

98-273

Environment Canada

Water Science and Technology Directorate

Direction générale des sciences
et de la technologie, eau

Environnement Canada

Review of Phosphate Mobility and Persistence
in Ten Septic System Plumes

By:

W. Robertson, S. Schiff, C. Ptacek

TD
226
N87
No. 98-
273

**REVIEW OF PHOSPHATE MOBILITY AND PERSISTANCE
IN TEN SEPTIC SYSTEM PLUMES**



prepared by:

W.D. Robertson¹, S.L. Schiff¹ and C.J. Ptacek²

¹University of Waterloo, Department of Earth Sciences
Waterloo, Ontario N2L 3G1

²National Water Research Institute
867 Lakeshore Road, Burlington, Ontario L7R 4A3

FOR SUBMISSION TO GROUND WATER

Fourth Draft

November, 1997

NWRI Cont. # 98-273

MANAGEMENT PERSPECTIVE

- Title:** Review of Phosphate Mobility and Persistence in Ten Septic System Plumes
- Authors:** W.D. Robertson, S.L. Schiff and C.J. Ptacek
- NWRI Publication#:** 98-273
- Citation:** Groundwater, in submittal.
- EC Priority/Issue:** This review describes the relationship between geochemical properties and phosphate mobility at 10 septic system sites in Ontario. The study was funded by the Ontario MOEE to provide a basis for evaluating the potential for phosphorous leaching from septic systems and for determining siting criteria. 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:** The paper summarizes several years of research on phosphorous mobility in groundwater. 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 has led to the development of plumes of phosphate-rich groundwater which have the potential to discharge to surface water bodies. This paper summarizes the most important geochemical parameters which need to be considered when determining phosphorous mobility in aquifer materials.
- Next Steps:** Evaluate phosphorous removal processes at additional septic system sites to develop an expanded conceptual model applicable to a broader set of conditions.

ABSTRACT

Review of phosphate distribution in ten mature highly monitored, septic system groundwater plumes migrating through diverse sediments in Central Canada, has shown that in six (primarily those on calcareous sands), large zones of enriched P concentrations (0.5 - 5 mg/L P, > 10 m in length) are present. In each case, phosphate migration velocity is highly retarded compared to the groundwater velocity (retardation factor, 20-100); however migration rates remain sufficiently fast (~1 m/a) to be of concern when considering long term operation and the normal minimum setback distance of septic systems from adjacent surface water bodies (~ 15m). Much smaller scale phosphate plumes (< 3m in length) are present at the acidic sites on non-calcareous sands and on silt and clay rich sediments.

Although distinct phosphate plumes are present at a number of these sites, in each case groundwater concentrations are lower than effluent values by amounts ranging from 23-99%. In general, observed phosphate concentrations are consistent with values expected based on the solubility constraints of the minerals vivianite in reducing zones (including the septic tank), and strengite and variscite in oxidizing zones. Strengite and variscite have the potential to limit P to very low concentrations (<0.1mg/L) under acidic conditions, consistent with field observations. However, oxidation of sewage effluent leads to acidic conditions only in non-calcareous terrain or beneath very old septic systems where calcium carbonate has been depleted. Recognition of the solubility constraints of P sequestering minerals and their sensitivity to variations in pH and Eh assists in identifying terrain that may be at risk from phosphate contamination and also leads to suggestions for modifying septic system design to achieve improved phosphate attenuation. The most sensitive terrain appears to be calcareous sands where we observe plumes with highest P concentrations (1-5 mg/L).

Overall phosphate plume migration velocities in groundwater appear to be controlled by adsorption processes, but the phosphate concentrations that are present in the plumes appear strongly controlled by mineral precipitation reactions that occur in close proximity to the infiltration pipes.

INTRODUCTION

High concentrations of phosphorus are normally found in sewage effluent (~5-10 mg/L) in contrast to much lower concentrations (~0.03 mg/L) that have been observed to stimulate algae growth in aquatic environments (Dillon and Rigler, 1974; Schindler, 1977). Thus, phosphorus is often the inorganic contaminant of greatest concern when septic systems are located close to sensitive surface water bodies. The mobility of phosphate in the subsurface remains somewhat uncertain, however, as a result of the considerable reactivity of this constituent. Phosphate is strongly adsorbed by most sediments (i.e. Parfitt et al., 1975; Rajan, 1975; Isenbeck-Schröter et al., 1993) and is capable of combining with a number of metal cations, particularly iron, aluminum, manganese and calcium to form a wide range of minerals that can be stable in low temperature aqueous environments (Nriagu and Dell, 1974; Stumm and Morgan, 1981).

Phosphate concentrations in uncontaminated groundwater are often extremely low (<0.01 mg/L, this review) as they are in most aquatic environments (0.003 to 0.1 mg/L, Stumm, 1973; Dillon and Rigler, 1974; Oglesby and Schaffner, 1975) whereas much higher concentrations of up to several milligrams per litre have been observed in groundwaters impacted by septic systems (Childs et al., 1974; Reneau and Pettry, 1976; Beek et al., 1977; Cogger et al., 1988; Robertson, 1995; Walter et al., 1995; Harman et al., 1996). Septic systems inject dissolved phosphorus below the surface creating subsurface environments that can be substantially enriched in phosphate. Moreover, because loading to septic systems is often relatively uniform over a period

of years, they can be considered somewhat analogous to constant-input tracer tests, capable of providing insight into the subsurface behaviour of phosphate to a degree that is not possible in other situations.

Uncertainty regarding the mobility of phosphate in septic system plumes arises from the relatively few detailed field studies that are available, and in these from the contrasting behaviour of phosphate in differing terrain types and geochemical environments. In a number of studies porewater P concentrations have been profiled in the sediments underneath sewage infiltration beds (e.g. Sawhney and Starr, 1977; Beek et al., 1977; Whelan, 1988) but relatively few have described conditions in the groundwater zone farther downgradient where attenuation reactions may still be important. Childs et al. (1974) delineated phosphate plumes at three septic systems on sand in Michigan and showed phosphate concentrations of ~ 0.3 mg/L P for distances of up to 100 ft (30 m) downgradient at one site and higher concentrations of $\sim 2-5$ mg/L P for distances of up to 50 ft (15 m) downgradient at the other two sites. Reneau and Pettry (1976) measured groundwater phosphate concentrations near two tile beds at shallow water table locations on clayey sand in Virginia and found ~ 1 mg/L P for a distance of up to 3 m downgradient at one site and ~ 0.3 mg/L P up to 6 m downgradient at the other site. Cogger et al. (1988) observed phosphate breakthrough at the water table below a set of variably-loaded infiltration beds located on sand on a coastal barrier island in North Carolina. After two years of operation, an aerobic bed (deep water table) had phosphate concentrations at the water table approaching the effluent value, (~ 6 mg/L P) whereas at a nearby anaerobic bed (shallow water table) phosphate concentrations at the water table plateaued at about one third the effluent value (~ 2 mg/L as P). Walter et al. (1995) provide a very detailed description of a plume emanating from a set of 50 year old sewage lagoons located on sand and gravel at Cape Cod, Massachusetts and showed a

mappable phosphate plume (1-3 mg/L P) extending 700 m downgradient. Thus, high phosphate concentrations have been observed previously in septic system plumes, but the degrees of P attenuation and the lengths of the plumes differ markedly.

In this study, the behavior of phosphate is reviewed at ten septic system sites in Central Canada that have been investigated during the past decade. These include systems servicing two seasonal use cottages (Killarney and Harp sites) three single family households (Cambridge, Muskoka and Paradise sites), two seasonal-use campgrounds (Long Point and Camp Henry sites), a tourist resort (Delawana site) and a public school (Langton site). All are mature septic systems that have been in operation for at least six years and in most cases very detailed groundwater monitoring networks have been installed so that flowpaths emanating from the septic systems have been identified with confidence. A variety of silt and sand sediments are represented and geochemical conditions in the plumes vary over a wide range of pH and Eh values which substantially influence phosphate behavior.

The objective of this paper is to compare phosphorus behaviour at all of these sites in order to consolidate the site specific results into a more comprehensive assessment of phosphorus attenuation in the sediments below conventional septic infiltration beds.

METHODS

At all of the sites on sand, the monitoring networks consist primarily of multiple piezometer bundles of the type described by Cherry et al. (1983). These are constructed of 3 to 10 mm diameter polyethylene or TEFLON tubes attached at varying depth intervals to a PVC centre pipe. In some cases these were installed with an auger drill rig, but most often, a portable percussion hammer was used in conjunction with removable 5 cm diameter steel casing which allowed for economical installation of very detailed monitoring networks. At the sites on silty

sediments, individual piezometers were installed in manually augered holes or drive point-type piezometers were installed with a percussion hammer. Piezometers were installed below the infiltration beds and for distances of up to 150 m downgradient, with greatest monitoring detail concentrated along the plume centrelines.

Plume configurations were determined by sampling, using a peristaltic pump, indicator parameters such as electrical conductance (EC) and Cl⁻ (Killarney, Long Point, Camp Henry, Harp Lake, Delawana sites), Na⁺ (Cambridge site) or NO₃⁻ (Muskoka and Langton sites). In most cases, more detailed sampling was then concentrated along the plume centrelines and generally included sampling for nutrients (NO₃⁻, NH₄⁺, PO₄), major ions (Ca²⁺, Mg²⁺, K⁺, Na⁺, Cl⁻, SO₄²⁻, HCO₃⁻), trace metals (Fe, Mn, Al) and dissolved organic carbon (DOC). These samples were field filtered (0.45 µm) and were normally accompanied by field measurements of alkalinity and pH. Alkalinity was determined by acid titration, while pH was determined using a portable meter with a combination electrode calibrated against buffers of pH 4 and 7. Plume redox conditions were established by field measurements, at most sites, of dissolved oxygen (DO) and/or Eh. DO was measured using the Winkler titration method (U.S. EPA, 1974) which provided a detection limit of 0.1 mg/L, while Eh was measured using a portable meter checked against Zobell's solution (Nordstrom, 1977). Samples for cation and trace metal analyses were acidified (pH <2) immediately after filtration whereas samples for anion analyses (except PO₄) were filtered into separate containers and were left untreated. Laboratory analyses were completed as quickly as possible, usually within one to two weeks of sample collection.

PO₄ was analyzed colourimetrically on field filtered and in most cases acidified (pH <2) samples using a COBAS FARA® infrared spectrometer which provided a lower detection limit of 0.01-0.02 mg/L P. In most cases only orthophosphate (PO₄) concentrations were measured since

this is the chemically reactive form. Although this may underestimate total phosphorus concentrations in high DOC waters such as the raw wastewater, in most of the plume zones this analysis represented the bulk of the phosphorus present in solution. Reneau and Pettry (1976) and Harman et al. (1996) have noted that PO_4 and total dissolved P concentrations are generally equivalent in aquifer zones impacted by septic systems. Fe was analyzed by inductively coupled plasma spectrometry (ICP) which provided a detection limit of 0.001 - 0.02 mg/L. Low level Al analyses were done by ICP - mass spectrometry with a detection limit of 0.005 - 0.01 mg/L.

At most of the sites phosphate distribution was measured on a number of occasions over monitoring periods of up to nine years. The most recent data are generally shown here.

At four of the sites (Cambridge, Long Point 1, Langton, and Muskoka) tracer tests were used to determine the residence time of the effluent in the vadose zone and to establish groundwater velocity. The tests were conducted by injecting 1-4 kg of NaBr into the plumbing systems and then monitoring Br^- concentrations in the groundwater zone. At the Muskoka, Long Point 2 and Killarney sites, groundwater velocities were measured by monitoring breakthrough of conservative constituents as the frontal parts of the plumes advanced. At the remainder of the sites velocities were estimated using the Darcy equation.

SITE DESCRIPTIONS

Table 1 summarizes the important characteristics of the field sites, all of which are located in the Province of Ontario. Most have been described in more detail in previous publications as indicated.

The Cambridge site is a conventional gravity-fed septic system that has been servicing a four person household since 1977. The infiltration bed is positioned 2 m above the water table in an unconfined aquifer of fine to medium calcareous sand (21 wt% CaCO_3 equiv.). In 1987 a

monitoring network, consisting of over 500 monitoring points in 49 multiple piezometer bundles, was installed at the site. The bromide tracer test and the distribution of a mobile plume solute (Na^+) established that the effluent resides for about one week in the aerobic unsaturated zone and then forms a horizontally migrating plume in the groundwater zone advancing at a rate of about 20 m/a. Plume characteristics have been described extensively in previous publications (Robertson et al. 1991; Robertson, 1995; Wilhelm et al. 1996; among others).

At the Langton site, a conventional septic system serviced a public school with about 300 students for a 44 year period prior to replacement of the infiltration bed in 1994. The infiltration tiles were positioned 2 m above the water table in a unconfined aquifer of medium sand. The sand below the water table is calcareous (28 wt% CaCO_3 equiv.) but much of the vadose zone is carbonate-leached (~0.5 wt% CaCO_3 equiv.). A monitoring network consisting of more than 500 monitoring points in 45 multiple piezometer bundles was installed at the site in 1991. It was determined from the tracer test and from estimates using the Darcy equation that the effluent resides in the aerobic unsaturated zone for about one week and then forms a horizontally migrating plume in the groundwater zone advancing at a rate of approximately 100 m/a. The plume is described in detail by Harman et al. (1996).

At the Long Point site, a conventional septic system services a campground comfort station that is used seasonally by up to 300 persons per day. For a 19 year period prior to 1990 the septic tank effluent was pumped to an infiltration bed (Tile Bed 1) positioned 4 m above the water table in an unconfined sand aquifer of fine to coarse calcareous sand (19 wt% CaCO_3 equiv.). In 1989 the site was instrumented with a monitoring network consisting of about 500 monitoring points in 31 multiple piezometer bundles. A tracer test established that during peak use in July and August, the effluent resides for about one week in the aerobic unsaturated zone

and then forms a horizontally-migrating plume in the groundwater zone, advancing at a rate of 30-60 m/a (Robertson and Cherry, 1992). In 1990 the entire flow from the comfort station was diverted to a second infiltration bed (Tile Bed 2) located on the same aquifer but at a shallower water table location. The infiltration pipes here are positioned only 1.5 m above the water table, thus effluent residency in the vadose zone is much less, only about 2 days, during peak use. Because of differences in vadose zone thickness and in the resulting difference in the degree of effluent oxidation that may result, the two infiltration beds are considered here as separate sites. Tile bed 2 was instrumented in 1990 with a monitoring network consisting of 134 monitoring points contained in 8 multiple piezometer bundles (Aravena and Robertson, 1997).

At the Muskoka site, effluent from a two person household has been discharged to a conventional septic system since 1987. The infiltration bed is positioned 3 m above the water table on an unconfined aquifer of fine to coarse non-calcareous sand (<1 wt% CaCO₃ equiv.). A monitoring network consisting of 250 sampling points in 23 multiple piezometer bundles was installed at the site in 1988, shortly after commissioning of the septic system. From observation of advancement of the frontal part of the plume and from estimates of loading rate, it was estimated that the effluent resides in the aerobic unsaturated zone for about two weeks and then forms a horizontally-migrating plume in the groundwater zone advancing at a rate of about 20 m/a (Robertson et al., 1991; Wilhelm et al., 1996).

At the Delawana site, effluent from a seasonal-use tourist resort, that has up to several hundred guests per day, is pressure-dosed to a bank of eight infiltration beds that are loaded sequentially and that have been in operation since 1986. The infiltration beds are located on an unconfined sand aquifer of fine to medium non-calcareous to slightly calcareous sand. Because of sloping terrain at the site and because of undulations in the water table, the infiltration pipes are

positioned at varying heights above the water table ranging from one to three meters. A monitoring network consisting of 73 sampling points in 17 multiple piezometer bundles was installed at the site in 1994 and 1995. Effluent residency in the vadose zone is variable depending on the sequence of loading and on the location of the respective infiltration beds. In the groundwater zone the effluent forms a horizontally migrating plume advancing at a rate of about 50 m/a based on estimates using the Darcy equation.

At the Killarney site, effluent from a seasonal-use cottage is discharged to a conventional septic system located on a two meter thick pocket of non-calcareous lacustrine silt and fine sand (1 wt% CaCO_3 equiv.) overlying bedrock. A monitoring network consisting of 47 piezometers was installed at the site beginning in 1987, at the same time that the septic system was commissioned. The water table varies seasonally from a position near surface during recharge events in the Spring and Fall to a depth of about 2 m during mid-summer. Monitoring of plume advancement demonstrated that the effluent resides in the silt overburden for about one year before migrating downward into the underlying bedrock flowsystem (Robertson and Blowes, 1995).

At the Paradise site, effluent from a single family household has been discharged to a conventional septic system since 1964. The infiltration bed tile lines are trenched into silt-rich calcareous till (35 wt% CaCO_3 equiv.) at a location where the water table varies seasonally from a position near surface to about 2 m depth. A monitoring network was installed at the site in 1993 consisting of a single piezometer nest of five drive point-type piezometers installed below the centre of the infiltration bed, but accompanied also by a very detailed profile of porewater chemistry obtained by hydraulic squeezing of undisturbed sediment cores. Downward hydraulic

gradients are present at the site causing the plume to migrate downward into the till at a rate determined to be about 0.4 m/a (Alpay, 1993).

At the Harp site, a conventional gravity fed septic system serviced a seasonal use cottage for a 29 year period prior to installation of a monitoring network consisting of 56 drivepoint-type piezometers in 1991-1992. The tile bed is constructed on non calcareous sandy sediments at a location 16 m from the shoreline of a moderately oligotrophic softwater lake. A sewage impacted zone has been identified downgradient of the tile bed (site A1, Wood, 1993), however this zone is very dispersed and transient compared to the other plumes in this study. This results from a number of site specific factors including; the heterogeneous nature of the sandy till present, the steep hillslope position which may allow periodic lateral migration via macropores in the soil zone, irregular loading (weekends during the summer) and in particular, seasonally variable flow directions and the vigorous regional groundwater flowsystem present (velocity ~1 m/day) which results in the development of a very thin plume, estimated to be on the order of only 3-30 cm in thickness in this case. Nonetheless, a downgradient sewage-impacted zone has been identified in which mobile sewage constituents are enriched compared to background groundwaters by factors ranging from about three for Na^+ and Cl^- to about 50 for inorganic nitrogen (Wood, 1993). Although the plume here is less well defined and is more dilute than at the other sites, it is included in this review because it represents a lakeshore site typical of central Ontario "cottage country" where P loading from septic systems is of great concern. In addition, a layer of substantial P solids enrichment was identified immediately below the infiltration pipes at this site, (Wood, 1993) which is a circumstance of particular interest.

At the Camp Henry site, a conventional gravity fed septic system serviced a camp that was utilized intermittently by up to 50 persons per day during a 16 year period prior to

decommissioning of the tile bed in 1995. The tile bed lies on a sand spit comprised of calcareous medium sand and is situated at a location 60 m upgradient from a wetland. A monitoring network consisting of 150 monitoring points in 24 multiple piezometer bundles was installed at the site in 1994 and revealed the presence of a septic system plume extending from the tile bed to beyond the wetland edge (Ptacek, 1997). Calculations using the Darcy equation suggest that groundwater velocity varies seasonally at this site and is in the range of 10-60 m/a.

RESULTS

Table 1 summarizes the important features of each of the sites including the wastewater source, septic system age, sediment type, groundwater velocity, and the characteristics of the phosphate plumes including plume lengths, phosphate concentrations and degree of phosphate retardation (R) relative to the groundwater velocity. At most of the sites, the phosphate plume lengths are arbitrarily defined and include all points exceeding the 0.1 mg/L P concentration level. Although this value represents only one to two percent of the average effluent value of 5-10 mg/L P, it remains more than an order of magnitude higher than background phosphate concentrations in most of these groundwaters (<0.01 mg/L P) and thus normally provides a good indication of septic system impact. Figure 1 shows the distribution of phosphate at the six oxidizing plume sites where mappable phosphate zones are present (Cambridge, Langton, Harp, Muskoka, Long Point 1, and Long Point 2 sites). Figure 2 shows the three reducing plumes where mappable phosphate zones are present (Camp Henry, Delawana, and Killarney sites), at two of the latter sites (Camp Henry and Delawana) oxidizing zones are also present as noted (Fig. 2). The sections shown on Figures 1 and 2 follow the plume centrelines as established from the distribution of the more conservative plume solutes (e.g. Na⁺, Cl⁻, NO₃⁻).

In Table 1, the phosphate concentrations presented are average values observed during recent sampling in the shallow water table zones immediately below the infiltration beds or within a few meters downgradient. Because of the mature age of these septic systems (6-44 yrs., Table 1) it is likely, for the sites on sands, that most of the sediment phosphate sorption capacity has already been consumed in the near-tile area. This suspicion is confirmed at several of the sites (Cambridge, Langton, Muskoka) where long term monitoring over periods of four to nine years has revealed that proximal plume core P concentrations remain steady and show a consistent degree of attenuation compared to effluent values. At the Long Point 2 tile bed, high phosphate concentrations (~ 3 mg/L P) reached the water table at 2 m depth after only two months of operation, providing additional evidence of the relatively rapid utilization of vadose zone sorption capacity at these sites compared to their long histories of usage. Thus, P values given in Table 1 are considered quasi-steady state values assuming that effluent concentrations have remained relatively constant as monitoring suggests. Observed differences in phosphate concentrations between the effluent and the shallow water table zones, after several years of operation, are considered to represent attenuation by processes other than fast reversible adsorption, presumably solid phase formation reactions (irreversible adsorption and/or mineral precipitation) that are occurring in the vadose zone. Table 2 compares differences in effluent and proximal plume core phosphate concentrations. Normalized plume concentrations range from C/Co values of 0.77 at Cambridge (6.4 vs 4.9 mg/L P) to 0.004 at Muskoka (12.1 vs 0.05 mg /L P).

Table 1 distinguishes oxidizing (Cambridge, Long Point, Langton, Muskoka, Harp) and reducing (Delawana, Killarney Henry) sites with the indicated redox condition pertaining specifically to the phosphate zones. Oxidizing plumes are identified either by the presence of detectable dissolved oxygen (> 0.1 mg/L) or by elevated Eh values (> 200 mV) while in the

reducing plume zones no detectable dissolved oxygen is present (< 0.1 mg/L) and /or Eh values are depressed (< 200 mV). Tables 3 and 4 list representative field DO values for the oxidizing sites where data is available. Although the Delawana site is listed as reducing in Table 2, this site also contains zones that are oxidizing in areas where the vadose zone is thicker (2-3 m). An oxidizing zone, characterized by Eh values > 300 mV, is identified on Figure 1 and is in contrast to the reducing zone where Eh values are lower (< 200 mV). The Long Point 1 plume also contains a reducing zone, but at a location further downgradient. This zone is characterized by an absence of detectable dissolved oxygen (< 0.1 mg/L) and by abrupt attenuation of nitrate due to denitrification (Robertson and Cherry, 1992). However, this zone does not overlap with the proximal phosphate zone which remains aerobic throughout (DO=0.1 - 3 mg/L). Thus, the Long Point 1 site is considered oxidizing for the purposes of this discussion.

Other parameters can also be used as redox indicators in these plumes particularly the redox couples $\text{NH}_4^+/\text{NO}_3^-$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$. Oxidizing conditions facilitate the conversion of NH_4^+ to NO_3^- and cause iron to be present in the ferric oxidation state (Fe^{3+}). At pH ranges of 5-9, Fe^{3+} concentrations are limited to very low concentrations (< 0.1 mg/L) by the solubility of ferric oxyhydroxide minerals such as ferrihydrite ($\text{Fe}(\text{OH})_3$) whereas Fe^{2+} iron can have substantially higher solubility. $\text{Fe} > 0.1$ mg/L is indicative of iron occurring as Fe^{2+} in most of these waters. The presence of > 2 mg/L NH_4^+-N and/or > 0.1 mg/L Fe are good indicators of reducing conditions in these plumes (Fig. 3).

At the Camp Henry site, a phosphate-rich plume core zone (1-3 mg/L P) extends about 10 m downgradient from the tile bed (Fig. 2) but then P concentrations decline abruptly to values below detection (< 0.01 mg/L) further downgradient. A second zone is present however, at the bottom of the aquifer where moderate P concentrations are also present (0.1-0.8 mg/L) and that is

distinctly more reducing ($Eh < 200$ mV) than the shallower aquifer. It also has enriched Fe concentrations (2-15 mg/L). This reduced zone may be an artifact of an earlier period of heavier loading or higher water table conditions at the site, or it may be derived from other sewage sources which were released nearby in the past. Alternatively, it may occur naturally as a consequence of the relatively high organic carbon content of the nearby wetland sediment (Ptacek, 1997).

At the acidic Muskoka site (pH ~ 4.5), phosphate concentrations in the shallow groundwater zone are normally below detection (<0.01 mg/L P) except during the seasonal high water table condition after spring snow melt, when the water table rises to within about 1.5 m of the infiltration pipes. Several piezometers in this shallow zone consistently show low, but detectable phosphate concentrations in the range of 0.02-0.1 mg/L (Fig.1). Because similar phosphate concentrations have now been observed in this zone during four successive high water table episodes (1993-1997) and because these values are not increasing, it appears that these concentrations reflect steady state values.

DISCUSSION

PO₄ Sorption

The phosphate plumes shown on Figures 1 and 2 range in length from 1 m (Killarney) to 75 m (Langton) but in each case they are restricted in size compared to the plumes associated with the more mobile solutes (e.g. NO₃⁻, Cl⁻, Na⁺). By comparing the indicated rates of advance of the phosphate plumes to the estimated groundwater velocities, retardation factors ranging from <20 to 100 can be calculated for PO₄ migration at these sites (Table 1). These relatively large retardation factors presumably reflect the widely recognized affinity of PO₄ for sorption onto

mineral surfaces, particularly the metal hydroxides that possess positive surface charges at normal pH ranges (Parfitt et al., 1975; Rajan, 1975). Although substantial retardation is observed, at more than half of the sites (Cambridge, Camp Henry, Langton, Long Point, Delawana) the rates of PO_4 migration remain sufficiently fast (~ 1 m/a) to be of concern when considering the normal minimum set back distance of septic systems from surface water bodies (15 m) and their often long periods of usage.

PO_4 Solids

The observation that phosphorus solids tend to accumulate, at several of these sites (Cambridge, Langton, Muskoka, and Harp), within discrete narrow zones occurring immediately below the infiltration pipes (Wood, 1993; Harman et al., 1996; Zanini et al., 1997) rather than being uniformly dispersed along the plume flowpaths, indicates that processes other than conventional reversible adsorption must also be active at these sites. The distribution of these zones of P enrichment and the morphology of the P solids, as grain coatings, as grain overgrowths and as discrete secondary grains (Zanini et al., 1997) suggests that the precipitation of secondary phosphate minerals, or their amorphous precursors, is actively occurring at most of these sites. Thus, although sorption processes may be important in controlling the rate of phosphate migration, the concentrations that persist may be influenced by the constraints of phosphate mineral solubility.

During tertiary sewage treatment, phosphate concentrations are commonly controlled by the addition of metal salts such as alum, lime, ferric chloride, or ferrous chloride in order to promote the precipitation of phosphate minerals such as hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$), variscite ($\text{Al PO}_4 \cdot 2\text{H}_2\text{O}$), strengite ($\text{Fe PO}_4 \cdot 2\text{H}_2\text{O}$), vivianite ($\text{Fe}_3 (\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$), or their amorphous precursors (Jenkins et al., 1971; Sedlak, 1991). Chemical speciation models such as PHREEQE

(Parkhurst et al., 1985) can be used to assess the possibility of phosphate control by these mineral precipitation reactions in these plumes. Tables 3 and 4 list representative examples of effluent and phosphate plume water chemistry at each of the sites and provide calculated saturation indices (SI) for vivianite, hydroxyapatite, variscite, and strengite as well as several other mineral phases that may influence the concentrations of the important metal cations such as; Ca^{2+} (calcite), Fe (siderite, ferrihydrite) and Al^{3+} (gibbsite, jurbanite). For these analyses, pe values were assigned which provided compatibility with the observed condition of the redox pairs $\text{NH}_4^+/\text{NO}_3^-$ and $\text{Fe}^{2+}/\text{Fe}^{3+}$. For oxidizing plume zones, a pe value of +10 was normally used while in reducing zones, and for the effluent, a value of 0.0 was normally used.

Vivianite saturation indices for the septic tank effluents are given in Tables 3 and 4 and are shown on Figure 4 in conjunction with effluent Fe and PO_4 concentrations. SI values ranging generally from -3 to +2 indicate that in many cases vivianite saturation is approached or exceeded suggesting that vivianite precipitation may occur within the septic tank. This would cause phosphate solids to accumulate in the sludge at the bottom of the tank. This circumstance raises the possibility that the relative consistency of phosphate concentrations in septic tank effluent (3-10 mg/L P, Fig. 4) may be at least partly the result of equilibrium with vivianite. Reducing plume zones (Killarney, Delawana, Henry) also exhibit supersaturation with respect to vivianite (SI = 0.4 to 3.1, Table 4), but in addition have Fe concentrations (1-20 mg/L, Table 4, Fig. 5c) that are much higher than effluent values (generally 0.1 - 1 mg/L, Fig. 4). Enrichment in Fe occurs invariably in the reducing plumes, as a result of reductive dissolution of ferric oxyhydroxide minerals present in the sediments (Hem, 1992). Further increases in iron concentration in solutions already at equilibrium with vivianite (i.e. the effluent) would be expected to cause additional precipitation of vivianite. Thus the decreases in phosphate concentrations observed in

all three reducing plumes ($C/C_0 = 0.02 - 0.51$, Table 2) may potentially be attributable to additional vivianite precipitation. Nriagu and Dell (1974) identified authogenic vivianite grains in anaerobic Lake Erie sediments and established that the sediment porewater, containing Fe of 1-8 mg/L and PO_4 -P of 0.03 - 0.3 mg/L was near equilibrium with respect to vivianite. Because all three reducing plumes have Fe (1-20 mg/L) and PO_4 -P concentrations (0.1 - 3 mg/L) as high or higher than those in the above lake sediments and have the same pH range (6.5 - 7.5), it is reasonable to expect that vivianite also limits phosphate concentrations in reducing septic system plumes. Other workers also implicate vivianite as the main control on phosphate in reducing lake sediments (e.g. Emerson and Widmer, 1978; Wersin et al., 1991). A more detailed assessment of vivianite equilibrium at the Camp Henry site is presented by Ptacek (1997).

The highest phosphate concentrations (4-5 mg/L P) occur in the plumes that are oxidizing and are on calcareous sand at near neutral pH (Cambridge, Long Point 2, Tables 1-3, Fig. 6a). A common feature of both plumes is that they exhibit a high degree of supersaturation with respect to hydroxyapatite (SI 1.4 - 3.4, Table 3) and the degree of supersaturation persists along the flowpaths. Jenkins et al. (1971) suggest that the solubility of freshly precipitated amorphous hydroxyapatite and impure phases may be several orders of magnitude higher than that of the crystalline form which is used in the PHREEQE data base ($K_{sp} = -3.4$ at 25°C). Alternatively, hydroxyapatite precipitation may be kinetically limited, but Zanini et al., (1997) found little evidence of secondary solids containing Ca and P at these sites. Thus, the field data suggest that crystalline hydroxyapatite is relatively ineffective at controlling phosphate concentrations in these plumes. Moore and Reddy (1994) suggest that a more soluble calcium phosphate mineral, beta tricalcium phosphate (β - $Ca_3(PO_4)_2$), may control phosphate concentrations in Lake Okeechobee, Fl., sediments.

The solubility curves for variscite and strengite shown on Figure 6 imply that low phosphate concentrations should occur in acidic plumes that may be present in non-calcareous terrain. In addition, adsorption of PO_4 onto oxide surfaces is enhanced at lower pH (Goldberg and Sposito, 1984). The strengite solubility curve includes the assumption that in oxidizing environments, ferric iron concentrations are controlled by the solubility of amorphous $\text{Fe}(\text{OH})_3$ (e.g. Whittemore and Langmuir, 1975) and for variscite, that Al concentrations are primarily controlled by the solubility of gibbsite ($\text{Al}(\text{OH})_3$) (van Grinsven et al., 1992; Appelo and Postma, 1994). However, at very acidic values, it has been suggested that aluminum concentrations in some waters will be controlled by the solubility of the mineral jurbanite ($\text{Al OH SO}_4 \cdot 5\text{H}_2\text{O}$) (Nordstrom, 1982; Appelo and Postma, 1994). With respect to the Muskoka plume water chemistry given in Table 3, chemical equilibrium modelling suggests that jurbanite rather than gibbsite, controls Al concentrations at pH values <4.9 , as is indicated on Figure 5b. Thus, the variscite solubility curve shown on Figure 6 assumes Al concentrations are controlled by gibbsite equilibrium at pH >4.9 but by jurbanite at lower pH values. A comparison of plume Al concentrations and the gibbsite/jurbanite solubility curve (Fig. 5b) suggests that these assumptions may be reasonable for both reducing and oxidizing plumes. Substantially elevated Al values (0.2-5 mg/L) are observed as pH drops below 5.5. For Fe^{3+} however, the assumption of concentrations limited by amorphous $\text{Fe}(\text{OH})_3$ solubility appears less valid in these plumes. At the Muskoka site for example, low pH plume waters are substantially undersaturated with respect to amorphous $\text{Fe}(\text{OH})_3$ (Fig. 5c). Fe at this site is perhaps limited by some other less soluble mineral such as goethite. Nonetheless the data set is generally consistent with PO_4 solubility controlled by variscite and/or strengite including the important result that lower phosphate concentrations occur at lower pH values (Fig. 6).

Few data points substantially exceed variscite solubility. Two data points from Muskoka that do exceed the variscite solubility curve (1.55 and 0.34 mg/L PO₄-P) were retrieved, during recent sampling in 1997, from the same sampling point (piezometer 32-1), which is the shallowest point in the monitoring network (1.0m below the infiltration pipes). The first sample (1.55 mg/L PO₄-P) was obtained at the end of the spring snow melt period (April 22) while the second sample was retrieved one month later (May 20). The much lower P value in the second sample (0.35 mg/L) suggested that the porewater at this location may not have been at a condition of equilibrium with respect to phosphate during this period, possibly due to the close proximity of the sampling point to the infiltration pipes and due to the rapid infiltration rates that normally accompany spring snow melt.

Nriagu and Dell (1974), Martin et al. (1988) and Moore and Reddy (1994) describe other secondary phosphate minerals such as rockbridgite (Fe₃(PO₄)₃(OH)₅), reddingite (Mn₃(PO₄)₂·3H₂O), griphite (Fe₃Mn₂(PO₄)_{2.5}(OH)₂, and beta tricalcium phosphate (β - Ca₃(PO₄)₂), among others, than can be stable in low temperature aqueous environments and that may also be important in limiting phosphate concentrations in septic system plumes. However, the potential for their formation has not been rigorously evaluated in this study because adequate thermodynamic data for these minerals are generally lacking.

Irrespective of the actual pure or amorphous mineralogical phases limiting P concentrations in these plumes, it is clear from these data and from the accompanying compositional analyses of the zones of P-solids enrichment (Zanini et al., 1997), that Fe and Al solids appear to be important in affecting P concentrations, hydroxyapatites are less important and that lower P concentrations occur in more acidic environments.

IMPLICATIONS

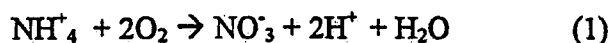
If the minerals indicated on Figure 6 (strengite, variscite, hydroxyapatite and vivianite) are valid controls on phosphate in septic system plumes, then it can be seen that the highest phosphate concentrations should be present in the neutral pH plumes that occur in calcareous terrain, whereas much lower concentrations should be present in non calcareous terrain if plume zones are present in which pH values drop below about 6. This is particularly so if the hydroxyapatite control is rendered ineffective as a consequence of kinetic limitations or as result of the greater solubility of impure or amorphous phases of this mineral. Generally, the field data support this pH dependency, with highest phosphate concentrations (~ 5 mg/L P) occurring in the two oxidizing plumes at pH ~ 7.0 (Cambridge, Long Point 2). The reducing plumes at neutral pH (Delawana, pH 6.6; Camp Henry, pH 7.2) have substantially lower phosphate concentrations however (0.1-1 mg/L P), possibly as a result of the greater effectiveness of the vivianite control in reducing environments. Thus, at neutral to slightly alkaline pH values, it appears that oxidizing plumes can have higher phosphate concentrations than reducing plumes. Interestingly, this relationship is the opposite to that normally reported in lake and marine sediments where higher porewater phosphate concentrations are generally associated with the deeper reducing zones compared to the more oxidizing shallower sediments (Nriagu and Dell, 1974; Moore and Reddy, 1994). In lake sediments this occurs, because at the redox boundary, oxidation of Fe^{2+} to Fe^{3+} causes precipitation of ferric oxyhydroxide minerals and the subsequent sorption of P onto fresh surfaces and/or the precipitation of sparingly soluble ferric phosphate minerals. It is likely that similar attenuation of P will occur when reducing plume waters, high in Fe^{2+} , discharge to oxidizing surface water environments.

It can be seen from Figure 6 however, that the aerobic/anaerobic relationship suggested above is reversed at lower pH, because at pH values below about 6 the vivianite control becomes less effective unless Fe values are exceedingly elevated (>10 mg/L). However, it should be noted that the occurrence of acidic (pH<6) reducing plumes is unlikely because septic system effluent normally has high alkalinity (150-500 mg/L as CaCO₃, Tables 3 and 4) and near neutral pH (6.5 - 7.5, Fig. 4) so that substantial oxidation of the effluent is necessary to effect a decrease in pH. This is evident at the Delawana site where pH in the reducing plume zone is higher (6.6) than in the oxidizing zone (6.3, Table 2) and has also been noted in the Cape Cod sewage plume where pH in the anaerobic zone (~6.5) is substantially higher than in the aerobic zones and in the background groundwater (~5.7, Walter et al., 1995).

In general, the field data indicate that P is "buffered" to moderate concentrations in reducing zones, whereas in oxidizing zones greater contrasts in P concentrations are exhibited. Patrick and Khalid (1974) reported similar behavior in laboratory batch tests in which P was added incrementally to a set of four soils (pH range 5.4 - 6.8) under both aerobic and anaerobic conditions. In this study, soil solution P values in the untreated soils were initially higher under anaerobic conditions, however as P was added, solution P values eventually became substantially higher under aerobic conditions.

Consideration of the mineral solubility controls discussed above can be useful in the development of alternative septic system designs to improve attenuation of phosphorus. For example, the possibility of achieving lower phosphate concentrations at more acidic pH values, invites design modifications that promote zones of decreased pH, provided that such zones do not adversely affect other treatment reactions. This can be done by recognizing that properly

functioning septic systems normally generate acidity by oxidation reactions such as the nitrification of ammonium;



Using acid/base accounting in a manner similar to that described by Wilhelm et al. (1996) it can be seen from Table 5 that oxidation of effluent NH_4^+ is, by itself, sufficient to consume most or all of the alkalinity available in most of these effluents. Furthermore, other reactions such as the oxidation of organic nitrogen and reduced sulfur compounds may cause further alkalinity consumption. Based on observed increases in plume SO_4^{2-} concentrations, Wilhelm et al. (1996) estimated that oxidation of reduced sulfur compounds in the Muskoka and Cambridge effluent would consume an additional 0.4 -0.8 meq of alkalinity. Thus it is likely that the thorough oxidation of most septic tank effluent will result in relatively complete consumption of available alkalinity and will cause the development of acidic conditions. At most sites however, low pH conditions do not develop as a consequence of the buffering reactions that occur in the sediments, particularly carbonate mineral dissolution reactions, that buffer pH to near neutral values. Only at the Harp and Muskoka sites, where sediment buffering capacity is limited, do pH values decline to below 6 (Table 1). When constructing infiltration beds, it should be possible to specifically engineer localized low pH zones simply by using non-calcareous fill material. This may be feasible particularly when constructing raised filter beds (e.g. Converse and Tyler, 1990) where import of fill material is normally required. Other simple mitigation measures follow. For example, at sites where phosphate loading is the primary concern, septic systems should be designed to allow for maximum oxidation at locations where the sediments have limited buffering capacity, but in calcareous terrain it may be more prudent to provide a lesser degree of oxidation

so that anaerobic plumes develop, although moderate P concentrations (~1 mg/L) would likely persist in the latter case.

SUMMARY

Review of phosphate distribution in ten mature septic system plumes reveals that in six cases relatively large scale phosphate zones are present (>10 m in length) where PO_4 concentrations (0.5-5 mg/L P) are about two orders of magnitude higher than normally found in uncontaminated aquatic ecosystems. At the other four sites, which are those on non calcareous and silt and clay rich sediments, above background phosphate concentrations are limited to within three metres of the infiltration pipes. Although phosphate plume migration velocities are substantially retarded compared to the groundwater velocities at all of the sites ($R = <20-100$), the phosphate migration velocities at the sites on calcareous sands remain sufficiently fast (~1 m/a) to be of concern with respect to the normal minimum setback distance of septic systems from surface water bodies.

Although phosphate is persistent and moderately mobile in a number of these plumes, phosphate concentrations at all sites are attenuated compared to effluent values by amounts ranging from 23 to 99%. Observed plume concentrations are generally consistent with the constraints imposed by the solubilities of the minerals vivianite, strengite and variscite, but not hydroxyapatite. Plumes at near neutral pH consistently exhibit a high degree of hydroxyapatite supersaturation possibly as a consequence of kinetic limitations or as a result of amorphous and impure forms of the mineral being more soluble than crystalline forms. In general, in reducing plumes, pH values appear to be maintained at near neutral values similar to that of the effluent and phosphate concentrations appear to be buffered to the ~ 1 mg/L P range, consistent with vivianite equilibrium. This represents a moderate amount of P attenuation compared to effluent

concentrations. In oxidizing plumes, pH values vary considerably depending on sediment buffering capacity with the result that phosphate concentrations also vary. In calcareous terrain PO_4 concentrations (2-5 mg/L P) exhibit only minor attenuation compared to effluent concentrations whereas in non-calcareous terrain almost complete attenuation of phosphate appears possible if acidic conditions develop.

The dominant mineral precipitation reactions appear to occur rapidly after the effluent enters the subsurface and are largely completed within the vadose zones at these sites. This results in the accumulation of phosphorus rich solids within discrete narrow depth intervals occurring in close proximity to the infiltration pipes. At the Langton site approximately 85% of the total sewage P remains retained within the 2 m thick vadose zone, even after 44 years of effluent loading, demonstrating the considerable longevity of these attenuation reactions.

Recognition of the constraints imposed by the solubilities of the secondary phosphate minerals opens up the possibility of modifying septic system design to achieve improved phosphate attenuation.

ACKNOWLEDGEMENTS

Funding for the site investigations and data review was provided by the Ontario Ministry of Environment and Energy, The Waterloo Centre for Groundwater Research, The Procter and Gamble Co., Environment Canada, Parks Canada and the Natural Sciences and Engineering Research Council of Canada. Access to the sites was kindly provided by D. Kitchen, H. and I. Kueper, B. Jessop, M. and B. Dykeman, P. Grise, D. and E. Robertson, Ontario Ministry of Natural Resources, Parks Canada and Norfolk County Board of Education. Development of such an extensive data set was made possible only by the diligent efforts of the

students and assistants who undertook the detailed site investigations; S. Wilhelm, J. Harman, J. Wood, S. Alpay, L. Zanini, and L. Durham.

REFERENCES

- Alpay, S. 1993. Fate of wastewater nutrients (N and P) beneath septic tile fields in low permeability sediments. B.Sc. thesis, University of Waterloo, Waterloo, Ontario, 80p.
- Appelo, C.A.J. and D. Postma, 1994. Geochemistry, groundwater and pollution. A.A. Balkema Publishers, Rotterdam, Netherlands, 536 pp.
- Aravena, R. and W.D. Robertson, 1997. Use of multiple isotope tracers to evaluate denitrification in groundwater: A case study of nitrate from a large-flux septic system plume. *Ground Water*, accepted.
- Beek, J., F.A.M. de Haan and W.H. Riemsdijk, 1997. Phosphates in soils treated with sewage water: II. Fractionation of accumulated phosphates. *J. Environ. Qual.* v. 6, pp. 7-12.
- Cherry, J.A., R.W. Gillham, P.E. Johnson, 1983. Migration of contaminations in groundwater at a landfill: A case study, 2. Groundwater monitoring devices. In: J.A. Cherry (Guest-Editor), *Migration of Contaminants in Groundwater at a Landfill: A Case Study*, *J. Hydrol.*, v. 63: pp. 31-49.
- Childs, D.E., S.B. Upchurch, and B. Ellis, 1974. Sampling of variable, waste-omigration patterns in ground water. *Ground Water*, v. 12, pp. 369-376.
- Cogger, C.G., L.M. Hajkjar, C.L. Moe and M.D. Sobsey, 1988. Septic system performance on a coastal barrier island. *J. Environ. Qual.* v. 17, pp. 401-408.
- Converse, J.C. and E.J. Tyler, 1990. Wisconsin mound soil absorption system: Siting, design and construction manual. Small scale waste management project, University of Wisconsin, Madison, WI, 40 P.

- Dillon, P.J. and F.H Rigler, 1974. The phosphorus - chlorophyll relationship in lakes. *Limnology and Oceanography*, v. 19, pp. 767-773.
- Emerson, S. and G. Widmer, 1978. Early diagenesis in anaerobic lake sediments: II Thermodynamic and kinetic factors controlling the formation of iron phosphates. *Geochim. Cosmochim. Acta*, v. 42, pp. 1307-1316.
- Goldberg, S. and G. Sposito, 1984. A chemical model of phosphate adsorption by soils: I. Reference oxide minerals. *Soil Sci. Soc. Am. J.* v. 48, pp. 772-778.
- Harman, J., W.D. Robertson, and J.A. Cherry, 1996. Impacts on a sand aquifer from an old septic system: Nitrate and phosphate. *Ground Water*, v. 34, pp. 1105-1114.
- Isenbeck-Schroter, M., U. Doring, A Moller, J. Schroter, and G. Matthes, 1993. Experimental approach and simulation of the retention processes limiting orthophosphate transport in groundwater. *J. Contam. Hydrol.* v. 14, pp. 143-161.
- Jenkins, D., J.F. Ferguson and A.B. Menar, 1971. Chemical processes for phosphate removal. *Water Res.* v. 5, pp. 369-389.
- Martin, R.R., R. St. C. Smart, and K. Tazaki, 1988. Direct observation of phosphate precipitation in the goethite/phosphate system. *Soil Sci. Soc. Am. J.* v. 62, pp. 1492-1500.
- Moore, P.A. and K.R. Reddy, 1994. Role of Eh and pH on phosphorus geochemistry in sediments of Lake Okeechobee, Florida. *J. Environ. Qual.* v. 23, pp. 955-964.
- Nordstrom, D.K., 1977. Thermochemical redox equilibria of Zobell's solution. *Geochim. Cosmochim. Acta*, v. 41, pp. 1835-1841.

- Nordstrom, D.K., 1982. The effect of sulfate on aluminum concentrations in natural waters: some stability relations in the system $Al_2O_3-SO_3-H_2O$ at 298°K. *Geochim. Cosmochim. Acta*, v. 46, pp. 681-692.
- Nrigau, J.O. and C. I. Dell, 1974. Diagenetic formation of iron phosphates in recent lake sediments. *American Mineralogist*, v. 59, pp. 934-946.
- Ogelsby, R.T. and W.R. Schaffner, 1975. The response of lakes to phosphorus. In: Nitrogen and phosphorus food production, waste and the environment, K. S. Porter, Ed., Ann Arbor Science, Ann Arbor, Michigan, pp. 25-57.
- Parfitt, R.L., R.J. Atkinson, and R.S.C. Smart, 1975. The mechanism of phosphate fixation by iron oxides. *Soil Sci. Soc. Am. J.* v. 39, pp. 837-841.
- Parkhurst, D.L., D.C. Thorstenson and L.N. Plummer, 1985. PHREEQE-A Computer program for geochemical calculations. U.S.G.S. Water-Resources Investigation 80-96, rev. 1985.
- Patrick, W.H. and R.A. Khalid, 1974. Phosphate release and sorption by soils and sediments: Effect of aerobic and anaerobic conditions. *Science*, v. 186, pp. 53-55.
- Ptacek, C.J., 1997. Geochemistry of a septic-system plume in a coastal barrier bar, Point Pelee, Ontario, Canada. *J. Contam. Hydrol.*, accepted, 7/97.
- Rajan, S.S.S., 1975. Absorption of divalent phosphate on hydrous aluminum oxide. *Nature*, v. 253, pp. 434-436.
- Reneau, R.B., Jr. and D.E. Pettry, 1976. Phosphorus distribution from septic tank effluent in coastal plains soils. *J. Environ. Qual.* v. 5, pp. 34-38.
- Robertson, W.D., 1995. Development of steady-state phosphate concentrations in septic system plumes. *J. Contam. Hydrol.* v. 19, pp. 289-305.

- Robertson, W.D. and D.W. Blowes, 1995. Major ion and trace metal geochemistry of an acidic septic system plume. *Ground Water*, v. 33, pp. 275-283.
- Robertson, W.D. and J.A. Cherry, 1992. Hydrogeology of an unconfined sand aquifer and its effect on the behaviour of nitrogen from a large flux septic system. *J. Applied Hydrogeol.* v. 1, pp. 32-44.
- Robertson, W.D., J.A. Cherry and E.A. Sudicky, 1991. Groundwater contamination from two small septic systems on sand aquifers. *Ground Water*, v. 29, pp. 82-92.
- Sawhney, B.L. and J.L. Starr, 1977. Movement of phosphorus from a septic system drainfield. *J. WPCF*, v. 49, pp. 2238-2242.
- Schindler, D.W., 1977. Evolution of phosphorus limitation in lakes. *Science*, v. 195, pp. 260-262.
- Stumm, W. and J.J. Morgan, 1981. *Aquatic Chemistry*. John Wiley and Sons, New York, NY, 780 pp.
- Sedlak, R.I. (Editor), 1991. *Phosphorus and nitrogen removal from municipal wastewater: principles and practice*. The Soap and Detergent Assoc. New York, NY, 240 pp.
- U.S. Environmental Protection Agency, 1974. *Methods of chemical analysis of water and wastes*. Technical Report, Office of Technology Transfer, Washington, D.C., pp. 105-106.
- Van Grinsven, H.J.M., W.H. van Riemsdijk, R. Otjes, and N. van Breemen, 1992. Rates of aluminum dissolution in acid sandy soils observed in column experiments. *J. Environ. Qual.* v. 21, pp. 439-447.
- Walter, D.A., B.A. Rea, K.G. Stollenwerk, and J. Savoie, 1995. Ground-water quality, geochemistry of phosphorus on aquifer sediments, and transport of phosphorus in a sewage contaminated sand and gravel aquifer near Ashumet Pond, Cape Cod,

Massachusetts, U.S. Geological Survey, Open File Report 95-?, Marlborough, Massachusetts, 156 pp.

Wersin, P., P. Hohener, R. Giovanoli, and W. Stumm, 1991. Early diagenetic influences on iron transformations in a freshwater lake sediment. *Chem. Geol.*, v. 90, pp. 233-252.

Whelan, B.R., 1988. Disposal of septic tank effluent in calcareous sands. *J. Environ. Qual.* v. 17, pp. 272-277.

Wilhelm, S.R., S.L. Schiff and W.D. Robertson, 1996. Biochemical evolution of domestic waste water in septic systems: 2. Application of a conceptual model in sandy aquifers. *Ground Water*, v. 34, pp. 853-864.

Whittemore, D.O. and D. Langmuir, 1979. The solubility of ferric oxyhydroxides in natural waters. *Ground Water*, v. 13, pp. 363-365.

Wood, J.S.A., 1993. Migration of septic system contaminated groundwater to a lake in a Precambrian shield setting: A case study. M.Sc. thesis, University of Waterloo, Waterloo, Ontario, 275 pp.

Zanini, L., W.D. Robertson, C.J. Ptacek, S.L., Schiff and T. Mayer, 1997. Phosphorus characterization in sediments impacted by septic effluent at four sites in Central Canada. *J. Contam. Hydrol.*, in submission.

Table 1 Ten septic system plumes in central Canada of sufficient age to develop P zones.

Site	Septic System			P-plume				Sediment Type
	age (a)	source	G.W. vel. (m/a)	PO ₄ -P ¹ (mg/L)	length ² (m)	R ³	pH	
Oxidizing - Calcareous								
Paradise	25	house	0.4	0.3	0.3	30	8.0	silt
Cambridge	20	house	20	4.9	25	20	7.0	m. sand
Camp Henry	16	campground	10-60	1.1	15	20	7.0	c. sand
Long Point 2	6	campground	40	4.8	>10	<20	6.9	m. sand
Long Point 1	18	campground	40	2.8	6-16	100	6.6	m. sand
Langton	44	school	100	1.3	70	40	6.6	m. sand
Oxidizing - Non Calcareous								
Harp 1	29	cottage	400	0.03	15	-	5.9	sand till
Muskoka	10	house	20	0.05	3	50	4.5	f.-c. sand
Reducing								
Delawana	10	resort	70	0.61	>25	<40	6.6	m. sand
Killarney	10	cottage	3	0.95	1	>50	6.1	silt, f. sand

- 1) average of recent data from shallow water table zone below tile bed or immediately downgradient.
- 2) plume front defined by 0.1 mg/L P concentration level.
- 3) Phosphate retardation factor (R) = groundwater velocity/phosphate velocity.

Table 2. Phosphate attenuation in the vadose zone; comparison of effluent and proximal plume core PO₄ concentrations.

Site	PO ₄ -P (mg/L)				C/C ₀	Plume pH
	effluent ¹	plume ²				
Oxidizing-Calcareous						
		N		N		
Cambridge	6.4	21	4.9	26	0.77	7.0
Camp Henry	11.8	1	1.1	9	0.09	7.0
Long Point 2	7.1	1	4.8	16	0.68	6.9
Long Point 1	6.2	12	2.8	13	0.45	6.6
Langton	8.2	6	1.3	10	0.16	6.6
Oxidizing-Non-Calcareous						
Delawana	1.2	3	0.30	15	0.25	6.3
Harp 1	8.9	2	0.03	3	0.003 ³	5.9
Muskoka	12.1	10	0.05	27	0.004	4.5
Reducing						
Camp Henry	11.8	1	0.19	7	0.02	7.2
Delawana	1.2	3	0.61	10	0.51	6.6
Killarney	7.5	8	0.95	12	0.13 ³	6.1

- 1) average effluent PO₄ concentration except total dissolved phosphorus at Harp and Henry sites. (N = 3-21, except 1 for Long Point 2, Camp Henry, 2 for Harp 1)
- 2) average of recent data from shallow water table zone below tile bed or immediately downgradient. (N = 7-27, except 3 for Harp 1)
- 3) conservative constituents (Na⁺, Cl⁻) indicate that proximal plume core is affected by dilution at these sites (See tables 3 and 4).

TABLE 3: OXIDIZING PLUMES

Sample Point	Delawana		Camp Henry		Long Point 2		Langton		Cambridge		Muskoka		Paradise 2		HARP - 1	
	EFF	4:1	EFF	7:4	EFF	10FA-10	EFF	31-1	EFF	33-1	EFF	32-3	EFF	PL2-2	EFF	35
x (m) ¹	0	2	0	7	0	2	0	2	0	2	0	3	0	13	0	8
Date	10/95	11/95	5/95	6/94	10/95	10/95	10/91	10/91	10/95	10/95	5/95	5/95	8/93	10/92	91-92	5/92
Na (mg/L)	31	29	43	11	23	27	114	101	75	71	54	51	55	30	35	9
K	7	3	21	9	16	17	49	62	7	8	12	15	24	3	22	1
Ca	36	72	84	106	112	199	12	249	33	74	10	34	37	110	10	10
Mg	6	7	13	9	17	20	26	30	15	13	3	4	12	32	4	3
AlK(as CaCO ₃)	147	150		520	350	230	452	210	261	270	202	<1	402	401	310	14
SO ₄	35	35	34	47	38	44	44	66	42	45	17	47	11	23	1	21
Cl	24	24	57	112	42	57	228	209	21	26	41	36	53	20	50	11
SiO ₂	5	10	10				8	57	21	20	15	20	10	10		
PO ₄ -P	1.8	0.04	11.8 ²	1.4	7.1	4.2	8.5	1.5	7.7	4.6	6.7	0.08	7.6	<0.01	10.3 ²	0.03 ²
NO ₃ -N	0.05	13	0.05	18	0.6	69	<0.05	131	0.9	14	<0.05	37	<0.05	<0.05	0.1	3.2
NH ₄ -N	17	0.2	98	0.4	57	<0.1	135	0.06	19	<0.05	34	0.05	58	0.1	69	0.08
Fe	1.2	0.03	0.60	0.004	0.12	<0.02	0.2	<0.02	0.12	0.02	0.14	0.03	0.37	<0.02	25	0.11
Mn	0.06	0.11	0.48	1.0			0.14	2.2	0.05	<0.01	0.02	0.37	0.11	0.36		
Al	<0.10	0.16	0.10	<0.01					0.047	0.01	0.066	3.5			0.18	
DOC	9	5	32	13			28	0.7	40	4	81	3	26	5	65	4
DO					0.2		0.3		8		3					
pe ⁴	0.0	10	0.0	10	0.0	10	0.0	10	0.0	10	0.0	10	0.0	10	0.0	10
pH	7.15	6.25		7.00	7.5	6.9	7.35	6.55	7.1	6.9	6.57	4.3	6.9	7.75	7.5 ³	5.9
Calcite SI	-0.6	-1.2		-0.3	0.4	-0.1	0.4	-0.4	-0.5	-0.4	-1.7	-5.7	-0.5	0.7	0.0	-3.5
Siderite	-0.3	-6.1		-6.3	-0.8	<-6.9	-0.6	-6.6	-1.2	-6.8	-1.8	-11	-0.7	<-7.8	1.6	-6.2
FeOH ₂ ^α	-1.6	0.7		0.8	-1.7	<-1.1	-1.9	0.8	-2.8	1.1	-4.4	-1.3	-2.9	<-1.7	0.7	0.9
Gibbsite	<-1.1	1.4							0.8	-0.1	0.6	-1.0			1.4	
Jurbanite ⁵	<-4.0	-2.1							-4.1	-4.6	-3.5	-0.2			-6.0	
Hydroxyapatite ⁶	0.8	-7.9		0.2	5.6	3.4	5.5	0.3	2.0	1.4	-4.0	-2.2	1.1	-1.9	4.5	-15
Vivianite ⁷	1.4	-20		-18	-0.1	<-18	0.2	-18	-0.8	-15	-2.2	-30	0.1	<-27	7.2	-17
Strengite ⁸	-2.2	-0.3		<-1.0	-2.5	<-1.1	-2.3	<-0.8	-2.7	1.3	-3.6	0	-2.5	-2.3	0.2	0.1
Variscite ⁹	<0.0	-0.3							0.4	-0.3	1.2	-0.1			0.3	

- 1) flowpath length between infiltration pipes and sampling point
- 2) total dissolved P
- 3) lab measurement
- 4) assumed values
- 5) jurbanite, $Al(OH)SO_4 \rightarrow Al^{3+} + OH^- + SO_4^{2-}$, $\log K_p = -17.8$ (Appelo and Postma, 1994)
- 6) hydroxyapatite, $Ca_5(PO_4)_3OH + 4H^+ \rightarrow 5Ca^{2+} + 3HPO_4^{2-} + H_2O$, $\log K_p = -3.421$ (PHREEQE database)
- 7) vivianite, $Fe_3(PO_4)_2 \cdot 8H_2O \rightarrow 3Fe^{2+} + 2PO_4^{3-} + 8H_2O$, $\log K_p = -36.0$ (PHREEQE database)
- 8) strengite, $FePO_4 \cdot 2H_2O \rightarrow Fe^{3+} + PO_4^{3-} + 2H_2O$, $\log K_p = -26$ (Stumm and Morgan, 1981)
- 9) variscite, $AlPO_4 \cdot 2H_2O \rightarrow Al^{3+} + PO_4^{3-} + 2H_2O$, $\log K_p = -21$ (Stumm and Morgan, 1981)

Table 3: Oxidizing plumes: comparison of effluent and proximal plume chemistry. Presented are recent data considered representative of average conditions. Mineral saturation indices (SI) determined using the chemical speciation model PHREEQE (Parkhurst et al., 1985).

TABLE 4: REDUCING PLUMES

Sample Point	Killarney		Delawana		Camp Henry	
	EFF	61-0.8	EFF	6-2	EFF	6-1
x (m) ¹	0	0.4	0	2	0	30
Date	10/95	11/95	10/95	3/96	5/96	5/94
Na (mg/L)	58	31	31	28	43	27
K	43	18	7	5	21	4
Ca	11	10	36	37	84	161
Mg	6	5	6	6	13	17
AlK(as CaCO ₃)	360	400	147	131		
SO ₄	11	<2	35	31	34	104
Cl	89	34	24	21	57	52
SiO ₂	7	7	5	15	10	
PO ₄ -P	14.2	3.1	1.8	0.14	11.8 ²	0.34
NO ₃ -N	<0.05	<0.05	0.05	0.07	<0.05	<0.01
NH ₄ -N	111	73	17	3	98	0.58
Fe	0.88	18	1.2	10	0.60	10.3
Mn	0.10	0.42	0.11	0.16	0.48	0.37
Al	<0.1	0.075	<0.10		0.10	<0.01
DOC	83	44	9	7	32	7
pe ⁴	0.0	0.0	0.0	0.0		0.9
pH	6.50	6.50	7.15	6.68		7.28
Calcite SI	-1.5	-1.5	-0.6	-1.3		0.45
Siderite	-0.9	0.5	-0.3	0.1		1.1
Fe(OH) ₃ α	-3.9	-2.5	-1.6	-2.2		0.59
Gibbsite	0.8	0.7	1.1			<0.1
Jurbanite ⁵	<-3.4	-4.3				<-4.9
Hydroxyapatite ⁶	-3.6	-5.9	0.8	-6.0		1.5
Vivianite ⁷	0.3	3.1	1.4	0.4		2.5
Strengite ⁸	-2.8	-2.1	-2.2	-3.4		-1.1
Variscite ⁹	<1.7	0.9	<0.0			<-2.1

See Table 3 footnotes.

Table 4: Reducing plumes; comparison of effluent and plume chemistry.

TABLE 5

	Effluent Alkalinity (meq/L)	Alkalinity Consumed by NH ₄ ⁺ Oxidation (meq/L)
Long Point 1	9.8	-9.7
Langton	9.0	-19
Paradise	8.0	-8.3
Killarney	7.2	-16
Long Point 2	7.0	-8.1
Harp 1	6.2	-9.9
Cambridge	5.2	-2.7
Muskoka	4.0	-4.9
Delawana	2.9	-2.4

Table 5: Alkalinity of septic tank effluent compared to alkalinity consumption expected from oxidation of effluent NH₄⁺ (Data from Tables 3 and 4).

OXIDIZING PLUMES - PO₄ - P

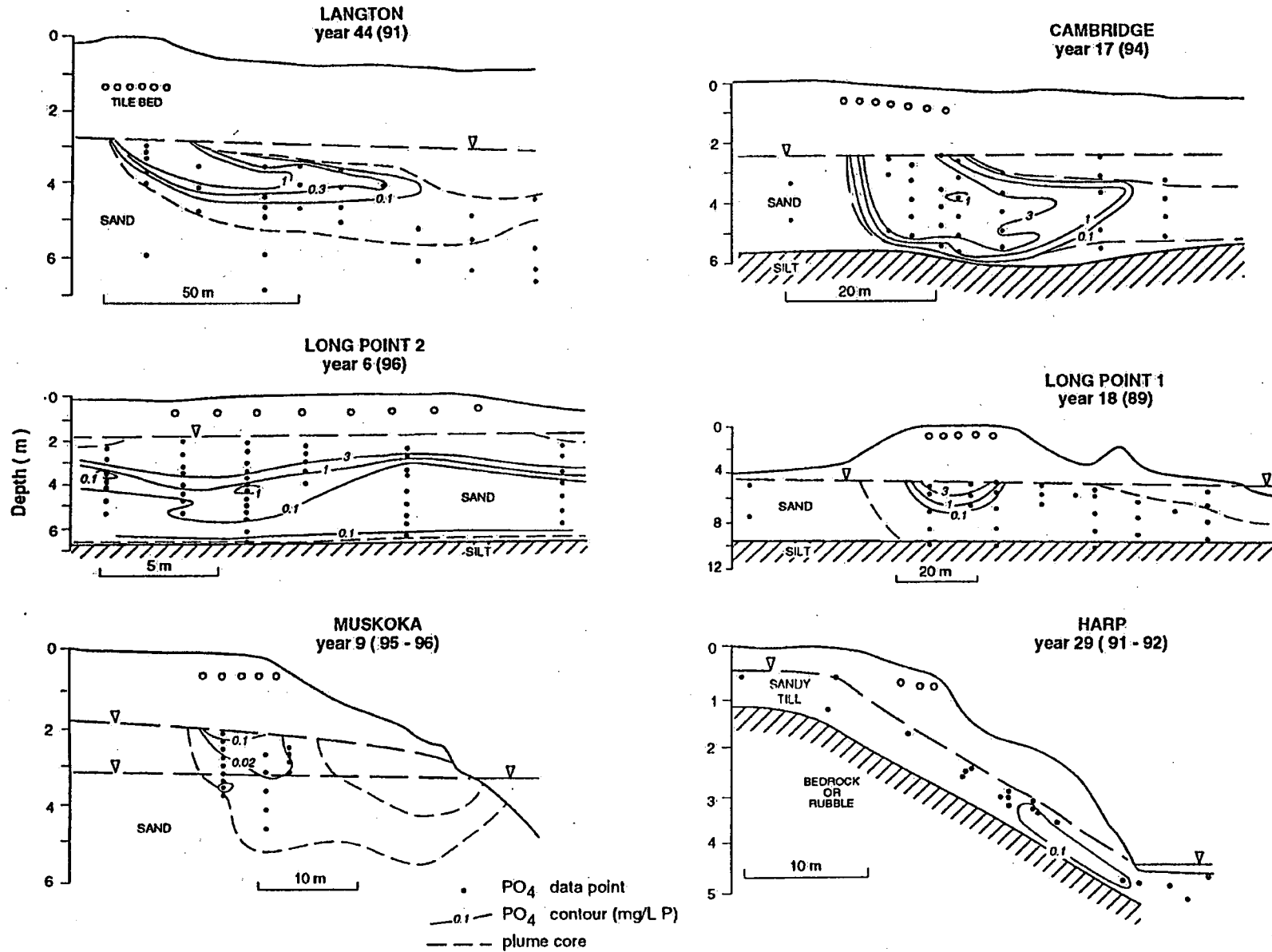


Figure 1. Phosphate zones in six oxidizing septic system plumes in central Canada. Dashed lines denote plume boundaries defined by mobile solutes (Cl⁻, Na⁺, NO₃⁻).

REDUCING PLUMES - PO₄-P

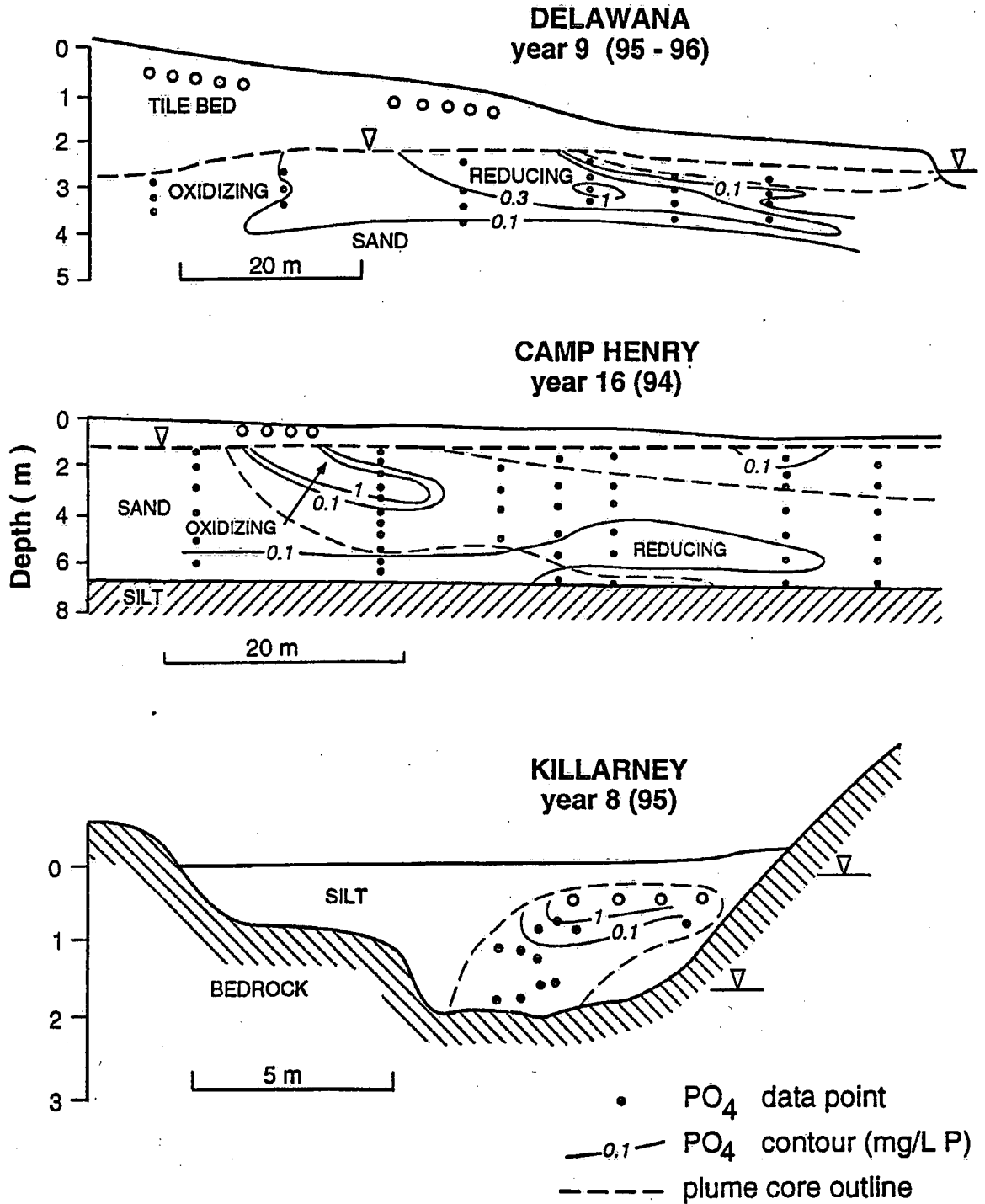


Figure 2. Phosphate zones in three reducing septic system plumes in central Canada. (Note: At Delawana and Camp Henry sites, reducing zones are characterized by Eh < 200 mv and are NH₄⁺ rich; adjacent oxidizing zones have Eh > 300 mv and are NO₃⁻ rich).

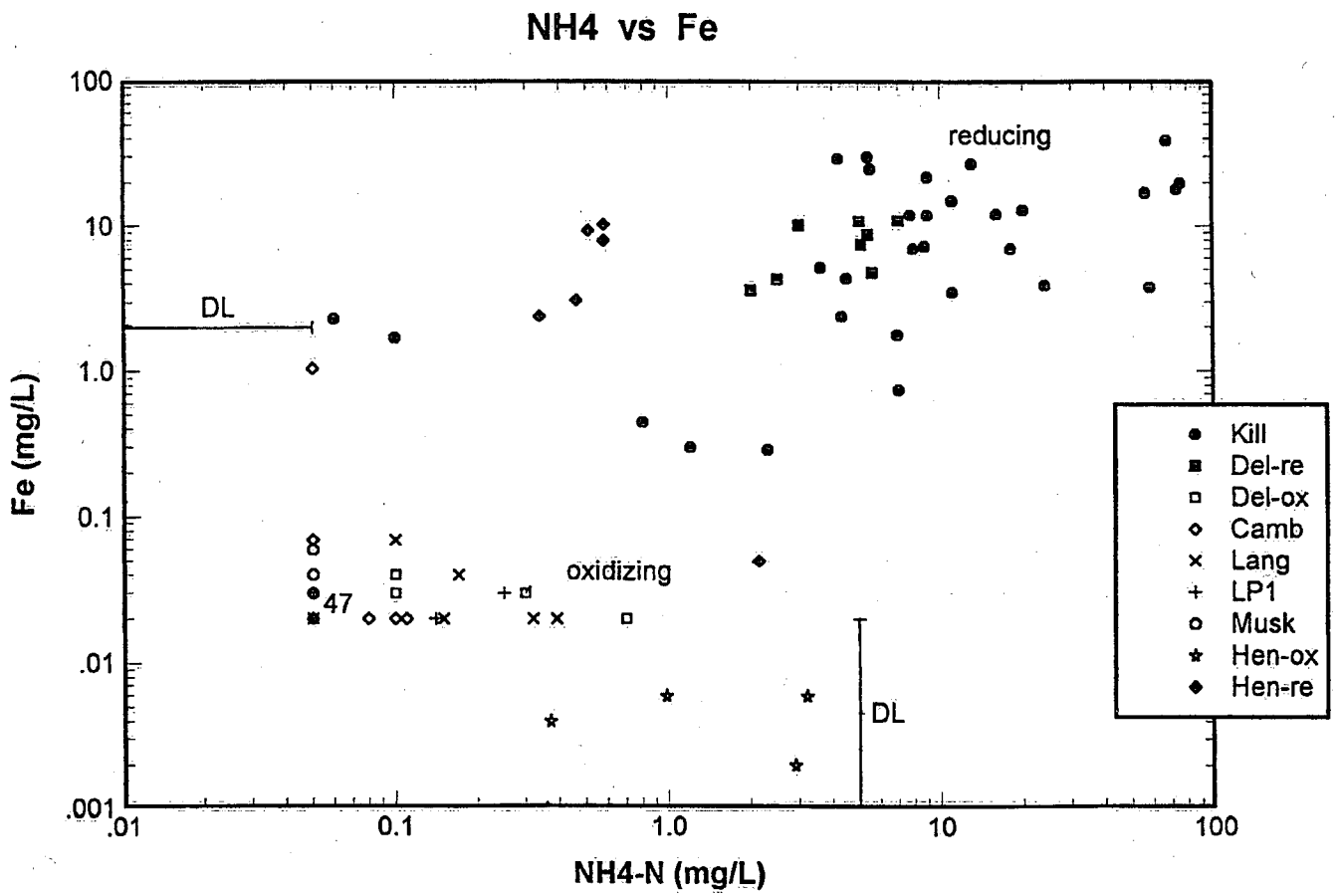


Figure 3. Comparison of NH_4^+ and Fe concentrations in oxidizing (open symbols) and reducing (closed symbols) plume core zones.

Septic Tank Effluent

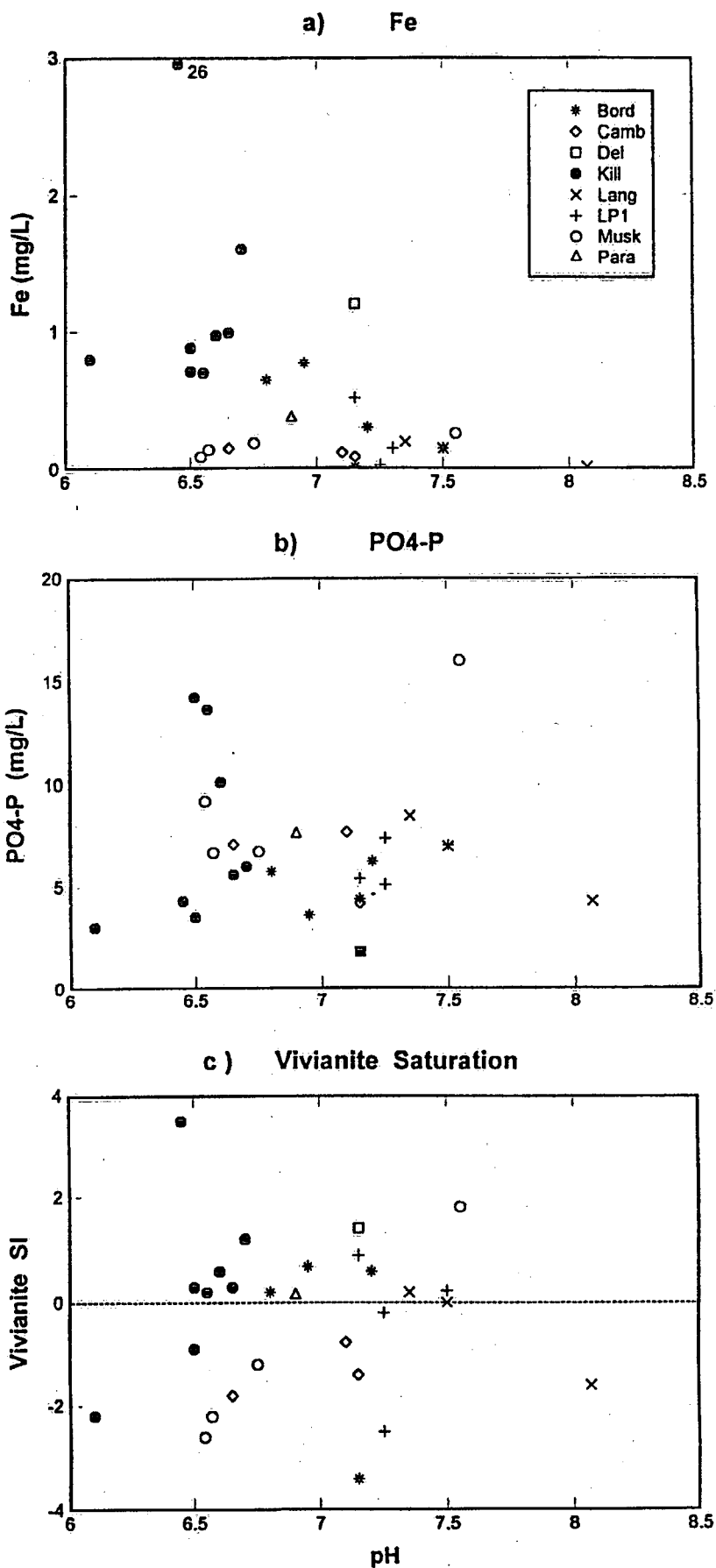


Figure 4. Vivianite saturation indices in septic tank effluent in relation to Fe and PO₄ concentrations.

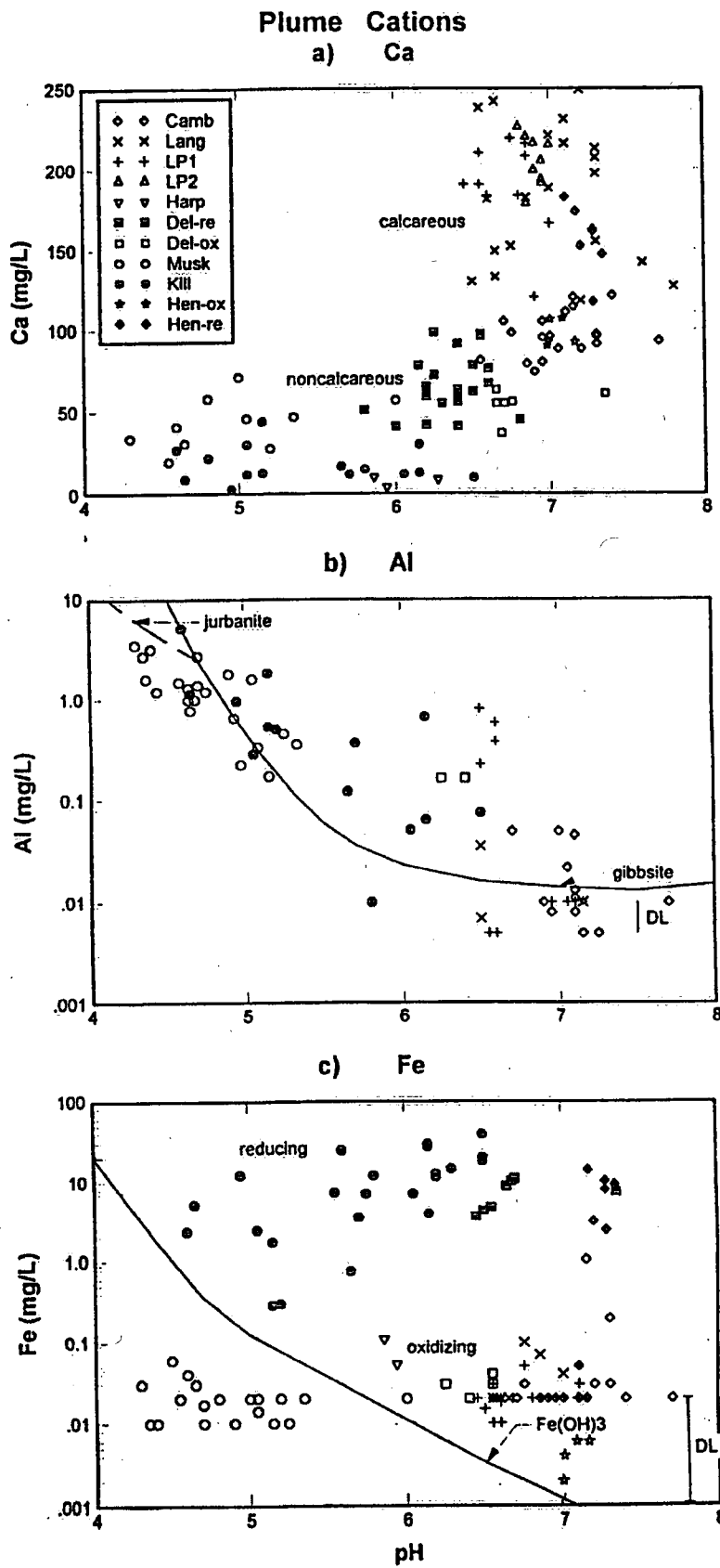
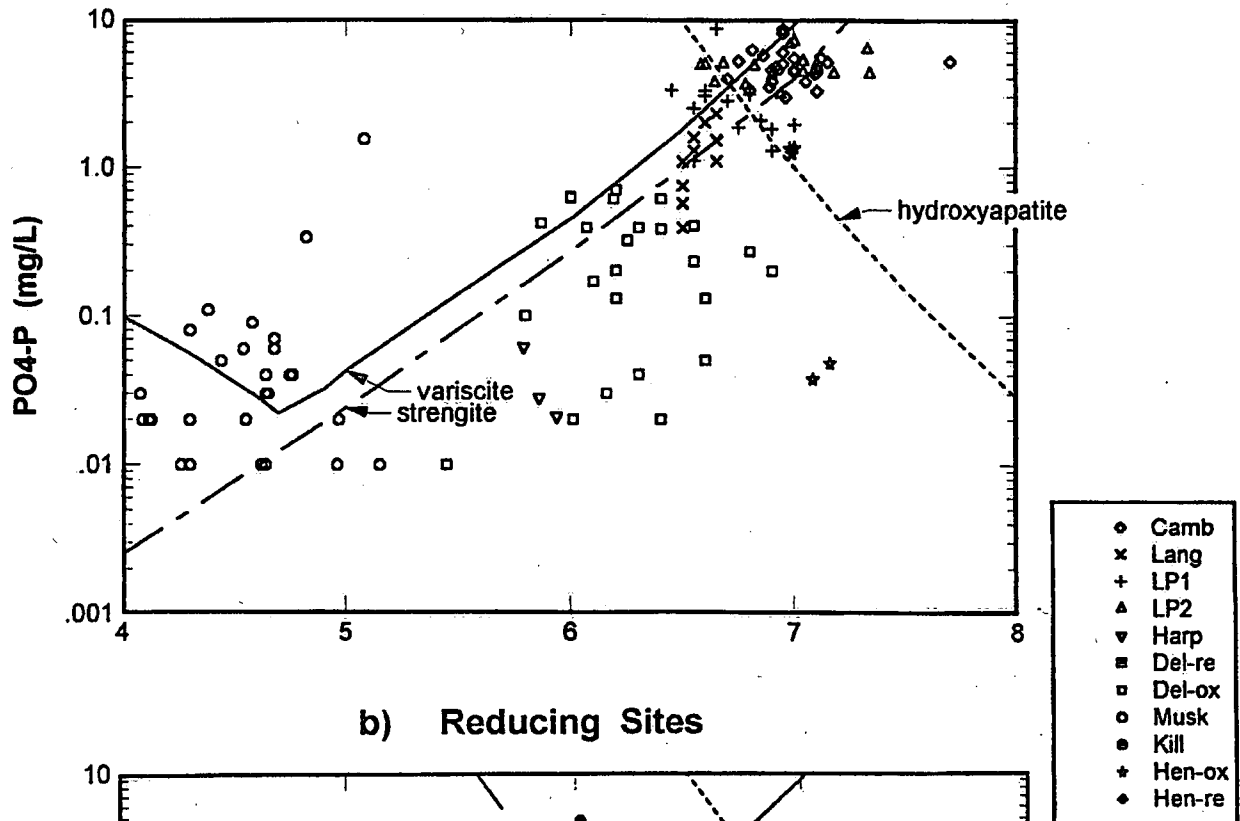


Figure 5. Concentrations of several cations (Ca, Al, Fe) that may react with PO_4 in septic system plumes. Closed symbols denote reducing plumes, open symbols denote oxidizing plumes. Al concentrations are compared to the gibbsite/jurbanite solubility curve calculated using Muskoka plume water composition and Fe concentrations are compared to the amorphous $\text{Fe}(\text{OH})_3$ solubility curve calculated using Cambridge plume water composition.

PLUME PHOSPHATE CONCENTRATIONS

a) Oxidizing Sites



b) Reducing Sites

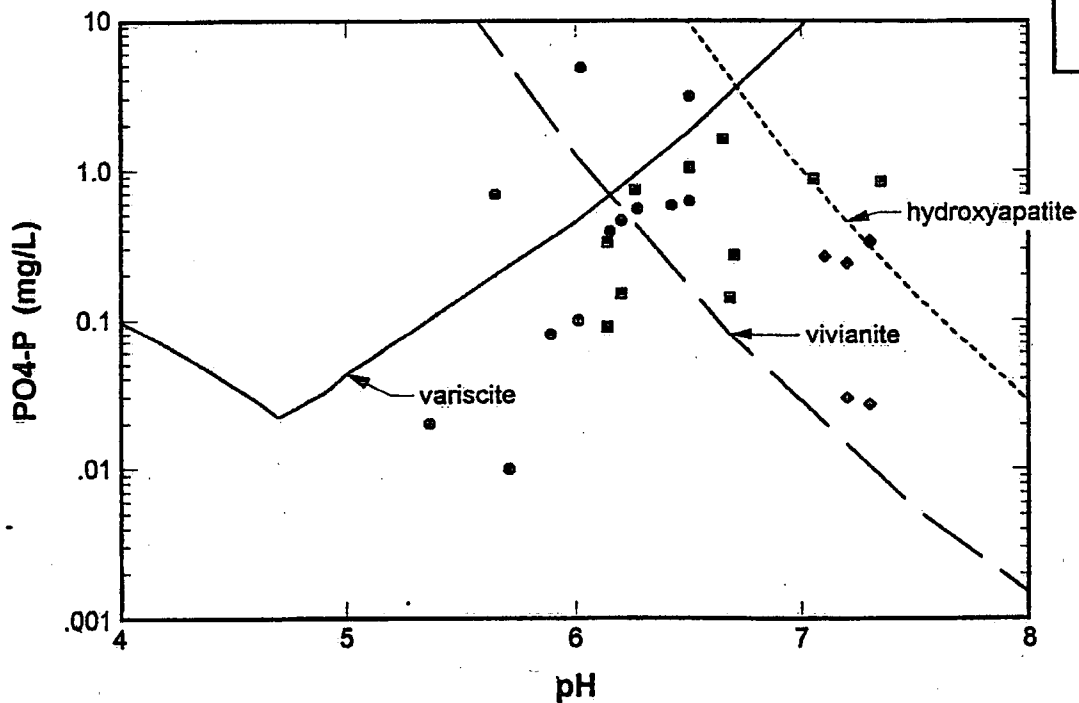


Figure 6. Phosphate concentrations in proximal plume core zones compared to solubility curves for hydroxyapatite, strengite, variscite and vivianite for a) oxidizing and b) reducing plumes. Included are recent data from proximal plume core zones. Hydroxyapatite curve calculated using Cambridge plume water composition ($\text{Ca}^{2+} = 74 \text{ mg/L}$); vivianite curve calculated using Delawana reducing plume water compositions ($\text{Fe} = 10 \text{ mg/L}$); strengite curve calculated using Cambridge plume water composition assuming equilibrium with amorphous $\text{Fe}(\text{OH})_3$; variscite curve calculated using Muskoka plume water composition assuming equilibrium with gibbsite at $\text{pH} > 4.9$ and jurbanite at $\text{pH} < 4.9$.

Environment Canada Library, Burlington



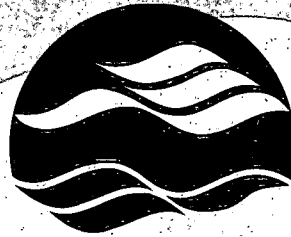
3 9055 1017 7245 6

PRINTED IN CANADA
IMPRIMÉ AU CANADA



ON RECYCLED PAPER
SUR DU PAPIER RECYCLÉ

National Water Research Institute
Environment Canada
Canada Centre for Inland Waters
P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada



**NATIONAL WATER
RESEARCH INSTITUTE**
**INSTITUT NATIONAL DE
RECHERCHE SUR LES EAUX**

Institut national de recherche sur les eaux
Environnement Canada
Centre canadien des eaux intérieures
Case postale 5050
867, chemin Lakeshore
Burlington, Ontario
L7R 4A6 Canada

National Hydrology Research Centre
11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

Centre national de recherche en hydrologie
11, boul. Innovation
Saskatoon, Saskatchewan
S7N 3H5 Canada



Environment Canada **Environnement Canada**

Canada