

94-21

Environment Canada

Water Science and
Technology Directorate

Direction générale des sciences
et de la technologie, eau
Environnement Canada

Adsorption and Mineralization of Phosphate from
Septic System Effluent in Aquifer Materials

By:

C. Ptacek, D. Blowes, W. Robertson, M. Baker

TD
226
N87
No. 94-
21

94-21

Ptacek, C.J., Blowes, D.W., Robertson, W.D., and Baker, M.J., 1994. Adsorption and mineralization of phosphate from septic system effluent in aquifer materials. Proceedings of the Waterloo Centre for Groundwater Research Annual Septic System Conference, "Wastewater Nutrient Removal Technologies and Onsite Management Districts", Waterloo Ontario, June 6, 1994, pp. 25-44.

Management Perspective

The release of nutrients and other dissolved constituents from septic system tile beds is a common occurrence in humid, temperate climates. This release can lead to the development of large plumes of nonpotable groundwater containing elevated concentrations of nitrate, ammonia, phosphate and other dissolved constituents. Discharge of this septic system leachate to surface water bodies can lead to the development of eutrophic conditions in the receiving waters. Geochemical mechanisms controlling the movement of septic-system derived phosphate in aquifer materials below tile beds are evaluated. Detailed geochemical studies conducted at two field sites are presented to illustrate the highly variable behaviour of phosphate in aquifer materials. At one site, groundwater concentrations of phosphate exceed 5 mg/L up to 20 m downgradient of the tile bed. This phosphate is relatively mobile, moving at a velocity 1/20 of the groundwater flow rate. At a second, higher use site, groundwater concentrations of phosphate are generally < 1 mg/L adjacent to the tile bed area and decline to levels < 0.05 mg/L within 20 m of the tile-bed area. An in situ technique for treating groundwater containing elevated concentrations of phosphate is presented. This technique involves the use of porous reactive geochemical barriers that are installed vertically in the path of the flowing groundwater by excavating the aquifer materials and replacing them with porous materials that chemically remove the phosphate as it moves through the reactive materials. Results of laboratory column tests suggest this treatment system has the potential to effectively remove phosphate from simulated groundwater (>95% removal) at representative groundwater flow rates for sustained periods. Larger scale performance of this system for removing phosphate from groundwater at a septic system site in southern Ontario currently is being evaluated.

Adsorption and Mineralization of Phosphate from Septic System Effluent in Aquifer Materials

Carol J. Ptacek¹, David W. Blowes², William D. Robertson², and Michael J. Baker²

*¹National Water Research Institute
Environment Canada
Burlington, Ontario
L7R 4A6*

*²Waterloo Centre for Groundwater Research
University of Waterloo
Waterloo, Ontario
N2L 3G1*

Introduction

The release of nutrients from septic systems to groundwater and adjacent surface water bodies is a common occurrence in humid, temperate climates. The principal nutrient released from septic system beds is nitrogen, but in some cases phosphorous can also migrate long distances from the septic system source (Harman, 1992). The movement of nitrogen away from the septic beds is controlled by a series of reactions. These reactions typically follow the sequence of organic-matter and NH_4^+ oxidation in the unsaturated zone to release NO_3^- , followed by removal of NO_3^- through denitrification reactions below the water table (e.g., Robertson and Cherry, 1992). Robertson and Cherry describe sites where the oxidation of NH_4^+ above the water table is incomplete, leading to its direct release to the groundwater zone, and sites where denitrification of NO_3^- is incomplete in the groundwater zone. At some sites NO_3^- can be highly mobile, moving at approximately the same rate as the flowing groundwater.

The second principal nutrient derived from septic system effluent is phosphorous. The geochemical mechanisms controlling the transport of phosphorous differ substantially from those controlling nitrogen. In the unsaturated zone, organic-bound P and soluble

P, generally in the form of PO_4 , are released directly from the septic system beds. Both forms are biologically utilized, and a high degree of attenuation typically is observed in the near-surface soil zone (Reneau and Perry, 1976). However, some soluble P forms can be released to the groundwater zone, typically as ortho-phosphate (PO_4). Based on the analysis of a large number of groundwater samples collected in the vicinity of septic system leaching beds, several authors (e.g., Sawhney and Starr, 1977; Jones and Lee, 1979) concluded that PO_4 does not generally migrate long distances from septic beds, with decreases in PO_4 concentrations of more than 95% of the influent concentration being common. There are sites, however, where PO_4 has been observed to migrate long distances from the septic system source area. The release of even very low concentrations of PO_4 can lead to the development of eutrophic conditions in surface water bodies (Schindler, 1977; Pictcairn and Hawkes, 1973). Phosphorous is a key element controlling the growth of algae and plants in aquatic ecosystems. Algae require from 0.001 - 0.01 mg/L to grow; above 0.5 mg/L, P is no longer a limiting nutrient (Tomson and Vignona, 1984). Studies evaluating the geochemical mechanisms controlling PO_4 migration in aquifer materials provide information that can be used to evaluate the migration of PO_4 , both in the short and long term.

A summary of principal geochemical mechanisms controlling the migration of PO_4 in aquifer materials is described here. Results of two case studies on PO_4 migration in the groundwater zone underlying and adjacent to septic beds, which indicate highly different behaviour for PO_4 attenuation, are presented. Also presented are preliminary results of an *in situ* treatment system for removing phosphate from flowing groundwater in areas where natural attenuation processes are insufficient to maintain low PO_4 concentrations.

Geochemical Background

Geochemical Conditions in the Vicinity of Septic Systems

When septic system effluent enters the subsurface a series of processes occurs, both physical and chemical, which leads to the development of plumes of dissolved constituents downgradient from the source area (Figure 1). These processes include physical advection and dispersion of the septic system leachate and chemical transformation of the components. As the effluent migrates through the unsaturated zone, a series of oxidation reactions occurs transforming the reduced septic system effluent components to oxidized species (Figure 2). This altered effluent, together with rainfall and snowmelt, migrate downward to the groundwater zone. Once in the groundwater zone, it migrates downward and laterally from the site in the direction of the flowing groundwater (in unconfined aquifers, in the direction of the sloping water table).

In the unsaturated zone, the principal oxidant of the organic carbon contained in the septic system effluent is gaseous oxygen. Below the water table, transport of O_2 is in the dissolved form. The solubility of O_2 is low (8-13 mg/L at typical groundwater temperatures), therefore extensive oxidation of septic effluent by O_2 is limited to the unsaturated zone. If septic effluent is incompletely oxidized in the unsaturated zone, its further oxidation in the saturated zone is limited by mixing with dissolved O_2 at the fringes of the septic effluent plume or by the extent of oxidation by other oxidant sources (e.g., Fe(III) and Mn(IV) oxides and (oxy)hydroxides). Attenuation of dissolved PO_4 along the groundwater flow path is highly dependent on the changing geochemical conditions that result from these oxidation reactions. Changes in pH and alkalinity occur along the flow path. Degradation of the organic wastes in the effluent leads to the production of CO_2 , alkalinity, and alteration of the pore-water pH. These chemical changes also influence PO_4 migration from the source area.

Geochemical Controls on Phosphate Mobility

The discussion that follows will focus on the principal geochemical mechanisms that potentially can influence the rate of PO_4 migration in the groundwater zone. Specific geochemical mechanisms controlling the movement of PO_4 in the septic system environment include adsorption/desorption and precipitation/dissolution reactions.

Adsorption Reactions

Phosphate potentially can be adsorbed by a number of minerals and amorphous phases present in the aquifer solids. Phosphate is a protolytic acid with PO_4^{3-} protonating to form HPO_4^{2-} , $H_2PO_4^-$, and $H_3PO_4^0$ (Table 1). Polyphosphate species, derived from detergents and other sources, may also be present. This discussion will focus on the more dominant orthophosphate species. Under normal groundwater pH conditions, the dominant forms of PO_4^{3-} are HPO_4^{2-} and $H_2PO_4^-$, both of which are anions. The adsorption of these anions requires the presence of positively-charged mineral surfaces. The surface charge on minerals is typically pH-dependent, and is closely related to the zero-point of charge of the mineral (Stumm and Morgan, 1981; Table 2). For a clean mineral surface, on which no adsorption has occurred, the pH of the zero point of charge is the pH at which the mineral surface has equal positive and negatively charged sites. Above this pH, negative sites dominate and below this pH positive sites dominate. Because PO_4 occurs as an anion under normal groundwater pH conditions, solids that are positively charged in the intermediate pH range become the dominant candidates for PO_4 adsorption. The principal solids present in aquifers that meet these criteria include Al-, Mn(IV)- and Fe(III)-containing oxides and (oxy)hydroxides and some clay minerals.

Studies on the adsorption of PO_4 onto mineral surfaces indicate that the adsorption process is pH-dependent and that PO_4 is strongly adsorbed, referred to as 'specific' or 'inner sphere' adsorption (Hingston et al., 1967, 1972; Parfitt, 1978; Hingston, 1981; Goldberg and Sposito, 1985). The process leads to a tight bond between the PO_4

species and the mineral, which, in some cases, is so strong that the surface charge is substantially altered as a result of the adsorption process. Under very low-pH conditions ($\text{pH} < 2.2$), H_3PO_4^0 , a neutral species, is the dominant form of phosphate (Table 1), leading to a decrease in PO_4 adsorption under very acidic conditions. The result, therefore, is an adsorption envelope with the maximum dependent on the dissociation constants for PO_4 and the surface charge of the mineral.

In natural soils and sediments, oxides and (oxy)hydroxides of Al, Mn(IV), and Fe(III) are common, as are clay minerals. When partially oxidized septic-system leachates rich in organic carbon enter a soil or aquifer system, there is the potential for the reductive dissolution of oxidized solids, in particular, Mn(IV)- and Fe(III)-bearing solids. Reduction of Mn(IV)- and Fe(III)-bearing solids leads to increased concentrations of dissolved Fe(II) and Mn(II). If a large unsaturated zone is present, this Fe(II) and Mn(II) may reoxidize, leading to the reprecipitation of Fe(III)- and Mn(IV)-bearing solids further along the flowpath. In the case of an oxygen-limited septic system, where reducing conditions are maintained to the water table, dissolved organic carbon and reduced Fe(II) and Mn(II) can enter the groundwater zone and migrate long distances in the groundwater zone (Robertson and Blowes, 1994). The release of these components from septic systems results in the migration of redox fronts, analogous to that observed in a landfill setting by Lingkilde and Christensen (1992) and Heren and Christensen (1994). As reductive dissolution reactions occur, some of the natural PO_4 attenuation capacity of the soil or aquifer solids may be depleted. To predict the rate of movement of the zones of stability for the mineral adsorbents, a complete understanding of the redox buffering capacity of the system is required. Various methods for assessing redox buffering capacity in aquifer materials are currently being developed (*e.g.* Heren and Christensen, 1994).

Other solids, including Al-containing solids and clays are expected to be more stable under reducing conditions. If present, these solids can contribute to the PO_4 adsorption capacity, even if the system is highly reducing.

Precipitation/Dissolution Reactions

The second major process influencing the migration of PO_4 in natural systems is the precipitation and dissolution of PO_4 -containing solid phases. There are numerous PO_4 phases that occur in nature (Nriagu, 1984), the most common being Al, Fe, and Ca solids (Table 3). Because of the protolytic nature of PO_4 , and because many of these phases contain OH and CO_3 , consideration of the groundwater pH conditions in the changing septic system environment is needed to determine their solubility. As well, because some of the low solubility phases contain cations in multiple oxidation states, information on the changing Eh conditions are also required.

Solids commonly proposed to be major controls on dissolved PO_4 concentrations in natural systems include hydroxyapatite, fluorapatite, strengite, variscite and vivianite,

or closely related amorphous and hydrated solid phases (Table 2). The latter two phases contain Fe in the Fe(III) and Fe(II) forms, respectively. In lake sediments, supersaturated conditions with respect to hydroxyapatite have been documented (*e.g.*, Emerson, 1976; Wersin et al., 1991). Under reducing conditions, the formation of vivianite has been proposed to be an important control on PO₄ concentrations (Nriagu and Dell, 1974; Emerson, 1976; Wersin et al., 1991).

Attenuation of PO₄ can be through a combination of geochemical processes. There often is a rapid initial uptake through adsorption reactions, followed by a slower mineralization step. For example, initial adsorption of PO₄ by Fe(OH)₃ surfaces can be followed by recrystallization to FePO₄·nH₂O, provided the conditions for its formation are favoured (Stumm and Morgan, 1981). A similar series of reactions is expected for adsorption of PO₄ onto Al oxide and (oxy)hydroxide surfaces. Following the adsorption step, recrystallization to AlPO₄·2H₂O (variscite) may also be expected. Similarly for the PO₄ carbonate phases, precipitation of a structurally less complex amorphous precursor, such as brushite (CaHPO₄·2H₂O) or octacalcium phosphate (Ca₈H₂(PO₄)₆·5H₂O), is expected to occur, followed by the gradual conversion to stable hydroxyapatite (Posner et al., 1984).

Adsorption reactions are usually rapid. There is, however, a finite adsorption capacity for most aquifer materials, unless adsorbent surfaces are being freshly regenerated through other geochemical processes. Precipitation reactions that remove PO₄ through conversion of a preexisting phase in the aquifer solids also have a finite capacity. Geochemical conditions that initially favour the removal of PO₄ through precipitation and adsorption reactions, such as in the advancing front of a high PO₄ plume, may later change to conditions that favour the redissolution or desorption of PO₄. Structural uptake of PO₄ in a highly insoluble solid phase will lead to the highest likelihood that release rates will be low over the long term. The exception is if the insoluble phase is not stable under changing Eh conditions and is oxidized, such as vivianite, or reductively dissolved, such as FePO₄·2H₂O. Predictions of PO₄ mobility, both short and long term, need to address the geochemical evolution of the complete solid and aqueous system at a given site.

Case Studies

We here discuss two cases, one where septic leachate is almost completely oxidized in the unsaturated zone prior to its infiltration into the groundwater zone, and the second where the septic system leachate is only partially oxidized. In the case of nearly complete oxidation, the effluent contains primarily highly oxidized species (NO₃⁻ and PO₄) and recalcitrant organic matter. In the case of incomplete oxidation, the effluent contains a combination of reduced species (organic matter, NH₄⁺, Fe²⁺ and Mn²⁺) and oxidized species (CO₂, NO₃⁻, NO₂⁻, PO₄³⁻, SO₄²⁻ and O₂). Infiltration of this water type into an aquifer containing oxidized solids will lead to the continued oxidation of

the septic leachate below the water table.

Cambridge Site

At the Cambridge site, Cambridge, Ontario, domestic wastewater from a single household has been disposed of using a conventional septic system since 1977 (Robertson et al., 1991). The infiltration bed is positioned in a 2 m-thick unsaturated zone overlying an unconfined aquifer of carbonate-rich medium sand. Groundwater flow in the aquifer is primarily horizontal at a rate of about 20 m/yr. In 1987 (year 10 of operation), a detailed groundwater monitoring network revealed the presence of a long, narrow contaminant plume (> 130 m in length) that was little affected by dispersive dilution. During monitoring in year 10, a PO_4 plume was delineated in the groundwater zone, but its distribution was limited to the area immediately underlying the infiltration bed (Figure 3).

Subsequent monitoring in year 14 (1991) and 17 (1994), however, revealed slow but progressive advancement of the PO_4 plume. During the latter monitoring episode, the PO_4 plume ($\text{PO}_4\text{-P} > 1 \text{ mg/L}$) had advanced to a location 20 m downgradient from the infiltration bed (Figure 3). The apparent PO_4 plume migration velocity of about 1 m/yr represents retardation by a factor of 20, compared to the groundwater velocity. Phosphate concentrations in the plume reach a maximum of about 5 mg/L as P, representing a substantial fraction (70%) of the amount found in the raw wastewater (about 7 mg/L as P). Plume behaviour during long-term monitoring suggests that PO_4 mobility in the groundwater zone at this site is controlled primarily by sorption processes.

Pelee Site

A study was initiated to determine the fate of septic-system derived effluent in the shallow groundwater zone at Point Pelee National Park, near Leamington, Ontario. The Park is located on a narrow peninsula extending southward into Lake Erie. A groundwater sampling network was installed in the vicinity of a septic-system tile bed located at Camp Henry, to determine the groundwater flow-field in the vicinity of the bed and to obtain samples of groundwater for geochemical analysis. The tile bed at Camp Henry was installed in the 1930's and has been receiving wastewater from a washroom facility on a variable basis since then. Below the tile bed is a poorly graded coarse sand unit containing thin lenses of pebbly material (upper 7-8 m) which overlays a dense clay unit. The maximum population is estimated to be 50, and the maximum day water use is estimated to be 2500 L/day (MacLaren Engineers, 1989).

In winter, 1994, a series of groundwater samples were collected and analysed to determine concentrations of NO_3+NO_2 , NH_4 , o-PO_4 , DOC, SO_4 , Cl, and conductance. The water table below the tile bed was < 1 m below the ground surface at the time of sampling. A plume of contaminated groundwater, as delineated by elevated concentrations of one or more of the nutrients, has developed downgradient

in an easterly direction from the tile bed. Results from piezometer nest CH14, 1.5 m north of the northern edge of the tile-bed, and three piezometer nests along a cross-section approximately parallel to the groundwater flow direction, CH7, 3.7 m east, CH5, 18.3 m east, and CH22, 37.8 m east of the eastern edge of the tile-bed. The location of the septic system plume at these piezometer nests, as indicated by increased specific conductance measurements, is 1.5 - 6.0 m below the ground surface at location CH14 and along the cross-section. The distribution of dissolved constituents (DOC, Cl, NO₃ and NH₄) derived from the septic system indicates water originating from the septic system has migrated beyond the location of piezometer nest CH22.

The highest concentrations of PO₄ are observed in the shallowest sampling points at piezometer nest CH14 (1 m) and at greater depth (1.5 m - 4.0 m) at CH7. Maximum PO₄ concentrations are on the order of 0.3 mg/L PO₄-P. At greater distance (CH5 and CH22), PO₄ concentrations decrease to < 0.05 mg/L PO₄-P, suggesting PO₄ is being attenuated along the flow path. Persistence of high concentrations of DOC and NH₄ suggest that the septic-system effluent at this site is not completely oxidized in the unsaturated zone.

The behaviour of PO₄ at the Camp Henry site, and reduced condition of the septic system effluent in the groundwater zone, contrasts with the extensively oxidized effluent at the Cambridge site. The differences in geochemical environments at these two sites suggest that different PO₄ attenuation mechanisms may be active. The low mobility of PO₄ observed at the Pelee site is similar to observations made at other sites receiving PO₄-containing wastewaters. For example, at a site where secondary-treated sewage water was disposed of on surface sand beds in Cape Cod, MA, PO₄ was attenuated to a much greater extent than other sewage related constituents, including detergents, NO₃, NH₃ and Cl and Na (LeBlanc, 1985).

In-situ Treatment of PO₄-Contaminated Groundwater

At sites where there is little natural attenuation capacity in the aquifer materials, or where this capacity has been exceeded, release of PO₄ to nearby streams and lakes can lead to the development of eutrophic conditions in these water bodies (Schindler, 1977; Pictcairn and Hawkes, 1973). Studies on the temporal behaviour of PO₄, such as at the Cambridge site, suggests that, if no action is taken, the distance of migration of PO₄ from the source area will increase with time. There are a number of possible remedial measures that can be taken. Some options include the use of alternative septic system designs that maximize P removal from the septic system effluent prior to its release to the groundwater zone, relocation of the septic beds to maximize the use of the natural attenuation capacity of the local aquifer materials, and the use of aquifer amendments in the form of *in situ* porous reactive walls to increase the capacity of the aquifer materials to attenuate PO₄. The first two options do not address the problem of

PO₄ plumes that have already formed and are now migrating. The last option is particularly valuable at sites where large PO₄ plumes already exist, or at sites where the natural attenuation capacity of local materials are inadequate for the attenuation of PO₄.

We have been conducting studies on the use of aquifer amendments to enhance the removal of inorganic contaminants from flowing groundwater (Blowes and Ptacek, 1992, 1994; Blowes et al., 1994). These amendments are added to the aquifer materials in the form of porous reactive walls that are installed in the path of the contaminant plumes (Figure 5). The contaminants are removed from the flowing groundwater as they pass through the reactive materials.

To be suitable candidates for use in a reactive wall, the solid phase must be sufficiently reactive to remove the contaminant within the residence time of the contaminant in the wall. The solid phase must also be sufficiently stable that it remains active and in place for a period of decades to make the technique economically viable. After the reactive capacity is exhausted, the material can be replaced if necessary.

For the treatment of PO₄ using a porous reactive wall, two materials have been evaluated as potential candidates for use as the solid-phase mixture (Baker, 1993). These materials were a Fe(III) (oxy)hydroxide adsorbent, and calcium carbonate in the form of crushed agricultural limestone. These materials were evaluated separately, and in combination, for their ability to remove PO₄ from water. Limestone was added to promote the precipitation of a mixed Ca-PO₄ carbonate solid. This precipitation reaction is favoured under intermediate- to basic-pH conditions. The Fe(III) (oxy)hydroxide was added to promote adsorption of PO₄ on the solid surfaces. This adsorption reaction is favoured under slightly acidic to slightly basic pH conditions. The purpose of combining the ferric solid and the limestone was to enhance the removal process over a broader pH range than if either was used alone. Coarse-grained sand was added to the mixture to increase its permeability.

Laboratory batch experiments were conducted for a variety of mixtures of reactive solids. A run in which a combination of solids was used is presented here. For this run, 500 g of 10 mg/L PO₄ (as P) solution was agitated with 2.5 g of Fe(III) (oxy)hydroxide solid, 22.5 g of agricultural limestone and 25 g of quartz sand. A 10 mL aliquot of the water was removed from the reaction flask at selected time intervals and the solution was filtered through a 0.45 μm filter and analyzed for PO₄ concentrations using a colourimetric technique. This run indicated removal of PO₄ by Fe(III)-(oxy)hydroxide was rapid, with > 99.9 % removed within 0.5 hrs (Figure 6). A separate run indicated removal of PO₄ by limestone alone was less rapid, with 96 % removed within 45 hrs. Tests using only Fe(III)-(oxy)hydroxide with quartz sand

yielded results that were similar to those obtained for the mixture combining the Fe(III) solid and limestone.

Laboratory column experiments were conducted to assess the rate of removal of PO_4 under dynamic flow conditions. Columns 15 cm in length and 6.5 cm in diameter were packed with a mixture of the Fe(III) solid (15 wt%), limestone (45 wt%) and quartz sand (50 wt%). Solution containing 10 mg/L PO_4 was pumped through the column at an average linear velocity of approximately 25 cm/day, and the column effluent was sampled at regular time intervals. For the first 50 pore volumes (volume of displaceable water in the packed column) of solution that were displaced, > 99.9 % of the PO_4 was removed from the flowing water (Fig. 7). For the next 400 pore volumes, the removal was less complete, with a slow increase in PO_4 concentration in the column effluent to levels currently approaching 3-7 % of the input solution concentration (93-97 % removal).

Limitations to the application of this PO_4 removal technique include potential clogging of the porous media due to the precipitation of PO_4 -bearing minerals and other solid phases. At sites where highly reducing conditions have developed, the potential for the reductive dissolution of the Fe(III) solids exists. Hindrances to continued access to the reactive surfaces may also limit the long-term effectiveness of this technology. A field trial designed to assess the potential effectiveness of this technology for removing PO_4 in an oxidized septic-system plume is currently underway. Materials suitable for use under reducing conditions also are being evaluated currently.

Conclusions

The principal geochemical mechanisms controlling PO_4 mobility in the subsurface environment include adsorption, precipitation and co-precipitation reactions. In many geochemical environments, interactions between PO_4 and natural soil and aquifer materials can lead to a high degree of PO_4 attenuation. In other geochemical environments, the attenuation of PO_4 by aquifer materials is much less effective at limiting the migration of PO_4 . Case studies demonstrate this variability in PO_4 behaviour. A potential technique for remediating existing plumes of PO_4 , the use of porous reactive walls, is currently being evaluated.

Acknowledgements

We thank J. Voralek, C. Hanton-Fong, A. Crowe, R. McCrea, and J. Harman for their contributions and helpful discussions.

References

- Baker, M.J. (1993) Laboratory investigations into the potential for solid mixtures containing industrial products to remove phosphates from solution. M.Sc. thesis, University of Waterloo, Waterloo, Ontario, 39 pp.
- Blowes, D.W. and Ptacek, C.J. (1992) Geochemical remediation of groundwater by permeable reactive walls: Removal of chromate by reaction with iron-bearing solids. *In* Proceedings Subsurface Restoration Conf., 3rd Internat. Conf. Ground Water Qual. Research, June 21-24, 1992, Dallas, Texas, 214-216.
- Blowes, D.W. and Ptacek, C.J. (1994) Redox curtain for groundwater remediation. US Patent.
- Blowes, D.W., Ptacek, C.J., Jambor, J.L. (1994) Remediation and prevention of low-quality drainage from tailings impoundments. *In* Jambor, J.L. and Blowes, D.W. (Eds.) MAC Short Course Handbook on Environmental Geochemistry of Sulfide Mine-Wastes, Waterloo, Ontario, May, 1994, pp. 365-379.
- Emerson, S. (1976) Early diagenesis in anaerobic lake sediments: chemical equilibria in interstitial waters. *Geochim. Cosmochim. Acta*, 40, 925-934.
- Goldberg, S. and Sposito, G. (1985) On the mechanism of specific adsorption by hydroxylated mineral surfaces: A review. *Commun. Soil Sci. Plant Anal.*, 16(8), 801-821.
- Harman, J. (1992) Impacts on a sand aquifer from a septic system at a school: nitrate, phosphate, and organic carbon. M.Sc. thesis, University of Waterloo, Waterloo, Ontario, 250 pp.
- Heren, G. and Christensen, T.H. (1994) The role of aquifer sediment in controlling redox conditions in polluted groundwater. *In*: Transport and Reactive Processes, Dracos, T.H. and Stauffer, F. (Eds.), Balkema, Rotterdam, pp. 73-78.
- Hingston, F.J. (1981) A review of anion adsorption. *In* Anderson, M.A. and Rubin, A.J. (Eds.) Adsorption of Inorganics at Solid-Liquid Interfaces. Ann Arbor Science, Ann Arbor, Michigan, pp. 51-90.
- Hingston, F.J., Atkinson, R.J., Posner, A.M. and Quirk, J.P. (1967) Specific adsorption of anions. *Nature*, 215, 1459-1461.

- Hingston, F.J., Posner, A.M. and Quirk, J.P. (1972) Anion adsorption by goethite and gibbsite. I. The role of the proton in determining adsorption envelopes. *J. Soil Sci.*, 23, 177-192.
- Jones, R.A. and Lee, F.G. (1979) Septic tank wastewater disposal systems as phosphorous sources for surface waters. *J. Wat. Poll. Cont. Fed.* 51:2764-2775.
- LeBlanc, D.R. (1985) Sewage plume in a sand and gravel aquifer, Cape Cod, Massachusetts. U.S. Geological Survey Water-Supply Paper 2218, 28 pp.
- Lingkilde, J. and Christensen, T.H. (1992) Redox zones of a landfill leachate pollution plume (Vejen, Denmark). *J. Contam. Hydrol.*, 10: 273-289.
- MacLaren Engineers (1989) Evaluation of sewage disposal systems Point Pelee National Park. A report to Environment Canada, Canadian Parks Service.
- Nriagu, J.O. and Dell, C.I. (1974) Diagenetic formation of iron phosphates in recent lake sediments. *Amer. Mineral.*, 59, 934-946.
- Nriagu, J.O. (1984) Phosphate minerals: Their properties and general modes of occurrence. *In: Nriagu, J.O. and Moore, P.B. (Eds.), Phosphate Minerals.* Springer-Verlag, New York, pp. 1-136.
- Parfitt, R.L. (1978) Anion adsorption by soils and soil materials. *Adv. Agron.*, 30., 1-50.
- Pictairn, C.E.R. and Hawkes, H.A. (1973) The role of phosphorous in the growth of *Cladophora*. *Water Res.*, 7, 159-171.
- Posner, A.S., Blumenthal, N.C. and Betts, F. (1984). Chemistry and structure of precipitated hydroxyapatite. *In: Nriagu, J.O. and Moore, P.B. (Eds.), Phosphate Minerals.* Springer-Verlag, New York, pp. 330-350.
- Reneau, R.B., Jr. and Perry, D.E. (1976) Phosphorous distribution from septic tank effluent in coastal plain soils. *J. Environ. Qua.*, 5:34-39.
- Robertson, W.D. and Blowes, D.W. (1994) Major ion and trace metal geochemistry of an acidic septic system plume in silt. *Ground Water*, accepted.
- Robertson, W.D. and Cherry, J.A. (1992) Hydrogeology of an unconfined sand aquifer and its effect on the behaviour of nitrogen from a large-flux septic system. *Appl. Hydrogeol.*, 1:32-43.

- Robertson, W.D., Cherry, J.A. and Sudicky, E.A. (1991) Ground-water contamination from two small septic systems on sand aquifers. *Groundwater*, 29:82-92.
- Sawhney, B.L. and Starr, J.L. (1977) Movement of phosphorous from a septic system drainfield. *J. Wat. Poll. Cont. Fed.* 49:2238-2242.
- Schindler, D.W. (1977) Evolution of phosphorous limitation in lakes. *Science*, 195, 260-262.
- Stumm, W. and Morgan, J.J. (1981) *Aquatic Chemistry*. Wiley-Interscience, New York, NY.
- Tomson, M.B. and Vignona, L. (1984) Precipitation of phosphate minerals in wastewater treatment systems. *In: Nriagu, J.O. and Moore, P.B. (eds.), Phosphate Minerals*, Springer-Verlag, New York.
- Wersin, P., Hohener, P., Giovanoli, R., Stumm, W. (1991) Early diagenetic influences on iron transformations in a fresh-water lake sediment. *Chem. Geol.*, 90, 233-252.

List of Figures

- Figure 1. Schematic diagram showing the development of a plume of dissolved constituents derived from a conventional septic system.
- Figure 2. Schematic diagram showing the sequence of reactions occurring in the vadose zone and groundwater zone in an unconfined aquifer underlying a conventional septic system.
- Figure 3. Distribution of $\text{PO}_4\text{-P}$ (mg/L) along the plume centreline at Cambridge during years 10, 14 and 17 of operation (dashed line represents plume boundary as defined by 40 mg/L Na contour).
- Figure 4. Specific conductance and concentrations of o-PO_4 (mg/L as P) versus depth for groundwater samples collected at three sites downgradient from a high-usage septic bed, Point Pelee National Park.
- Figure 5. Schematic diagram illustrating the use of a porous reactive wall to remove PO_4 from a septic system plume.
- Figure 6. Removal of PO_4 from solution *versus* time by reaction with a solid mixture containing $\text{Fe(III)(oxy)hydroxide}$, agricultural limestone, and quartz sand.
- Figure 7. Laboratory column test results showing normalized concentration of PO_4 in the column effluent water versus normalized time (pore volumes).

Table 1: Acidity constants for phosphate species.

Reaction	pK, 25°C
$\text{H}_3\text{PO}_4 = \text{H}_2\text{PO}_4^- + \text{H}^+$	2.2
$\text{H}_2\text{PO}_4^- = \text{HPO}_4^{2-} + \text{H}^+$	7.0
$\text{HPO}_4^{2-} = \text{PO}_4^{3-} + \text{H}^+$	12.0

Table 2: Common PO_4 minerals.

Phase	Formula
hydroxyl apatite	$\text{Ca}_5(\text{OH})(\text{PO}_4)_3$
fluorapatite	$\text{Ca}_5(\text{PO}_4)_3\text{F}$
carbonate fluorapatite	$(\text{Ca},\text{H}_2\text{O})_5(\text{F},\text{OH})(\text{PO}_4,\text{CO}_3)_3$
strengite	$\text{FePO}_4 \cdot 2\text{H}_2\text{O}$
variscite	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O}$
vivianite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$

Table 3: Zero point of charge for selected solid surfaces (after Stumm and Morgan, 1981).

Material	pH _{zpc}
α -Al ₂ O ₃	9.1
α -Al(OH) ₃	5.0
γ -AlOOH	8.2
α -FeOOH	7.8
γ -Fe ₂ O ₃	6.7
Fe(OH) ₃ (am)	8.5
Fe ₃ O ₄	6.5
δ -MnO ₂	2.8
β -MnO ₂	7.2
SiO ₂	2.0
Feldspars	2-2.4
Kaolinite	4.6
Montmorillonite	2.5
Albite	2.0

List of Figures

- Figure 1. Schematic diagram showing the development of a plume of dissolved constituents derived from a conventional septic system.
- Figure 2. Schematic diagram showing the sequence of reactions occurring in the vadose zone and groundwater zone in an unconfined aquifer underlying a conventional septic system.
- Figure 3. Distribution of $\text{PO}_4\text{-P}$ (mg/L) along the plume centreline at Cambridge during years 10, 14 and 17 of operation (dashed line represents plume boundary as defined by 40 mg/L Na contour).
- Figure 4. Specific conductance and concentrations of o-PO_4 (mg/L as P) versus depth for groundwater samples collected at three sites downgradient from a high-usage septic bed, Point Pelee National Park.
- Figure 5. Schematic diagram illustrating the use of a porous reactive wall to remove PO_4 from a septic system plume.
- Figure 6. Removal of PO_4 from solution *versus* time by reaction with a solid mixture containing Fe(III)(oxy)hydroxide, agricultural limestone, and quartz sand.
- Figure 7. Laboratory column test results showing normalized concentration of PO_4 in the column effluent water versus normalized time (pore volumes).

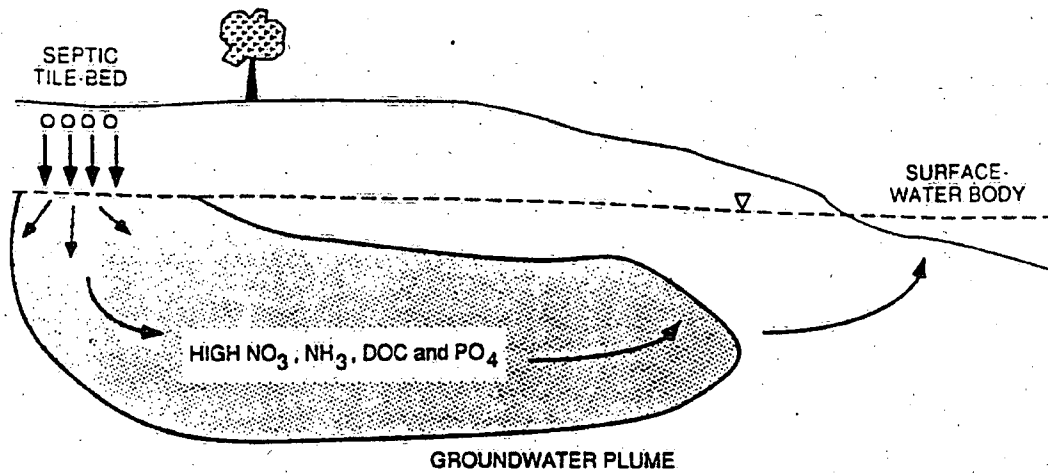


Figure 1. Schematic diagram showing the development of a plume of dissolved constituents derived from a conventional septic system.

SUMMARY OF GEOCHEMICAL REACTIONS

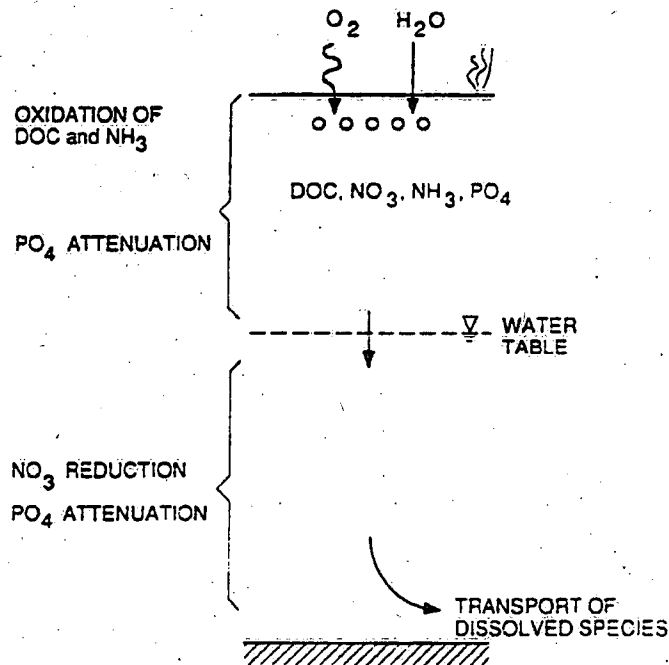
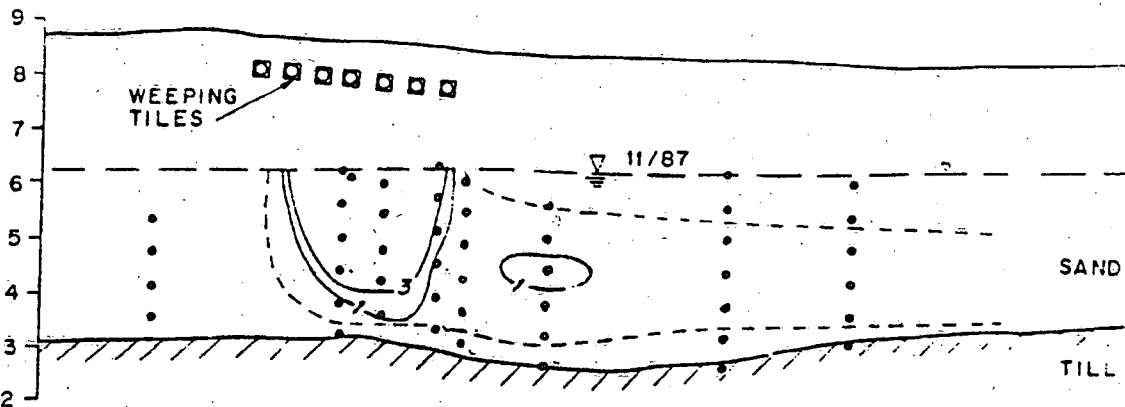
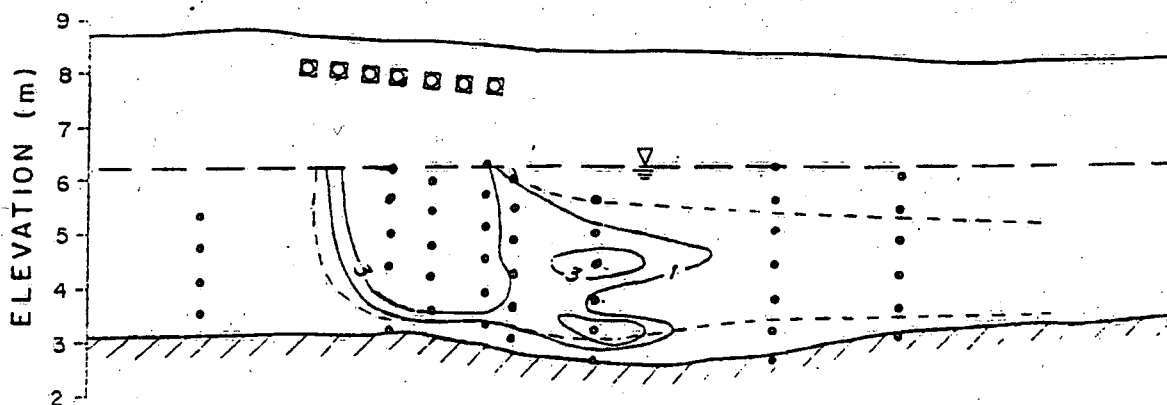


Figure 2. Schematic diagram showing the sequence of reactions occurring in the vadose zone and groundwater zone in an unconfined aquifer underlying a conventional septic system.

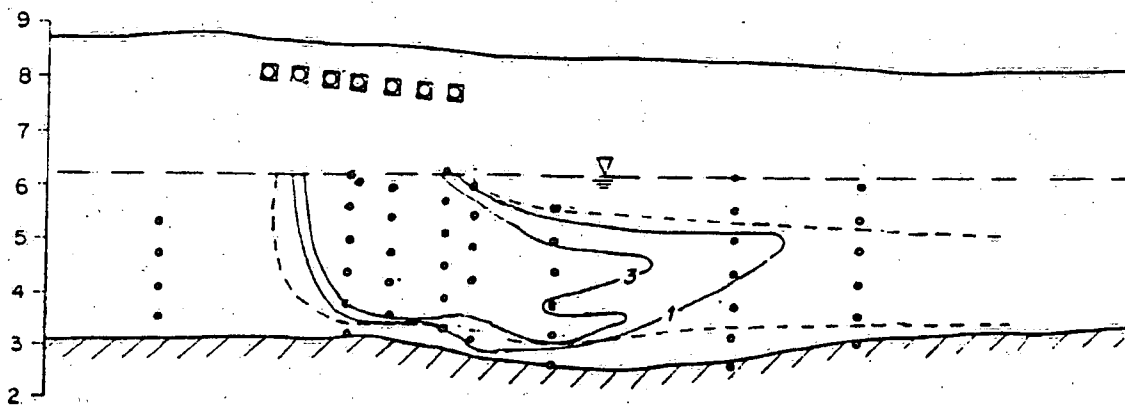
CAMBRIDGE SITE
YEAR 10



YEAR 14



YEAR 17



0 10 20 m

Figure 3. Distribution of $\text{PO}_4\text{-P}$ (mg/L) along the plume centreline at Cambridge during years 10, 14 and 17 of operation (dashed line represents plume boundary as defined by 40 mg/L Na contour).

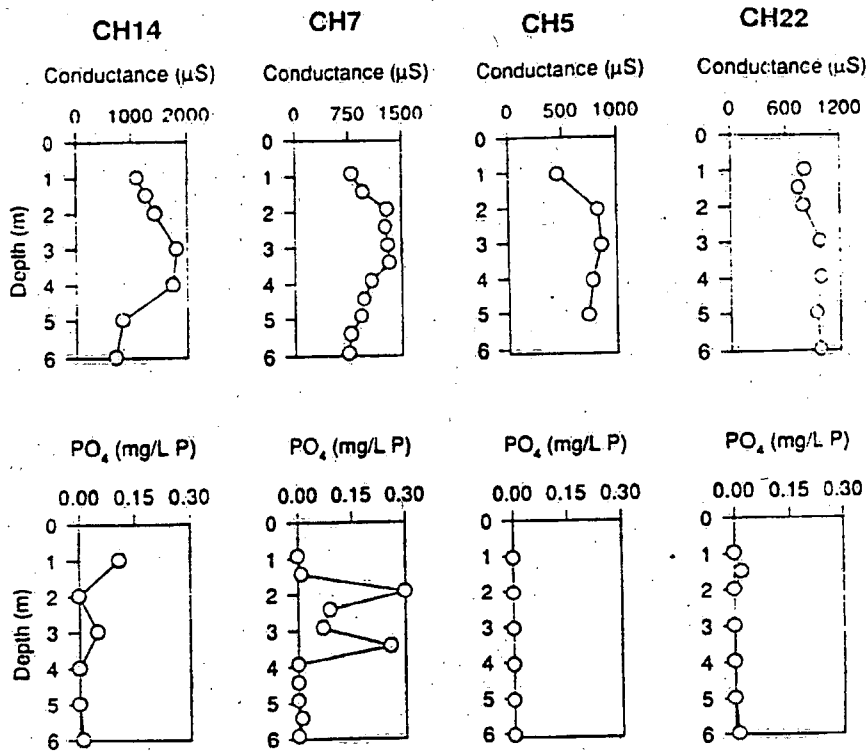


Figure 4. Specific conductance and concentrations of o-PO₄ (mg/L as P) versus depth for groundwater samples collected at three sites downgradient from a high-usage septic bed, Point Pelee National Park.

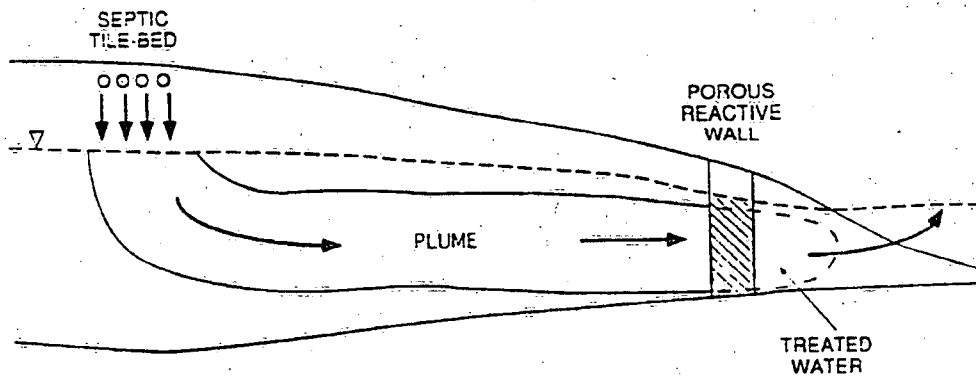


Figure 5. Schematic diagram illustrating the use of a porous reactive wall to remove PO₄ from a septic system plume.

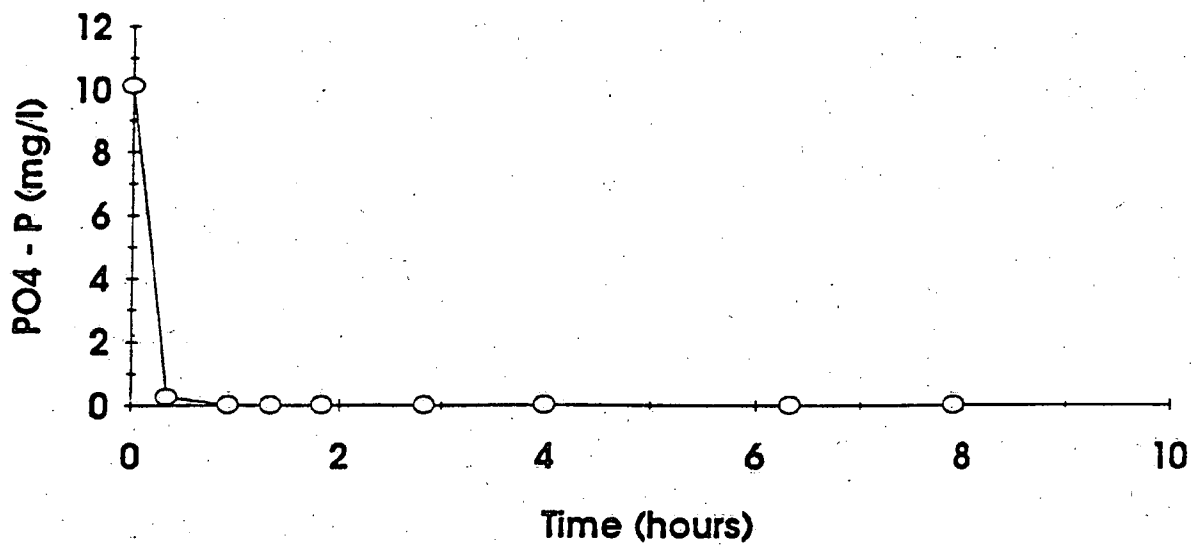


Figure 6. Removal of PO₄ from solution *versus* time by reaction with a solid mixture containing Fe(III)(oxy)hydroxide, agricultural limestone, and quartz sand.

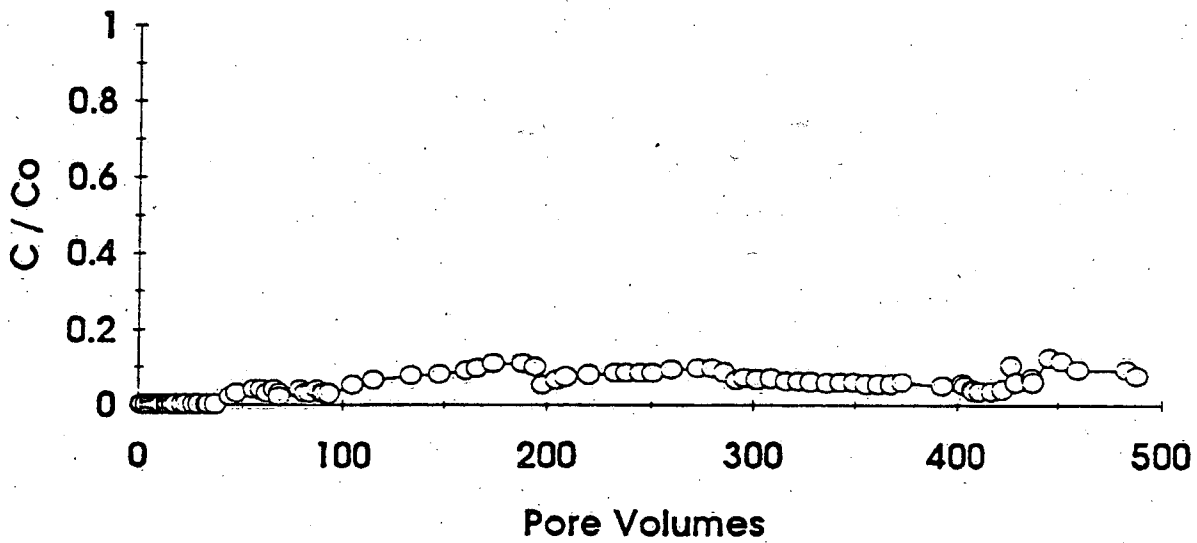


Figure 7. Laboratory column test results showing normalized concentration of PO₄ in the column effluent water versus normalized time (pore volumes).

Environment Canada Library, Burlington



3 9055 1017 7992 3



Environment
Canada

Environnement
Canada

Canada

Canada Centre for Inland Waters

P.O. Box 5050
867 Lakeshore Road
Burlington, Ontario
L7R 4A6 Canada

National Hydrology Research Centre

11 Innovation Boulevard
Saskatoon, Saskatchewan
S7N 3H5 Canada

St. Lawrence Centre

105 McGill Street
Montreal, Quebec
H2Y 2E7 Canada

Place Vincent Massey

351 St. Joseph Boulevard
Gatineau, Quebec
K1A 0H3 Canada

Centre canadien des eaux intérieures

Case postale 5050
867, chemin Lakeshore
Burlington (Ontario)
L7R 4A6 Canada

Centre national de recherche en hydrologie

11, boul. Innovation
Saskatoon (Saskatchewan)
S7N 3H5 Canada

Centre Saint-Laurent

105, rue McGill
Montreal (Québec)
H2Y 2E7 Canada

Place Vincent-Massey

351 boul. St-Joseph
Gatineau (Québec)
K1A 0H3 Canada