Nutrient transport in relation to redox transitions below a septic system tile-bed and in a sand aquifer

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Geochemical and mineralogical measurements were made at a high-capacity tile bed servicing Point Pelee National Park (PPNP). The analyses focus on the transitional redox zone directly below the tile lines and on nutrient transport in relation to changing redox conditions in the groundwater zone. The understanding gained from this study assists in the development of improved wastewater disposal systems and quantifying rates of nutrient loading into surface water bodies.

Study area

PPNP is located on the north shore of Lake Erie, Ontario, Canada, and receives over 0.5 million visitors annually. The Camp Henry tile bed, one of 30 tile beds servicing PPNP, was studied. Black water was fed from a holding tank to the tile bed for 16 years at an estimated rate of 2500 L/day. The tile bed is excavated directly into native barrier bar sands. These sands are 7-8 m thick locally and overlie dense clay till. Groundwater flow in the surficial sand aquifer ranges between 10 and 60 m/a.

Methods

Samples of groundwater were collected from multilevel bundle piezometers and analysed for NO_3 , NH_3 , PO_4 , total P, major ions, trace metals, Eh, pH, alkalinity, and dissolved O_2 , H_2S , CH_4 , and H_2 . Mineral saturation indices were calculated using the geochemical computer code MINTEQA2 (Allison *et al.*, 1990). Cores of aquifer material were collected next to a tile line and 5 m down gradient of the tile bed. Solid-phase P concentrations were determined by digesting 1 g crushed sample in 100 mL 1N HCl for 16 hours. The composition of solid-phase P was determined using secondary electron microscopy (SEM), energy-dispersive X-ray microanalysis (EDX), and X-ray photoelectron spectroscopy (XPS). Data collection and analysis techniques are described in Pratt (1997).

Unsaturated zone processes

Directly below the tile bed, NH₃ and DOC are oxidized and P is removed from the sewage water. Concentrations of NH₃-N decrease from > 90 mg/L in the effluent to < 15 mg/L in the underlying groundwater zone. Concentrations of NO₃ increase from < 0.05 mg/L to > 80 mg/L in the groundwater. These changes are a direct result of NH₃ oxidation to NO₃ in the aerobic unsaturated zone. Concentrations of DOC decrease from > 30 mg/L in the effluent to a maximum of 12 mg/L in the groundwater zone. Concentrations of P in the effluent decrease from 12 mg/L to < 1.5 mg/L at groundwater sampling points closest to the tile bed.

Solid-phase concentrations of P increase markedly from < 300 mg/kg above the tile lines to > 700 mg/kgjust below the tile line (0.5 m), and then decline gradually over the next 0.6 m to generally < 300 mg/kg (Fig. 1). This enrichment is consistent with P accumulations below tile lines observed at four other sites in Ontario (Zanini *et al.*, 1998).

XPS analysis of selected grains collected from the Camp Henry enrichment zone identifies the presence of two species of phosphate, one organic the other inorganic. The P(2p) spectrum is consistent with various Fe and Ca phosphate species, and an organic P compound. The Fe($2p_{3/2}$) spectrum indicates Fe binding to PO₄ is consistent with the spectrum observed for Fe(II)-PO₄ binding in vivianite (Pratt, 1997), and Fe present in an organic-PO₄ species.

SEM micrographs show the surfaces analysed by XPS are agglomerations of colloidal particles similar to those expected for mixtures of organic and inorganic particles. Formation of vivianite was suggested by Gschwend and Reynoldson (1987) as a control on PO₄ concentrations in a sand and gravel aquifer receiving PO₄ from incompletely oxidized wastewater.



FIG. 1. Solid-phase P concentrations. Position of water table ranges between 1 and 2 m below ground surface.

The sewage effluent at Camp Henry has insufficient Fe to account for the mass of Fe contained in the PO₄ enrichment zone. It is likely that Fe(II) is derived from reductive dissolution of Fe(III) coatings on the native sands. The presence of P in both organic and inorganic forms is consistent with a microbially-active zone directly below the tile lines. The ratio of organic P:PO₄ in this zone is higher than in the original effluent, further supporting the role of biological activity in removing P from the effluent.

Saturated zone processes

A plume of sewage-derived groundwater, > 60 m long, > 40 m wide and up to 7 m deep, is present at the site (Ptacek, 1998). The groundwater chemistry at the site can be divided into discrete redox zones (Fig. 2). There is a shallow, 2–3 m thick, suboxic zone close to the tile bed. This zone has elevated concentrations of dissolved Mn (1–3 mg/L versus 0.1 to 1 mg/L elsewhere), occasionally elevated concentrations of Fe, intermediate Eh values, and low concentrations of dissolved oxygen (< 1 mg/L). At the base of the aquifer there is 2–3 m thick reducing zone, characterized by consistently elevated concentrations of Fe(II) (1-14 mg/L), low Eh values (< 200 mV) and elevated concentrations of H₂ (0.6 to 2.4 nmol/L), H₂S (up to 14 g/L), and CH₄ (50 to 250 g/L).

Transport of NH₃, NO₃ and PO₄ is closely related to these redox zones. In the suboxic zone, concentrations of NH₃, NO₃ and PO₄ are high (NO₃-N: 5-80 mg/L; NH₃-N: 1-15 mg/L; PO₄-P: 0.1-1.5 mg/L) (Fig. 2).



FIG. 2. Contours of measured Eh and PO₄ concentrations along the plume centre line.

In the reducing zone, concentrations of PO_4 -P range between 0.1–0.8 mg/L and remain elevated up to 60 m from the tile bed indicating the generally greater mobility of P under reducing conditions. Concentrations of NO₃ are below detection (< 0.01 mg/L N), most likely due to removal by bacterial denitrification in the reducing zone.

The groundwater is near saturation with respect to calcite at most sampling locations. In the Mn-rich suboxic zone, the groundwater is close to saturation or supersaturated with respect to rhodochrosite, hydroxyapatite, and ferrihydrite. In the presence of excess carbonates, formation of rhodochrosite is expected as a result of Mn(II) release from reductive dissolution of Mn(VI) solids coupled to DOC oxidation. Groundwaters which contain PO_4 in contact with carbonate solids frequently are near saturated or supersaturated with respect to hydroxyapatite. There is potential for this phase or a more soluble precursor to be forming at these locations.

In the reduced zone, the groundwater is near saturation or slightly supersaturated with respect to siderite suggesting this carbonate phase is controlling the concentration of dissolved Fe. The groundwater is also near saturation or supersaturated with respect to vivianite, suggesting vivianite is also potential control on concentrations of dissolved PO_4 and Fe in the reduced zone. Solid phase analyses indicate P enrichments at locations with elevated PO_4 concentrations, supporting solid-phase controls on PO_4 concentrations.