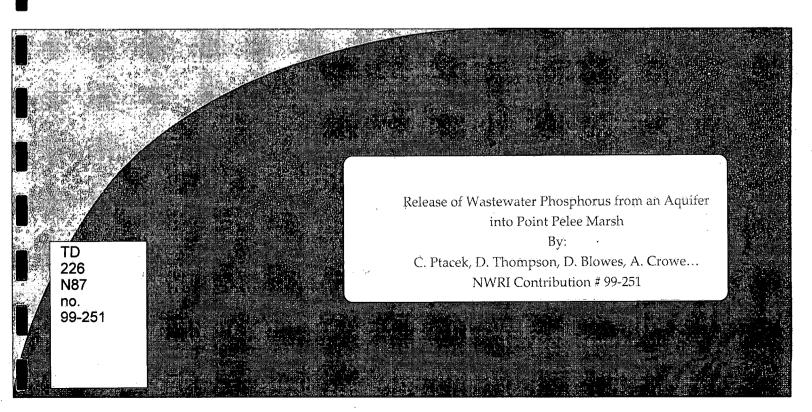
# Environment Canada

Water Science and Technology Directorate

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



### MANAGEMENT PERSPECTIVE

Title:

Release of Wastewater Phosphorus from an Aquifer into Point

Pelee Marsh

Authors:

C.J. Ptacek, D.L. Thompson, D.W. Blowes, A.S. Crowe, T. Mayer, and A.R. Pratt

**NWRI Publication#:** 

99-251

Citation:

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EC Priority/Issue:

This work was conducted as part of a larger study on the water quality of the Point Pelee coastal barrier bar/wetland complex funded by Parks Canada, and by the GL2000 program. The work supports the ESD issue "Conserving Canada's Ecosystems" (nutrients and wetlands). It supports the business plan deliverable Nature (nutrient loading, Great Lakes coastal wetlands). 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 describes hydrogeological, geochemical and microbiological controls on nutrient transport from active and abandoned wastewater disposal systems at Point Pelee National Park and in the shallow sand aquifer up to the edge of the marsh. Point Pelee National Park relies on tile beds for wastewater treatment for over 500,000 park visitors annually. Nutrient transport in relation to pH and redox zonation is evaluated. Long-term loadings of wastewater nutrients from active and abandoned sites and implications related to siting future disposal systems are discussed.

**Next Steps:** 

Comparison of nutrient fluxes for three tile beds located in different hydrogeological settings will be made. The results will assist in understanding contaminant transport in barrier bars, and in coastal settings in general.



Salt Lake City, Utah, November 16-17, 1999

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## RELEASE OF WASTEWATER PHOSPHORUS FROM AN AQUIFER INTO POINT PELEE MARSH

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ABSTRACT: Point Pelee National Park, Canada encloses the internationally protected Point Pelee marsh. Wastewater generated at the park is disposed using tile beds, most of which are excavated directly into native sands of the western barrier bar bordering the marsh. Detailed geochemical and hydrogeological studies conducted over the past 5 years indicate transport of wastewater nutrients correlates closely with changes in redox conditions. At two active tile bed sites, located within 60 m of the marsh, concentrations of NO<sub>3</sub> between 1 and 80 mg/L (as N) are present more than 40 m from the tile beds. In reducing zones at the marsh edge and at the base of the aquifer, NO<sub>3</sub> is removed to concentrations <0.01 mg/L N by bacterial denitrification. Phosphate concentrations approach 3 mg/L P up to 10 m from the tile beds, and range between 0.1 - 1 mg/L (as P) in reducing zones at the base of the aquifer up to the marsh edge. Elevated concentrations of NH<sub>3</sub> are present more than 60 m from the tile beds. At an inactive site which last received wastewater input 4 years ago, concentrations of NO<sub>3</sub> and NH<sub>3</sub> have declined, but concentrations of PO<sub>4</sub> remain virtually unchanged. At a site which last received wastewater input two decades ago, NO<sub>3</sub> is absent, but elevated concentrations of PO<sub>4</sub> and NH<sub>3</sub> persist in the groundwater zone close to the marsh edge. Solid-phase P analyses of aquifer materials impacted by wastewater are two to three times background values. These observations suggest that dissolvedphase PO<sub>4</sub> concentrations remain elevated after tile bed abandonment because of slow release from solid phase accumulations. The long-term release of PO<sub>4</sub> from the aquifer materials and the relatively high mobility of PO<sub>4</sub> in the reducing environment observed near marsh edges should be considered in marsh management programs.

#### INTRODUCTION

On-site wastewater disposal releases high concentrations of nutrients to groundwater. On-site disposal systems usually involve wastewater oxidation followed by infiltration to the subsurface. Disposal methods may also include direct discharge methods, such as subsurface flow to natural and constructed wetlands. These differing wastewater disposal systems can result in differences in the extent and rate of nutrient attenuation as the wastewater is transported away from the infiltration zone.

Geochemical processes occurring at the interface between upland and wetland areas are gaining increasing attention. This zone is characterized by large changes in hydrology, lithology, and geochemistry. This study evaluates

processes controlling the transport of nutrients from three wastewater disposal sites located close to the edge of a wetland. The study was initiated in response to increasing concern over excess phosphorus in open ponds of the internationally protected Point Pelee marsh within Point Pelee National Park, Ontario (Figure 1). Wastewater generated by 0.5 million park visitors and staff is disposed of in over 30 active tile beds. Past methods of wastewater disposal for up to one million visitors each year included conventional tile beds or latrines. Because of limited land space, wastewater disposal occurs close to the marsh edge.

Processes controlling transport of nutrients during the active stages of tile beds located within 60 m of the edge of Point Pelee marsh are described. At one site described previously (Ptacek, 1998), wastewater disposal was switched to a new raised tile bed to promote greater oxidation of the wastewater. The plume generated at the original tile bed site was monitored annually to assess the rate of plume dissipation. Results from a sampling program at a site abandoned more than two decades ago are also described. The results assist in predicting the long-term fate of nutrients derived from wastewater disposal systems located close to the geochemical transition zone at the edge of wetlands.

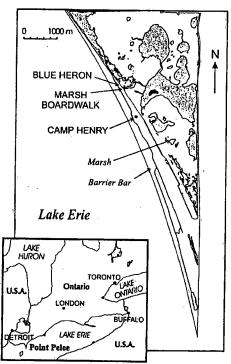


FIGURE 1. Maps showing location of Point Pelee National Park (inset), and western barrier bar, marsh, and Blue Heron and Camp Henry study areas.

#### MATERIALS AND METHODS

Bundle piezometers and conventional standpipe piezometers were installed for collection of hydraulic head data and samples of groundwater. Measurements of pH and Eh were made in the field using sealed flow-through cells. The pH electrodes were calibrated using pH 4, 7 and 10 buffers, and the response of Eh electrodes was checked using Zobell's solution, maintained at groundwater temperature. Samples for chemical analysis were filtered in-line using 0.45  $\blacksquare$ m filters. Alkalinity was measured shortly after sample collection using standardized H<sub>2</sub>SO<sub>4</sub> and a Hach digital titrator. Samples for PO<sub>4</sub> and NH<sub>4</sub> analyses were acidified with ultrapure H<sub>2</sub>SO<sub>4</sub>. Samples for cation analysis were acidified with HCl, and samples for anion analysis were left unacidified. Analyses were performed by the National Laboratory for Environmental Testing, Burlington. Cores were collected using a piston core barrel method. XPS and SEM analyses were conducted at Surface Science Western, University of Western Ontario (Ptacek and Pratt, 1998).

#### RESULTS AND DISCUSSION

Phosphorus Transport During Active Wastewater Disposal. Two active tile bed sites were instrumented, the Blue Heron site, where the barrier bar is 320 m wide, and the Camp Henry site, where the barrier bar is 450 m wide (Figure 1). Wastewater disposal at these sites occurred for close to two decades at the time of sampling and has lead to the development of distinguishable plumes of groundwater characterized by elevated concentrations of dissolved organic carbon, NO<sub>3</sub>, NH<sub>3</sub>, and PO<sub>4</sub>, depressed pH conditions and elevated concentrations of dissolved Mn(II) and Fe(II).

At the Blue Heron site, the wastewater plume is developed both toward the marsh and Lake Erie, in response to changing groundwater flow directions. Groundwater is directed toward Lake Erie for about 7 months of the year and toward the marsh for the remainder of the year. Close to the tile bed where wastewater discharge occurs, a subreducing zone is present which is characterized by low concentrations of dissolved O2, elevated concentrations of Mn(II), and occasional elevated concentrations of Fe(II). At the base of the aquifer (7 m below ground surface) and at the marsh edge, more strongly reducing conditions occur, as indicated by elevated concentrations of Fe(II), H2S, and CH4. In the subreducing zone, concentrations of NO<sub>3</sub> are elevated, and in the more strongly reducing zones concentrations of NO<sub>3</sub> decline to < 1.0 mg/L. The decline in NO<sub>3</sub>, and increase in Mn(II), Fe(II), H<sub>2</sub>S and CH<sub>4</sub> is attributed to progressive utilization of NO<sub>3</sub>, Mn(IV) and Fe(III) solids, and SO<sub>4</sub> as terminal electron acceptors during oxidation of DOC derived from the wastewater and aquifer solids. Concentrations of NH<sub>3</sub> are elevated above background values in the subreducing zone, and are slightly higher in the more strongly reducing zones. Concentrations of PO<sub>4</sub> exceed 1.0 mg/L close to the tile bed, and then decline to values <0.3 mg/L at the base of the aquifer and close to the marsh (Figure 2).

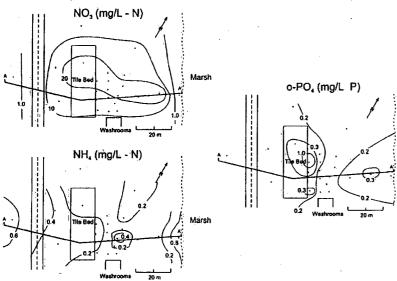


FIGURE 2. Maximum concentrations of NO<sub>3</sub>, NH<sub>3</sub>, and PO<sub>4</sub> in groundwater during active stages of Blue Heron tile bed.

At the Camp Henry site, the area of the plume is submerged below the marsh during periods of high water levels. Marsh water encroaches to within several meters of the tile bed. As a result, a very thin unsaturated zone is present below the infiltration pipes and oxidation of wastewater is limited. During low water levels, the marsh recedes to about 60 m away from the tile bed. Lower water table conditions prevail, and oxidation of the wastewater is more complete. The hydrological setting during high water levels is similar to subsurface flow wetlands that are commonly used for treatment of wastewater. The cyclical nature of the water level changes influences groundwater flow velocities, groundwater flow directions and redox processes occurring in the plume and at the discharge front (Ptacek, 1998; Ptacek and Pratt, 1998; Thompson, 1999).

Transport of N and P species is closely associated with changes in redox conditions. Close to the tile bed where subreducing conditions exist, concentrations of dissolved PO<sub>4</sub> are highest, up to 3 mg/L as P (Figure 3). Under the more strongly reducing conditions present near the base of the aquifer (5 to 7 m below ground surface), concentrations of PO<sub>4</sub> approach 0.8 mg/L (as P) in a zone extending from below the tile bed up to the marsh edge (Ptacek, 1998). The elevated concentrations of dissolved-phase PO<sub>4</sub> coincide closely with elevated concentrations of Mn(II) and Fe(II) and negative Eh values (not shown), similar to observations described by others for marsh and lake bottom sediments (e.g. Moore and Reddy, 1994; Mayer et al., 1998).

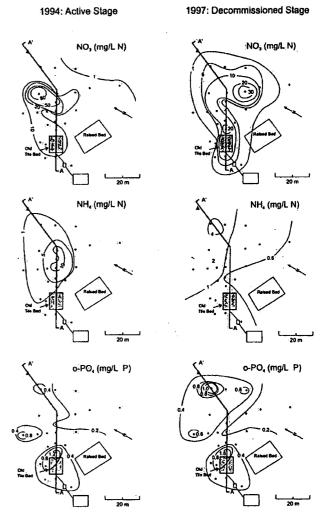


FIGURE 3. Maximum concentrations of nutrients in groundwater during active (left) and decommissioned stages (right) of Camp Henry tile bed.

Phosphorus Release after Tile-Bed Abandonment. Discharge of wastewater to the Camp Henry tile bed was terminated in 1995. The plume was sampled annually to evaluate the persistence of nutrients after the cessation of wastewater discharge. The concentrations of NO<sub>3</sub> and NH<sub>3</sub> declined each year, but concentrations of PO<sub>4</sub> remained nearly identical from year to year (Figure 3). The maximum concentration of NH<sub>3</sub> declined from > 30 mg/L (as N) in 1994 to < 5

mg/L in 1997. Concentrations of NO<sub>3</sub> declined from a maximum of 80 mg/L (as N) in 1994 to 30 mg/L in 1997. Concentrations of PO<sub>4</sub>, however, remained between 0.5 and 2.0 mg/L in the plume core in 1994, and in the first two years after abandonment. Slightly lower concentrations were observed in 1998, a maximum of 1.4 mg/L P. The persistence of PO<sub>4</sub> in the groundwater plume after cessation of wastewater disposal is attributed to PO<sub>4</sub> release from aquifer solids through desorption or dissolution processes. Continued release is expected to depend on the mass and form of phosphorus accumulated on the aquifer solids, and the overall geochemical evolution of the wastewater plume.

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Mass and Form of Phosphorus on Aquifer Solids. Solid-phase analysis of phosphorus on aquifer solids collected from the Camp Henry site indicate P accumulations occur directly below the tile lines and within the phosphorus plume (Figure 4). Solid-phase P concentrations observed in core material collected within the tile bed are < 300 mg/kg above the infiltration pipes, and then reach maximum values of > 700 mg/kg about 0.5 m below the tile bed. Downgradient of the tile bed in the core of the wastewater plume, solid-phase concentrations of phosphorus are also elevated to > 600 mg/kg. This enrichment in solid-phase P is consistent with observations at other wastewater disposal sites (Walter et al., 1995; Zanini et al., 1998). SEM and XPS analysis of the aquifer solids directly below the tile bed indicate P is present as both organic and inorganic Fe and Ca phosphate phases (Ptacek and Pratt, 1998). These accumulations are potentially available for long-term release, and the dissolution or desorption of bound PO<sub>4</sub> from these phases is a likely explanation for the elevated groundwater PO<sub>4</sub> concentrations after tile bed abandonment.

Long-term Potential for Phosphorus Release to Marsh. The Marsh Boardwalk area (Figure 1) last received wastewater discharge more than 20 years ago. This site was sampled to evaluate the potential for long-term nutrient release from latrines and vault toilets which had been used from the turn of the 20th century to the mid 1970's. Groundwater chemistry data show that reducing conditions prevail in this area, as indicated by low concentrations of dissolved O2 and NO3 (both < 0.05 mg/L), elevated concentrations of Mn(II), Fe(II), H<sub>2</sub>S and CH<sub>4</sub>. The redox conditions become increasingly reducing as the marsh edge is approached. For example, concentrations of SO<sub>4</sub> decline from > 80 mg/L a few meters inland to < 0.3 mg/L at the marsh edge. Concentrations of Fe(II) increase from < 1 mg/L 30 m inland to 80 mg/L at the marsh edge. Concentrations of CH<sub>4</sub> increase from < 0.01 mg/L inland to > 20 mg/L at the marsh edge, and H<sub>2</sub> concentrations increase from 0.9 nM inland to 6.3 nM at the marsh edge (Thompson, 1999). Concentrations of PO4 are elevated throughout most of the study area, with highest concentrations observed at locations of former latrines (Figure 5). The elevated concentrations of PO4 are attributed to release from former accumulations on aquifer solids. These results suggest that there is a potential for continued release of PO4 from aquifer solids more than two decades after wastewater disposal has ceased.

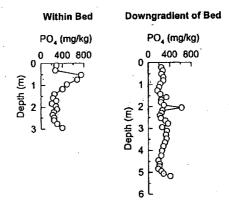


FIGURE 4. Mass of phosphorus accumulated on aquifer solids for cores collected within and 5 m downgradient of tile bed.

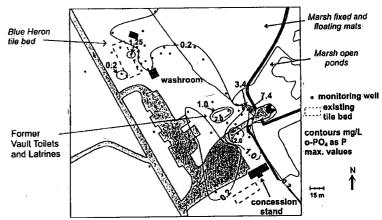


FIGURE 5. Concentrations of PO<sub>4</sub> at site which last received wastewater two decades ago.

#### CONCLUSIONS AND IMPLICATIONS

The concentrations of nutrients were similar at two active sites. Monitoring of two sites after cessation of wastewater disposal indicates concentrations of nitrate decline substantially, but PO<sub>4</sub> concentrations remain virtually unchanged. In both natural and constructed treatment wetlands, uptake of phosphorus by precipitation of P-bearing solids or adsorption of P onto mineral surfaces can decrease the amount of phosphorus available for immediate plant growth. The study results here suggest that a large portion of phosphorus is removed from flowing wastewater by reaction with mineral solids. Despite the initial removal, lower, but persistent, concentrations of phosphorus migrate

through aquifers and enter wetlands. These low concentrations can be released for decades or longer and will continue to contribute to the nutrient pool of wetlands. The potential requirement for ongoing wetland management long after wastewater disposal ceases should be considered in designs of wastewater disposal systems.

#### ACKNOWLEDGEMENTS

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# REMEDIATION OF CONTAMINATED SEDIMENTS IN THE VENICE INDUSTRIAL HARBOUR (ITALY)

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ABSTRACT: This project (basic design scale) regards the activities for the remediation of an industrial channel (630 meters long and 35 meters wide) situated in a big petrochemical site, connecting the Venice lagoon with the industrial area, and subject to strong tidal currents. The contamination is due to 30 years of various petrochemical and chemical plants activity with continuous discharge of wastewater into the channel. The amount of contaminated sediments is about 40000 cubic meters, to be dredged and treated in 64 months (included all activities from the plant construction to the final decommissioning).

Contaminants of concern are PAH, chlorinated solvents, PCB, PCDD and PCDF, aromatic amines, pesticides, heavy metals (Hg, Cu, Cr, Ni, Pb, Al, As). Potential risks during the remedial operations are: resuspension, transport and diffusion of contaminants during the dredging and remediation activities, both in the water environment of the lagoon and in air, with particular reference to on-site workers.

The basic design defines all the steps of the treatment process: a dredging system with special technical solutions studied to avoid secondary pollution, dredged material transportation with completely closed equipment in order to avoid air pollution, sediment treatment plant that includes a dewatering system, a drying system, a vitrification plant and off-gas combustion and treatment systems and a wastewater treatment plant.

The monitoring of water and air quality is foreseen during all the operations and every step of the treatment process.

#### INTRODUCTION

The present work describes a channel remediation project; the channel is situated inside the Venice lagoon(Italy).

This project was developed by Ambiente SpA (BASI) - ENI Group in 1998 after two years of extensive analytical activity and technical-economical feasibility studies.

The channel is about 630 m long and 35 m wide; another 30 m on each side of the channel have to be added to the treatment area as working area.

In the past decades big amounts of wastewater and contaminants were discharged into the channel, leading to a heavy contamination of the channel sediments and to a progressive reduction of the channel section.

The contaminants founded in the sediments, at various depths, are PAH, chlorinated solvents, PCB, PCDD and PCDF, aromatic amines, pesticides and heavy metals.





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