxidation of the effluent appears to be the dominant process controlling the formation of the P solids. The presence of Fe solids at these sites suggests that either the increase in Fe^{2+} promotes Fe^{2+}-P precipitation or the conversion of Fe^{2+} to Fe^{3+} at the redox front promotes Fe^{3+}-P precipitation. At the sites located on non-calcareous sediments, the decline in pH that results from effluent oxidation, may cause gibbsite dissolution and subsequent precipitation of Al-P solids. For example, concentrations of Al in the Muskoka groundwater below the septic bed are high (2 to 6 mg/L) compared to the low concentrations (0.008 to 0.06 mg/L) measured at the Cambridge and Langton sites (Harman et al., 1992, Robertson et al., 1997).

Few Ca and Mn bearing P solids have been observed at these sites even though chemical equilibrium modelling suggests that the vadose zone porewaters at Cambridge are highly supersaturated with respect to hydroxyapatite and other researchers have suggested that Mn-PO_4 minerals (e.g.

MnPO$_4$·1.5 H$_2$O) are most likely to precipitate as they are the least soluble of the secondary P minerals in soil systems at near neutral pH values (Boyle and Lindsay, 1986). Indeed, previous studies conducted using surface analytical techniques provided evidence for the formation of griphite (Fe$_3$Mn$_2$(PO$_4$)$_{2.5}$(OH)$_2$) in batch tests combining natural goethite and P-rich solutions (Martin et al., 1988). Thus, the formation of these minerals may be limited at these sites, possibly due to kinetic limitations or as a consequence of some other factor such as the higher solubility of amorphous or impure phases (Jenkins et al., 1971).

The source of the Fe in the Fe-PO$_4$ solids has not been determined with certainty in this study. It may be derived partly from the wastewater, however effluent Fe concentrations (0.02 - 0.14 mg/L, this study) appear insufficient in most cases to account for the amount of P mass loss occurring in the vadose zone. Previous monitoring at the Langton site (Harman et al., 1996, Robertson et al., 1997) indicated that approximately 7 mg/L-P (0.2 mmol) was attenuated in the vadose zone whereas an average of only 0.2 mg/L-Fe (0.004 mmol) was present in the effluent. Thus a larger supply of soluble Fe is needed to account for the observed Fe concentrated in the P-solids (1.2:1 Fe:P ratio). Additional Fe is likely solubilized at these sites as a result of reductive dissolution of ferric iron minerals (i.e. Fe(OH)$_3$) present in the sediments. When reducing septic effluent enters the subsurface reducing environments likely occur near the infiltration pipes causing the reductive dissolution of Fe from the sediments which can lead to greatly enriched Fe concentrations in solution. Increases in Fe concentrations of tens of milligrams per liter or more have been observed at other reducing septic system plumes (Robertson and Blowes, 1995; Ptacek, 1997, Robertson et al., 1997).

The Fe:P cation ratios in the P grains at Cambridge and Langton average 1.2:1 and 1.3:1 respectively (Table 1). These ratios are higher than would be expected for pure ferric minerals such as strengite (Fe:P = 1:1) but are low for pure ferrous minerals such as vivianite (Fe:P = 1.5:1). When the possibility of Fe exchange with other cations (Ca, Mn, Mg) is taken into account, the cation:P ratio approaches 1.5:1, consistent with vivianite. Since the effluent at these sites are at near equilibrium with respect to vivianite (Robertson et al., 1997), it is possible that PO$_4$ may precipitate as vivianite in reducing

environments near the infiltration pipes. However, Nriagu and Dell (1974) suggest that a group of ferric and ferrosoferric secondary PO_4 minerals containing Fe in both the ferrous and ferric oxidation states; lipscombite, $Fe_3(PO_4)_2(OH)_2$; rockbridgite, $Fe_5(PO_4)_3(OH)_5$; beraunite $Fe_6(PO_4)_4(OH)5\cdot6H2O$, tinticite, $Fe(PO_4)_2(OH)3\cdot3H2O$; and cocaxonite, $Fe_4(PO_4)_3$ $(OH)3\cdot12H2O$ and which also have Fe:P ratios of about 1.5:1, are the most stable forms in oxidizing and in intermediate Eh aqueous environments such as may occur near the redox boundaries at these sites. Although it is presently uncertain if the Fe in these solids exists in the ferrous or ferric oxidation state, the close association of the P enrichment zones with the redox boundary suggests that the P-solids likely contain at least some ferric iron.

If the cations available for co-precipitation with PO_4 are derived from the sediments, then the possibility exists that P accumulation will diminish with time as the cation supply is consumed. However, Wersin et al. (1991) provide an example, using a one dimensional kinetic model, where it would require about 1000 years to remove half of the Fe^{3+} minerals (~1.5 wt% Fe_2O_3) from a 20 cm depth interval of carbonate-rich freshwater lake sediments at typical rates of reductive dissolution of Fe^{3+}. The fact that the P accumulation zone at Langton, remains confined to within 30cm of the infiltration pipes and is effective at attenuating about 85% of the P mass even after 44 years of loading, provides a powerful example of the potential longevity of this process.

CONCEPTUAL MODEL

The conceptual model presented below considers the geochemical evolution of wastewater as it migrates from the septic tank into the subsurface with emphasis on the fate of septic derived P (Fig. 8).

The raw wastewater in most septic systems is reducing and inorganic P concentrations within the effluent are high (~8 mg/L; Robertson et al., 1997) existing as a soluble phosphate ion (PO_4) in the form of the orthophosphoric acids $H_2PO_4^-$ and HPO_4^{2-} (Fig. 8). In the septic tank the wastewater approaches or

16

exceeds saturation with respect to vivianite (Robertson et al., 1997). Thus, it is possible that vivianite precipitation begins initially in the septic tank, thereby limiting P concentrations occurring in the wastewater. When the effluent enters the subsurface, much of the effluent PO_4 will normally adsorb onto positively charged mineral surfaces. Also, reducing environments in the immediate vicinity of the infiltration pipes, may cause the liberation of additional Fe^{2+} as a result of the reductive dissolution of ferric (oxy)hydroxides present in the sediment. This may promote additional precipitation of vivianite. At properly functioning septic systems, the vadose zone will become aerobic at short distances from the infiltration pipes. Subsequent oxidation of the effluent would then convert Fe^{2+} to Fe^{3+}. Concentrations of Fe in solution will decrease as a result of the precipitation of ferric (oxy)hydroxides and ferric or ferrosoferric P solids. Phosphorous solids may either form by direct precipitation from solution or alternatively they may form by adsorption of PO_4 onto newly formed ferric (oxy)hydroxides) and subsequent incorporation into the mineral structure. Continued oxidation of the effluent also generates acidity as a result of the conversion of NH_4^+ to NO_3^-. This acid would normally consume most of the alkalinity contained in the wastewater and lead to the dissolution of carbonate minerals contained in the sediments (Robertson et al., 1997). At locations where the sediments have limited buffering capacity, acidic conditions will develop. If the pH drops below about 6, increases in Al concentrations resulting from gibbsite dissolution, can then cause the precipitation of Al-phosphate solids. If pH drops below about 5, the greatly elevated Al concentrations that can result (several milligrams per liter) have the potential to limit PO_4 concentrations to very low levels (<<1 mg/L, Robertson et al., 1997). Although, chemical equilibrium modelling suggests that Ca-PO_4 solids also have the potential to precipitate at near neutral or alkaline pH values, reaction rates for the formation of Ca minerals appear to be too slow to allow the P to be retained in close proximity to the infiltration pipes, in contrast to the reactions involving Fe and Al.

The findings suggest that the physical characteristics of the sediments will affect P attenuation. For example, finer grained sediments, with high water contents, are likely to allow more widespread development of reducing conditions near the tile lines by limiting O_2 penetration, and hence will promote

increase reductive dissolution of Fe (oxy)hydroxides. Thus, the following sequence is presented, rating the ability of different sediments to immobilize P assuming that Fe and Al (oxy)hydroxides are generally abundant in most sediment types: Fine grained, non calcareous (Al+Fe-P precipitates), > coarse grained, non-calcareous (Al-P precipitates), > fine grained, calcareous (Fe-P precipitates) > coarse grained, calcareous (minor Fe-P precipitates).

The sediment type that appears most susceptible, coarse grained calcareous sand, is widespread in many areas and indeed has been shown to be prone to the development of large scale PO_4 plumes at septic system sites such as at the Langton site (Robertson et al., 1997). In contrast, sites located on fine-grained non-calcareous sediments, such as those found in the Precambrian Shield "Cottage Country" in Ontario, should have a high ability to immobilize P. However, the depth and continuity of these sediments may impart limits to P immobilization. Recognition of the ability of some native sediment types to immobilize P, presents the possibility of modifying tile bed design to achieve improved P attenuation even where the local sediments have limited attenuation capacity.

The amount of P immobilization that occurs is likely to be controlled by a number of site specific factors including the composition of the effluent, particularly Fe, NH_4^+, and alkalinity levels, the amount of reductive dissolution of iron that occurs in the subtile sediments prior to oxidation, the degree of oxidation of the effluent and the buffering capacity of the sediments. The complexity of these factors makes it difficult to predict, a priori, the degree of P attenuation that will occur at a given site. The conceptual model developed as a result of this investigation provides a framework for the examination of P attenuation in the vadose zone below septic systems. The general applicability of the model requires testing at additional septic system sites in a variety of geologic settings.

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FIGURE LIST

Figure 5   Porewater pH and oxidation state in the vadose zones at Cambridge, Langton and Muskoka. Oxidation state inferred from proportion of inorganic N (NH_4^+ + NO_3^-) occurring as NO_3^-.

Figure 6   Porewater chemistry, Cambridge site (4/95); shallowest point is septic tank effluent.

Figure 7   Phosphate mineral saturation indices at the Cambridge site calculated using PHREEQE. (chemistry from Fig. 6)

Figure 8:   Conceptual model of P attenuation in the vadose zone below septic systems.

Table 1: Composition of representative P-grains determined by microprobe analyses

Cambridge:	Grain analyses (Fig. 3)		Grain analyses (Fig. 3)	
P	14.91	14.72	13.12	12.73
Fe	31.58	31.10	28.79	28.91
Al	0.2	0.13	0.89	0.35
Ca	1.15	1.65	0.77	0.65
Mn	2.32	0.91	1.73	0.70
Si	0.36	0.12	1.43	0.48

Langton:	Grain analyses (Fig. 3)	Coating analyses (Fig. 3)	
P	12.9	11.6	14.2
Fe	30.1	9.75	11.5
Al	0.06	9.50	8.72
Ca	3.15	1.04	4.07
Mn	0.00	0.00	0.00
Si	0.08	12.6	12.5

Muskoka:	Grain analyses (Fig. 4)			Coating analyses (Fig. 4)	
P	3.30	3.34	3.42	4.63	2.83
Fe	3.75	3.99	3.05	22.1	24.5
Al	18.1	17.2	17.4	13.4	13.8
Ca	0.95	0.80	0.92	0.61	4.03
Mn	0.00	0.02	0.03	0.33	0.00
Si	6.13	5.62	5.76	11.9	12.5

Harp Lake:	Grain analyses (Fig. 4)			
P	2.95	2.82	2.21	3.36
Fe	0.59	0.68	1.84	3.27
Al	11.8	9.32	7.11	10.3
Ca	0.71	2.03	0.62	0.59
Mn	0.01	0.00	0.03	0.03
Si	0.03	0.31	0.04	0.19

Table 2: Thermodynamic data used for geochemical speciation calculations

Mineral	Disassociation Reaction	Log K_{sp}	ΔH_r kcal/mole	Reference
Hydroxyapatite	$Ca_5(PO_4)_3(OH) + 4H^+ = 4Ca^{2+} + 3HPO_4^- + H_2O$	-3.421	-36.155	PHREEQE database
Vivianite	$Fe_3(PO_4)_2 \bullet 8H_2O = 3Fe^{2+} + 2PO_4^{3-} + 8H2O$	-36.0	0.0	PHREEQE database
Strengite	$FePO_4 \bullet 2H_2O = Fe^{3+} + PO_4^{3-} + 2H_2O$	-26	-6.49	K_{sp} (Stumm and Morgan, 1981); H_r (Woods and Garrels, 1987)
Variscite	$AlPO_4 \bullet 2H_2O + 2H^+ = Al^{3+} + H_2PO_4^- + 2H_2O$	-21	-2.24	K_{sp} (Stumm and Morgan, 1981); H_r (Woods and Garrels, 1987)

Figure 1

CAMBRIDGE
year 17 (94)

TILE BED

SAND

SILT

20 m

LANGTON
year 44 (91)

Depth (m)

SAND

50 m

MUSKOKA
year 9 (95 - 96)
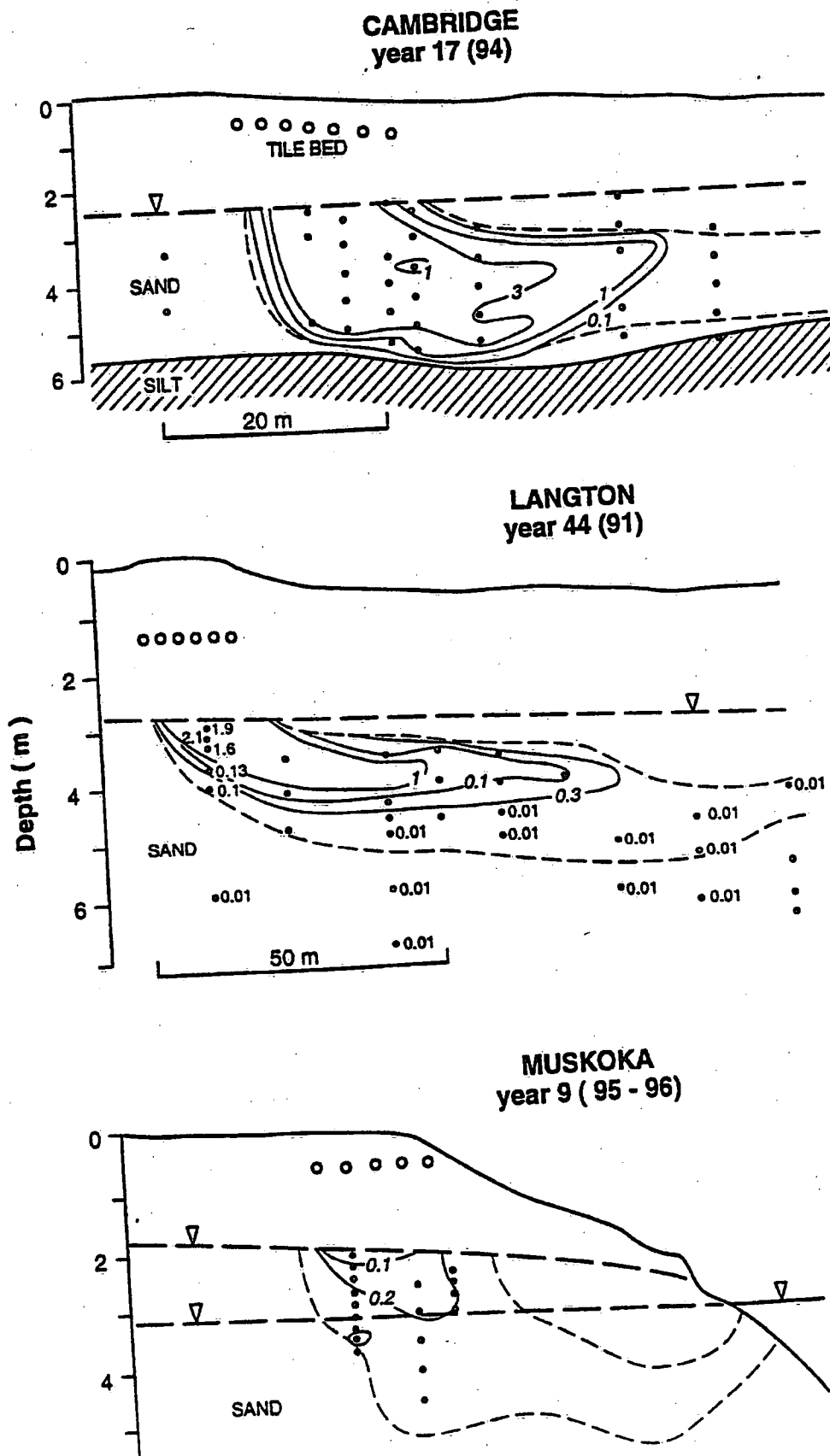
SAND

Figure 2

CALCAREOUS SITES

a) Cambridge
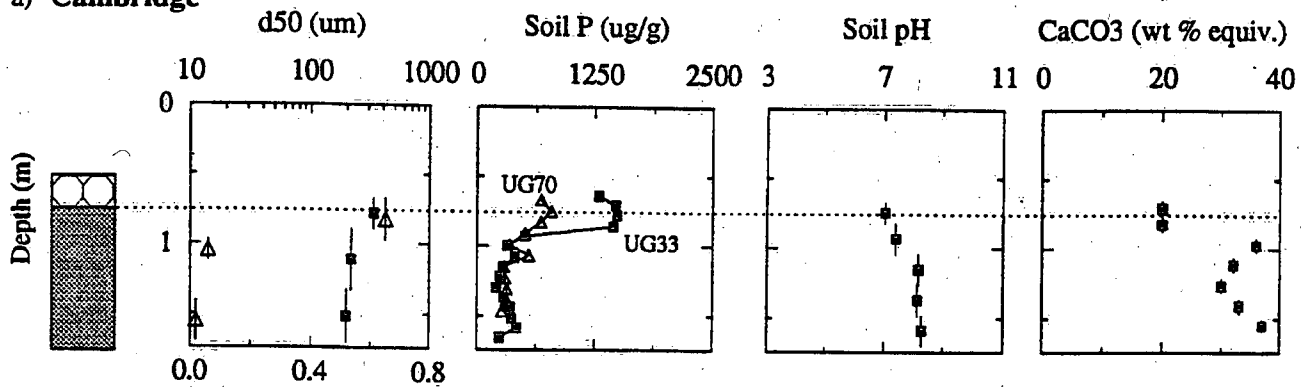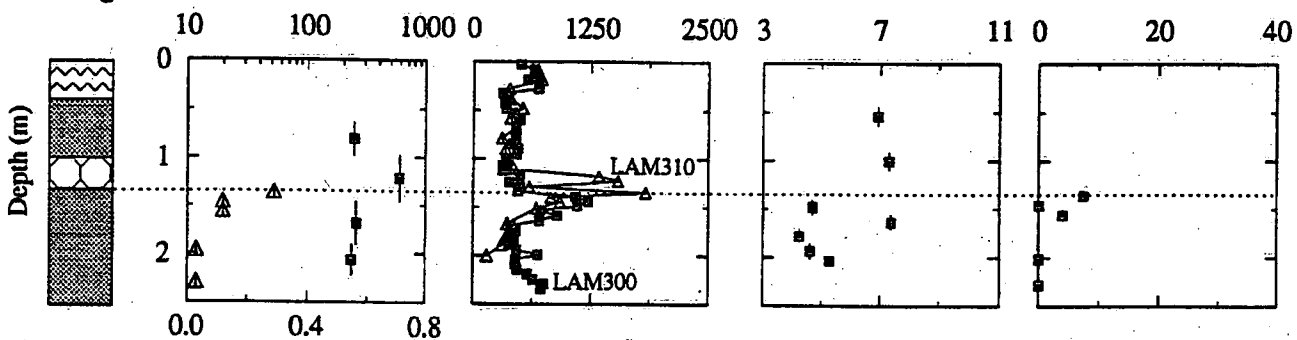
NON-CALCAREOUS SITES

c) Muskoka
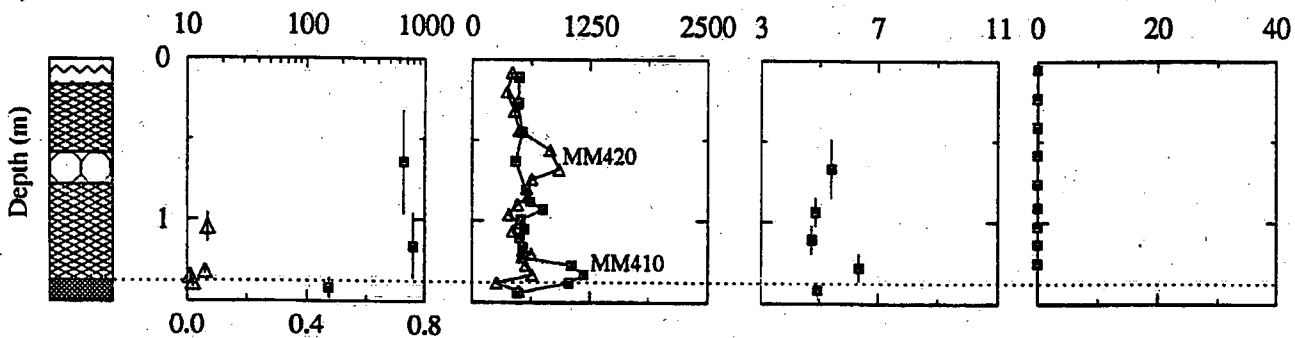
d) Harp Lake
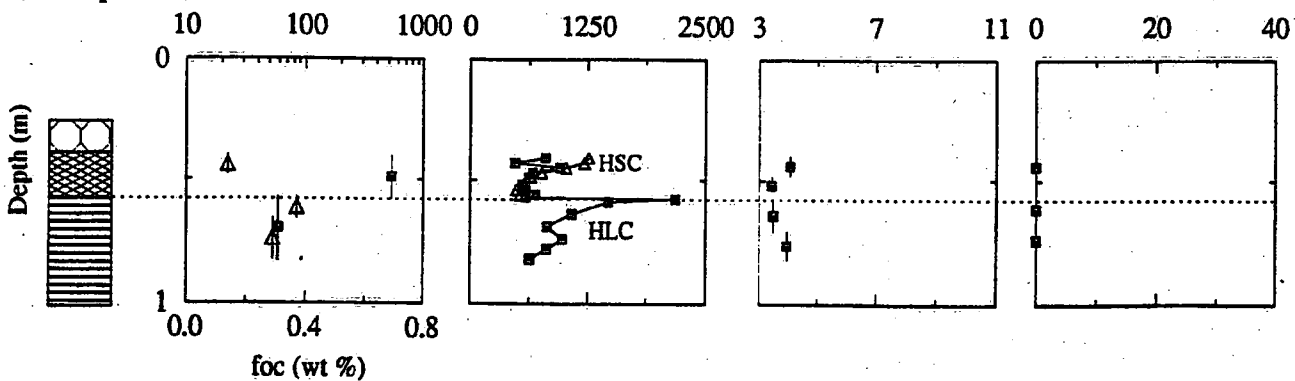
b) Langton

Legend:
Soil Zone   Tile Bed/Gravel Pack   Silty Sand   Fine/Medium Sand   Coarse Sand

Figure 3

Calcareous Sites
Cambridge

P-Grain
A) (0.8 -0.89 m depth)

P Grain
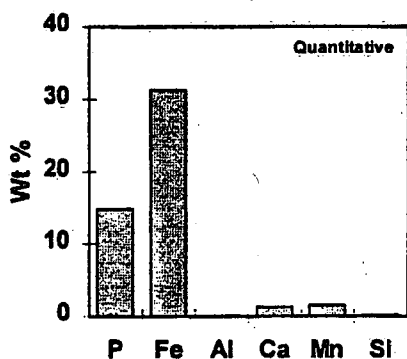
P-Grain
B) (1.03 - 1.11 m depth)
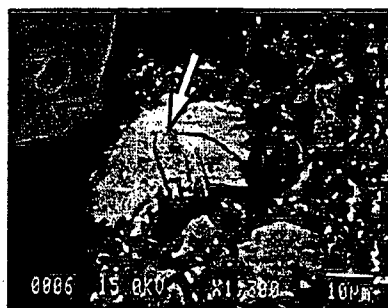
P Grain
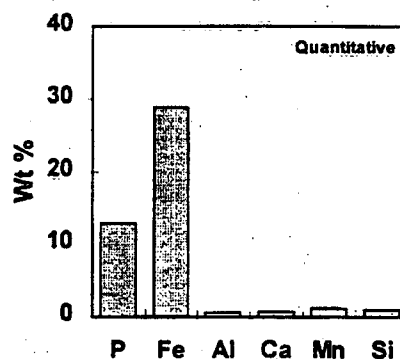
Langton

P-grain
C) (1.41-1.46 m depth)
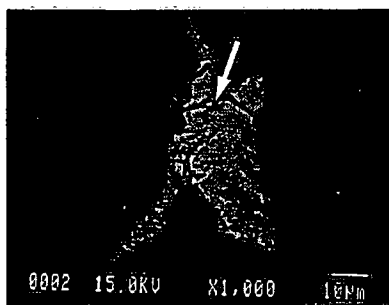
P Grain
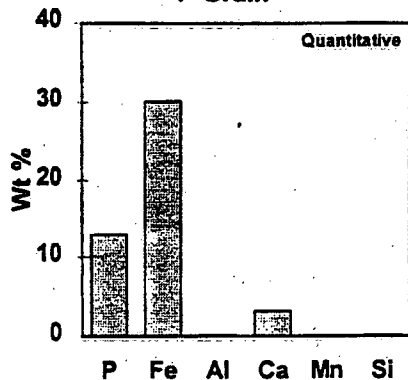
P-Coating
D) (1.41-1.46 m depth)

P Coating
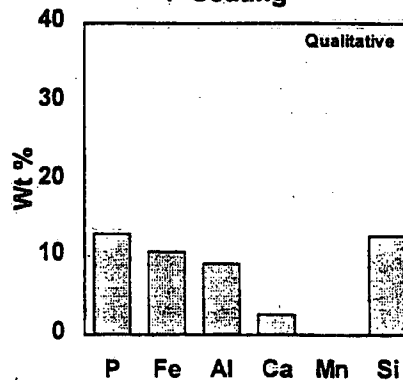
Figure 4

Non-calcareous sites

Muskoka

P-Grain

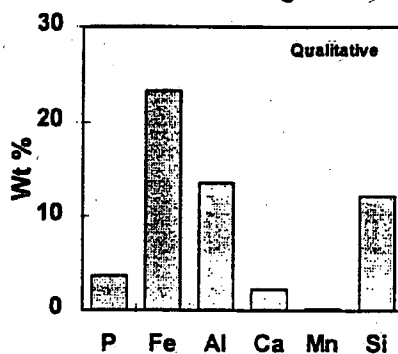**A) (1.35 - 1.41 m depth)**
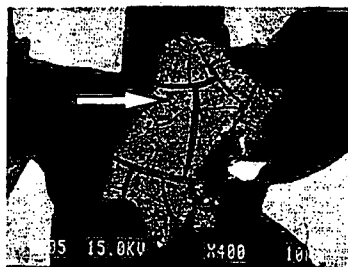
P-Coating

B) (1.25 - 1.30 m depth)
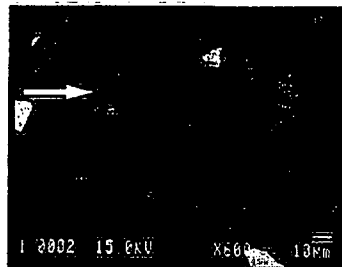
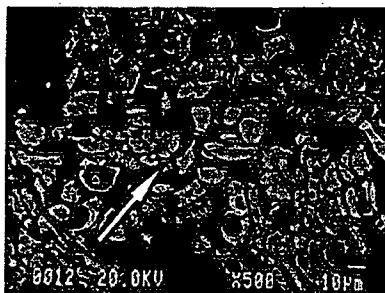**P Grain**
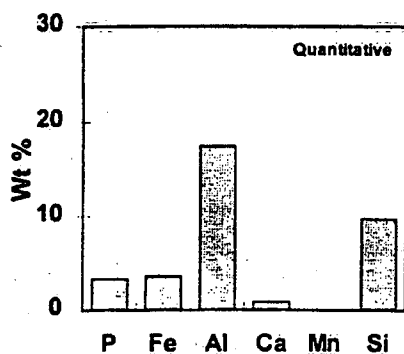
P Coating

Harp Lake

P-Grains

C) (1.25 - 1.30 m depth)

P Grain
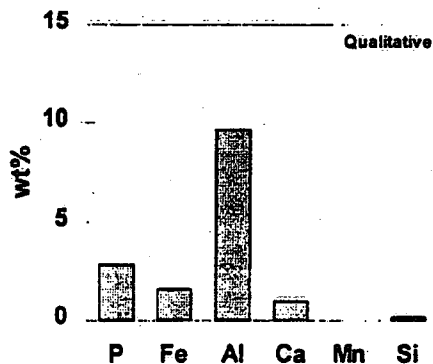
Figure 5
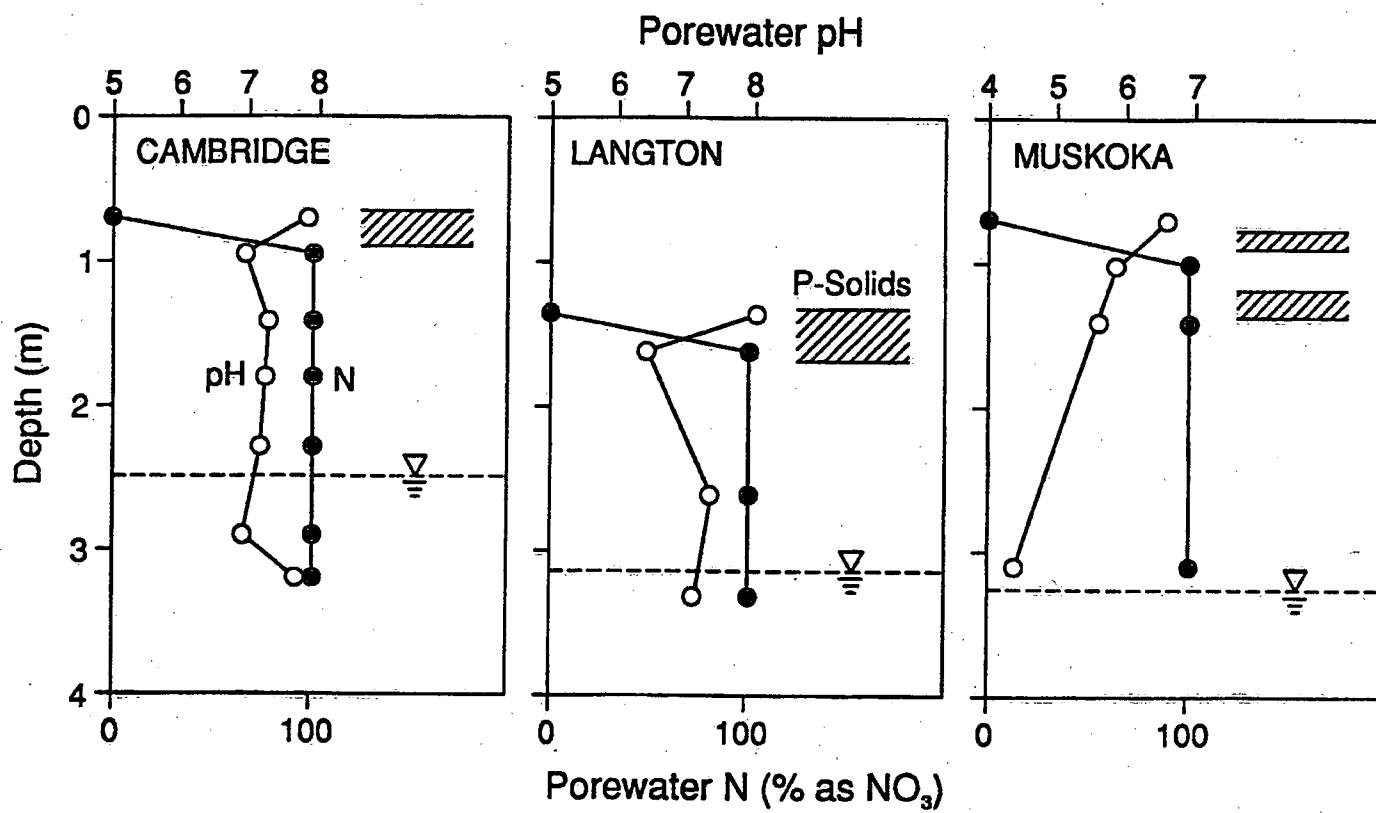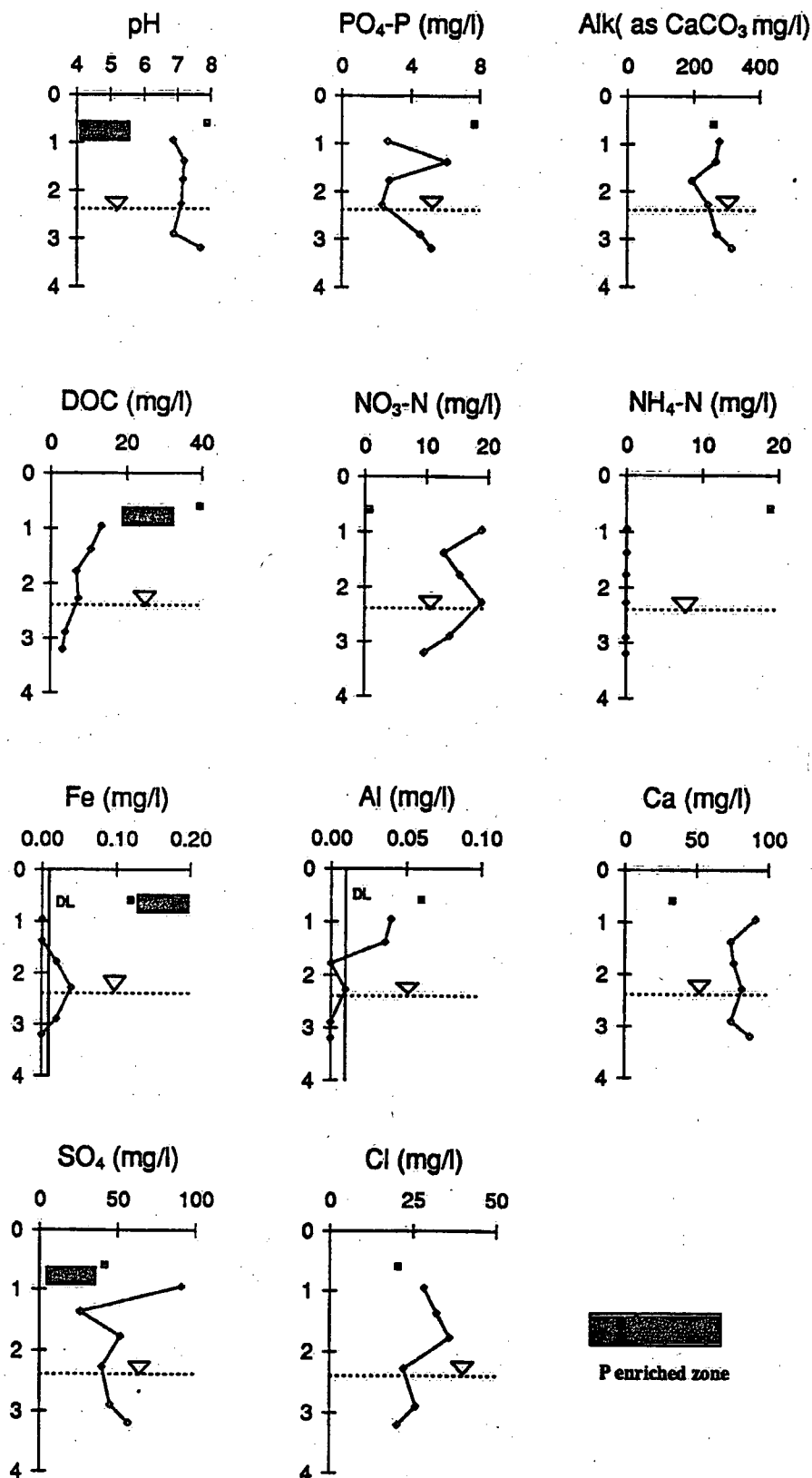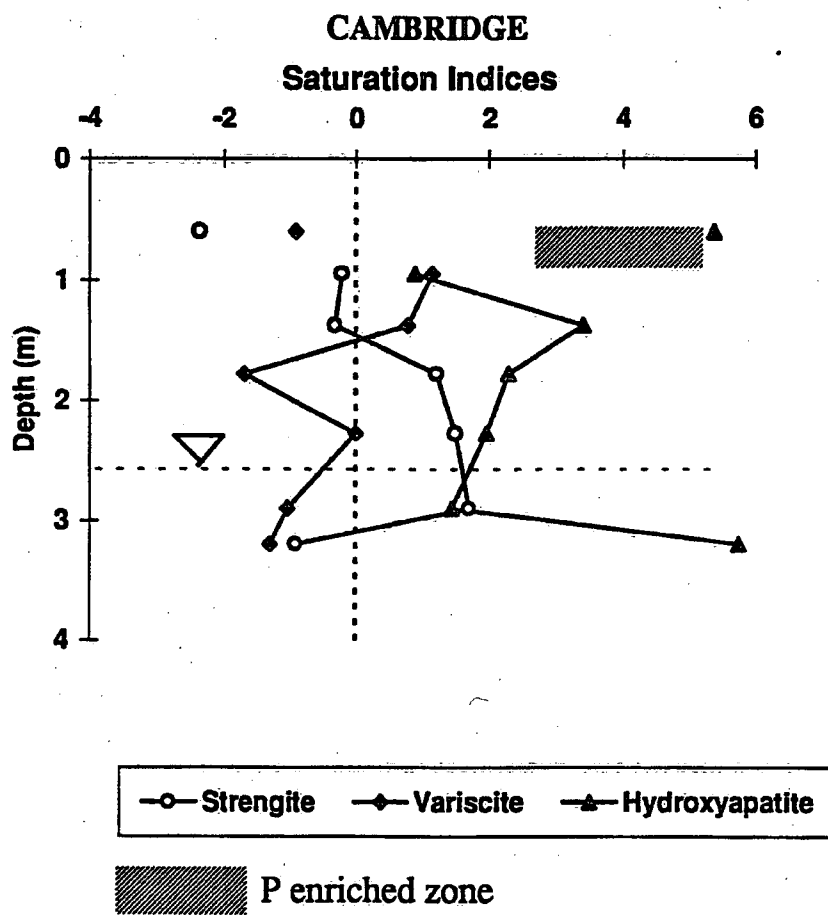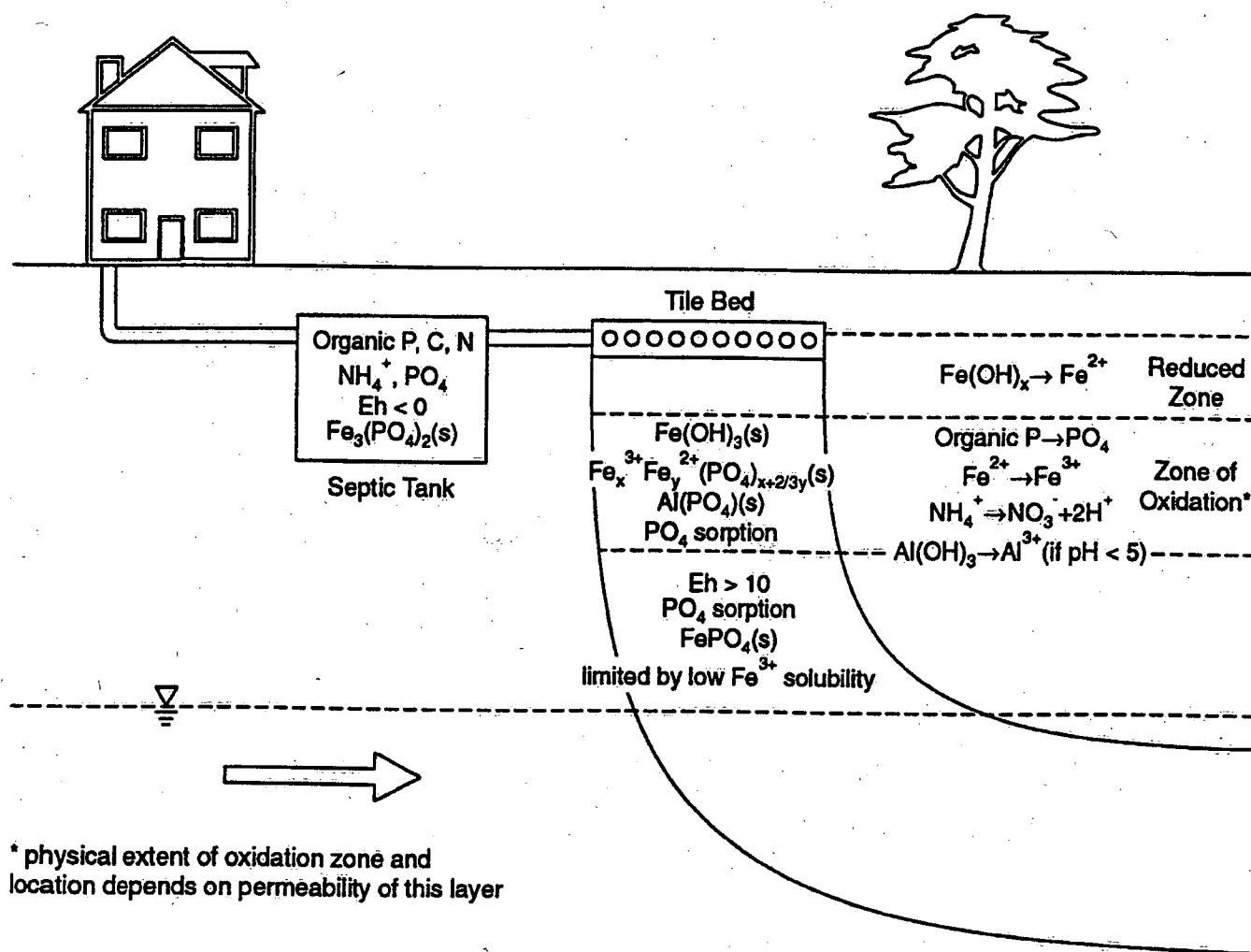
Porewater pH

CAMBRIDGE

pH N

LANGTON

P-Solids

MUSKOKA

Depth (m)

Porewater N (% as NO₃)

Figure 6

Figure 7

CAMBRIDGE

Saturation Indices

Figure 8

Tile Bed

Organic P, C, N
NH_4^+, PO_4
$Eh < 0$
$Fe_3(PO_4)_2(s)$

Septic Tank

$Fe(OH)_3(s)$
$Fe_x^{3+}Fe_y^{2+}(PO_4)_{x+2/3y}(s)$
$Al(PO_4)(s)$
PO_4 sorption

$Eh > 10$
PO_4 sorption
$FePO_4(s)$
limited by low Fe^{3+} solubility

$Fe(OH)_x \rightarrow Fe^{2+}$ Reduced Zone

Organic $P \rightarrow PO_4$
$Fe^{2+} \rightarrow Fe^{3+}$ Zone of
$NH_4^+ \Rightarrow NO_3^- + 2H^+$ Oxidation*
$Al(OH)_3 \rightarrow Al^{3+}$(if pH < 5)

* physical extent of oxidation zone and
location depends on permeability of this layer

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Environment   Environnement
Canada   Canada

Canada