97-144

Environment Canada

Water Science and Technology Directorate

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Environnement Canada

Phosphorous adsorption and precipitation in a permable reactive wall: Applications for wastewater disposal systems

By:
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MANAGEMENT PERSPECTIVE

Title: Phosphorous adsorption and precipitation in a permeable reactive wall: Applications for wastewater disposal systems.

Authors: M.J. Baker, D.W. Blowes, and **C.J. Ptacek**

NWRI Publication#: 97-144

Citation: Land Contamination & Reclamation, 1997, Vol. 5, No. 3, pp. 189-193.

EC Priority/Issue: This study supports the ESD issue Conserving Canada's Ecosystems (nutrients). It supports the EC Action Plan "Conserving Canada's Ecosystems" with the focus "Develop and implement strategies to conserve ecosystems". The study was initiated in 1991 and was funded by NSERC and the Waterloo Centre for Groundwater Research.

Current Status: The paper describes the results of laboratory and field tests to assess different reactive mixtures for removing phosphorous from wastewater. The release of phosphorous to surface water bodies is the single-most important factor leading to their eutrophication. The development of cost-effective methods for removing phosphorous from groundwater and wastewater is essential for maintaining the long-term health of surface water bodies.

Next Steps: This paper is a summary of several long-term (> 5 year) studies conducted to assess the effectiveness of various permeable reactive mixtures for removing phosphorous from flowing water. Future efforts will be directed toward the development of techniques for remediating other inorganic contaminants.

Abstract

A permeable reactive mixture has been developed using low-cost, readily available materials that is capable of providing effective, long-term phosphorous treatment in areas impacted by on-land wastewater disposal. The reactive mixture creates a geochemical environment suitable for P-attenuation by both adsorption and precipitation reactions. Potential benefits include significant reductions in phosphorous loading to receiving groundwater and surface water systems, and the accumulation of P-mass in a finite and accessible volume of material. The mixture may be applied as a component within surface treatment systems or in subsurface applications such as horizontal or vertical permeable reactive walls. The mixture averaged > 90% treatment efficiency over 3.6 years of continuous-flow laboratory column experiments. The mixture was further evaluated at the pilot-scale to treat municipal wastewater, and the field-scale to treat a well-characterized septic system plume using an *in situ* Funnel-and-Gate™ system. Average PO_4-P concentrations in effluent exiting the reactive mixture range between 0 - 0.3 mg/L. Mineralogical analyses have isolated the phases responsible for phosphorous uptake, and discrete phosphate precipitated have been identified.

Phosphorous Adsorption and Precipitation in a Permeable Reactive Wall: Applications for Wastewater Disposal Systems

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Abstract

A permeable reactive mixture has been developed using low cost, readily available materials that is capable of providing effective, long-term phosphorous treatment in areas impacted by on-land wastewater disposal. The reactive mixture creates a geochemical environment suitable for P-attenuation by both adsorption and precipitation reactions. Potential benefits include significant reductions in phosphorous loading to receiving groundwater and surface water systems, and the accumulation of P-mass in a finite and accessible volume of material. The mixture may be applied as a component within surface treatment systems or in subsurface applications such as horizontal or vertical permeable reactive walls. The mixture averaged > 90% treatment efficiency over 3.6 years of continuous-flow laboratory column experiments. The mixture was further evaluated at the pilot-scale to treat municipal wastewater, and the field-scale to treat a well-characterized septic system plume using an *in situ* Funnel and Gate™ system. Average PO_4-P concentrations in effluent exiting the reactive mixture range between 0 – 0.3 mg/L. Mineralogical analyses have isolated the phases responsible for phosphorous uptake, and discrete phosphate precipitates have been identified.

INTRODUCTION

Reactive materials which remove contaminants passively, under porous flow conditions are a promising new approach for the prevention and remediation of contaminated groundwaters. These materials may be utilized in surface applications under controlled conditions, or alternatively in subsurface applications, such as *in situ* permeable reactive walls.

Reactive materials focused on treating a wide range of groundwater contaminants are currently under development (Blowes *et al.* 1995). These materials may be classified into two distinct groups. The first type of material promotes chemical reactions that destroy the contaminant or transform it to a more benign species (e.g. reductive dehalogenation, denitrification, biodegradation); the second class attempts to provide sufficient levels of treatment by transferring contaminant mass from the aqueous phase to the solid phase using geochemical reactions (e.g. adsorption, ion exchange, precipitation).

Phosphorous contamination of soils, groundwater, and surface water from wastewater disposal practices is presently an important environmental concern in heavily developed riparian areas. Phosphorous is the limiting nutrient in most inland surface waters and excess inputs can adversely affect the natural trophic state of those waterbodies (Schindler 1977). Field studies have documented elevated phosphorous concentrations in groundwaters that receive wastewater effluent (Harman 1992; Robertson 1995; Walter *et al.* 1995). A reactive mixture has been developed (Blowes, Ptacek and Baker 1995) to provide long-term phosphorous treatment by coupling adsorption and precipitation reactions (Ptacek *et al.* 1994; Baker *et al.* 1996). The benefits of the system are two-fold. First, the effluent phosphorous concentrations reaching receiving soil and water systems are significantly reduced, and secondly, a significant mass of phosphorous is accumulated in a finite and accessible volume of material which allows for retrieval and future disposal, or alternatively, acceptable rates of release.

A permeable reactive mixture can be applied to areas of wastewater treatment in several ways. The mixture can be incorporated as a horizontal barrier to intercept and treat infiltrating wastewater (Figure 1A). Alternatively, a module-based system can provide phosphorous treatment prior to soil disposal (Figure 1B). In areas where a groundwater phosphorous plume has already developed, a vertical treatment wall can be placed perpendicular to the groundwater flow path upgradient of surface water discharge (Figure 1C).

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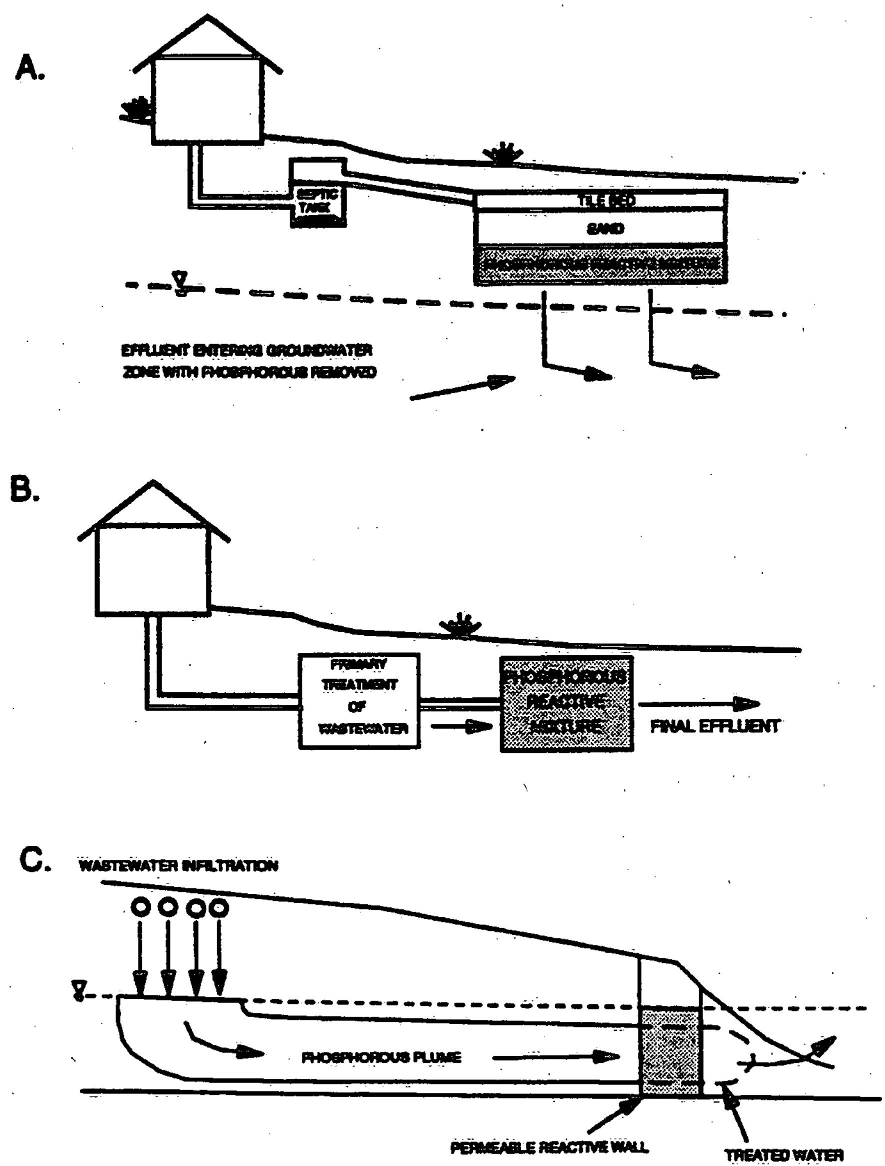

Figure 1. Potential applications of a permeable reactive mixture to remove phosphorous from wastewater discharges. A. Horizontal barrier underlying zone of infiltration in a conventional septic system. B. Modular unit which removes phosphorous from pre-treated effluent. C. Vertical *in situ* reactive wall installed downgradient of existing zone of contamination.

METHODS OF INVESTIGATION

Various materials were acquired and evaluated in the laboratory to assess the treatment efficiencies of adsorption and precipitation reactions. The most promising materials appear to be a specific group of alkaline metal oxides manufactured as by-products of steel manufacturing. A mixture containing 50 wt% silica sand, 45 wt% crushed limestone, and 5 wt% metal oxide was incorporated into a long-term laboratory column experiment under conditions of dynamic flow and cumulative phosphate loading. The column was constructed from acrylic plastic (20 cm long; 6.35 cm diameter) and a phosphate solution (3.30 mg/L PO_4-P) was administered through Teflon tubing connected to a multi-channel variable speed peristaltic pump (Figure 2A). The column received continuous inputs of the feed solution at representative groundwater velocities over a period of 3.6 years (1250 pore volumes) under saturated conditions. Flow rates and effluent chemistry were monitored over time. The column solids were sampled periodically and mineralogical analyses were performed to assess

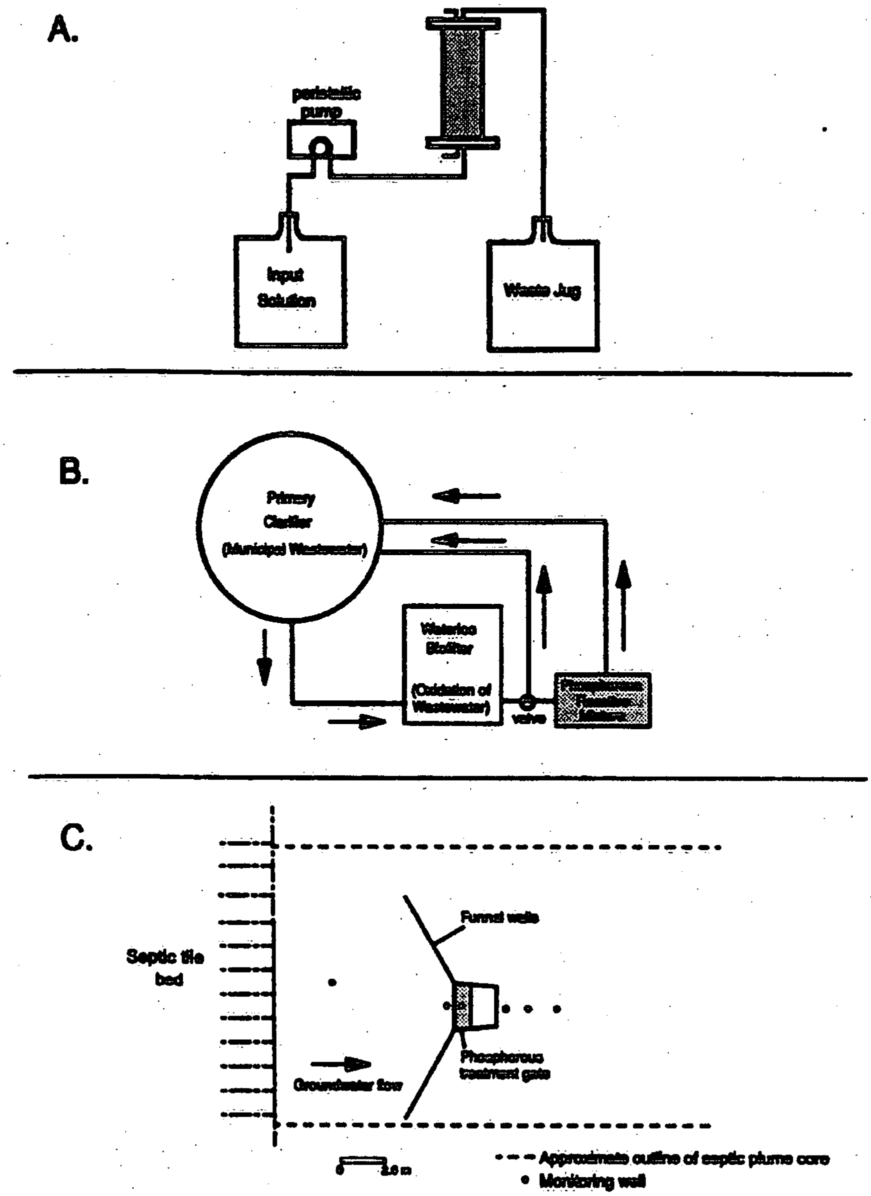

Figure 2. Methods of investigation during development of reactive mixture. A. Laboratory column experiment ; B. Pilot-scale treatment of municipal wastewater ; C. Field-scale funnel and gate *in situ* treatment system

the distribution of solid-bound phosphorous within the column, and to provide direct evidence of the geochemical reactions responsible for P-uptake.

The reactive mixture was further evaluated at the pilot-scale to test the reactive mixture under more realistic wastewater conditions. A porous flow treatment module was constructed to remove phosphorous from pre-treated municipal wastewater at the Waterloo sewage treatment plant. Primary clarifier effluent was first directed through a Waterloo biofilter™ for primary wastewater treatment and to provide an effluent suitable for porous flow. A portion of the biofilter effluent was then directed through a cylinder (0.5 m diameter; 0.5 m height), containing the reactive mixture. Wastewater was applied at an average flow rate of 26 L/day over a period of 133 days, or approximately 101 pore volumes of treatment (Figure 2B).

A Funnel and Gate™ *in situ* treatment system was installed to test the reactive mixture capabilities in removing phosphate from a well-characterized septic system plume, and also to evaluate the Funnel and Gate™ *in situ* design. The

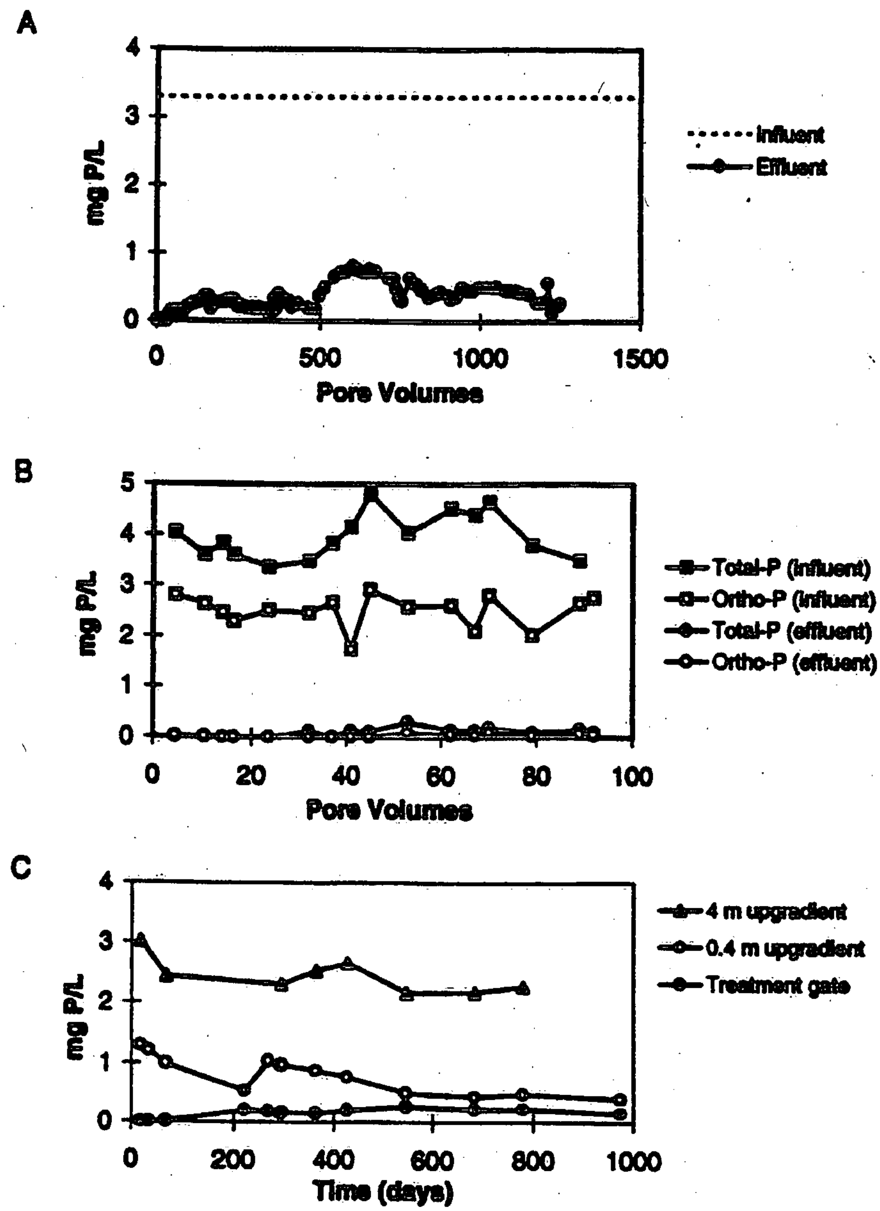

Figure 3. Breakthrough curves for laboratory and field tests. A. Laboratory column ; B. Municipal wastewater treatment system ; C. Funnel and gate system.

installation consisted of 1.67 m long inter-connected impermeable metal sheet piling (funnel) which directed groundwater flow through a permeable treatment gate (1.8 m length; 2.0 m width; 1.0 m depth) containing the phosphorous reactive mixture (Figure 2C). Chemical profiles of the groundwater at the site were monitored over a 779-day period.

RESULTS

Column experiments

Phosphate concentrations in the effluent solution remained below detection (< 0.01 mg/L PO_4-P) for approximately the first 50 pore volumes and then increased to low and steady concentrations over the remainder of the 3.6 year study period (Figure 3A). The average concentration in the effluent was 0.27 mg/L PO_4-P or > 90% phosphate removal efficiency over the course of the experiment. The shape of the breakthrough curve suggests that both adsorption and precipitation reactions are responsible for the observed reduction in phosphate. Geochemical speciation modelling performed using MINTEQA2 (Allison *et al.* 1990) indicate that the column effluent is supersaturated with respect to hydroxyapatite ($Ca_5(PO_4)_3OH$), and at saturation with respect to tricalciumphosphate β-$Ca_3(PO_4)_2$. Mineralogical analyses performed on the column solids reveal that the bulk of the phosphorous mass is preferentially concentrated at the base of the column and that phosphate is being accumulated on the surfaces of oxide phases as well as precipitated as microcrystalline hydroxyapatite, possibly by replacement of existing calcite.

Pilot-scale treatment cell

Breakthrough curves for the treatment module at the sewage treatment plant are shown in Figure 3B. The average influent concentrations into the unit were 3.93 mg/L (Total P) and 2.50 mg/L (Ortho-P). Average concentrations in the effluent were 0.14 mg/L (Total-P) and 0.05 mg/L (Ortho-P). Treatment efficiency of > 95% was achieved over the 133 day study period.

Funnel and Gate™ system

Breakthrough curves generated from the Funnel and Gate™ system are shown in Figure 3C, for monitoring wells 4 m and 0.4 m upgradient of the treatment gate, as well as directly inside the treatment gate. Concentrations within the plume core, 4 m upgradient of the treatment system remained high (2-3 mg/L). Concentrations 0.4 m upgradient of the treatment gate decreased over time from 1.5 mg/L to 0.40 mg/L. Similar reductions were observed for the more conservative solutes such as Cl, Na, and NO_3-. The dilution effect may be the result of complex groundwater flow paths that have developed due to the installation. For the first 221 days of operation, concentrations in the treatment gate were below detection (< 0.01 mg/L). For the duration of the 779 day monitoring period, average phosphate concentration in the wall remained steady and low (0.19 mg P/L).

CONCLUSIONS

Long-term laboratory, pilot, and field-scale experiments have demonstrated the potential for a permeable reactive mixture to remove phosphorous from wastewater effluent. Results from the field trials were consistent with results obtained from controlled laboratory experiments. Treatment efficiencies range between 85-100%. The reactive mixture, incorporating an alkaline iron oxide, removes phosphate from solution by accumulation on oxide surfaces and precipitation of microcrystalline hydroxyapatite ($Ca_5(PO_4)_3OH$). This technology has the potential to provide significant environmental benefits by preventing excess loading of phosphorous into soil, groundwater, and surface water systems. Current demonstration projects include incorporation of the reactive mixture into high efficiency domestic on-site wastewater disposal systems.

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