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The Role of Sediments in Nutrient Dynamics in Hyper-
Eutrophic Marshes of point Pelee, Onatrio, Canada

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**THE ROLE OF SEDIMENTS IN NUTRIENT DYNAMICS IN HYPER-EUTROPHIC
MARSHES OF POINT PEELE, ONTARIO, CANADA**

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MANAGEMENT PERSPECTIVE

Title: The Role of Sediments in Nutrient Dynamics in Hyper-eutrophic Marshes of Point Pelee, Ontario, Canada

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EC Priority/Issue: This work was conducted as part of a larger study on the hydrology and geochemistry 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 Thrust #1 under Conserving Canada's Ecosystems (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: This paper summarizes a geochemical study on nutrient cycling between the water column and marsh sediments in a hyper-eutrophic marsh pond at Point Pelee, Ontario. This marsh is a protected habitat for non-migratory and migratory species. The sediments in the studied pond contain very high concentrations of phosphate and ammonia, which are available for renewed cycling into the water column. The elevated concentrations are due to past and current nutrient loadings from sewage disposal practices, release from a major fire-burn conducted by duck hunters from the earlier part of the century, or a combination of processes. The study was initiated in 1995.

Next Steps: Evaluate whether current sewage disposal practices are leading to additional loadings of nutrients to the marsh, and evaluate potential remediation strategies.

THE ROLE OF SEDIMENTS IN NUTRIENT DYNAMICS IN HYPER-EUTROPHIC MARSHES OF POINT PELEE, ONTARIO, CANADA

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ABSTRACT

Elevated concentrations of nutrients, resulting in prolific algal growth, were reported in some open-water ponds in one of the finest surviving wetlands on the Lower Great Lakes, Point Pelee National Park, Ontario, Canada. A study was undertaken to identify the sources of nutrients to the most impacted pond in the complex, Sanctuary Pond. Specifically, inventories and spatial variability of phosphorus (P) in benthic sediments from Sanctuary Pond were investigated, to determine the role of benthic sediments in nutrient dynamics.

Sediment chemistry and, chemistry of interstitial water, also referred herein as porewater, was examined to determine the levels and spatial variability of nutrients. The results indicate high concentrations of dissolved nutrients (over 120 $\mu\text{mol/L}$ of P and over 1.5 mmol/L of N) in sediment porewater, a consequence of organic matter decomposition. Thermodynamic calculations were carried out to determine mineral equilibria of phosphate minerals controlling the concentrations of dissolved P in sediment porewater. The calculations suggest that P generated from organic matter decomposition should be reacting with Fe, Ca and Al to form authigenic mineral phases vivianite, hydroxyapatite and variscite. No spatial differences were observed between porewater profiles, nor in the levels of dissolved constituents. Likewise, sediment P concentrations were similar at both investigated sites.

The high levels of nutrients in porewater, the lack of spatial differences in sediment and porewater nutrients concentrations and the absence of known external

nutrients sources suggest that at the Sanctuary Pond internal regeneration of nutrients from sediments is responsible for the hyper-eutrophic conditions in the pond.

Key words - wetlands, sediments, interstitial water, nutrients, internal nutrients regeneration, mineral equilibria

INTRODUCTION

Wetlands are important ecosystems, as they play major roles in mitigating the impacts of excessive nutrient and toxicant loads to aquatic ecosystems. Moreover, wetlands supply food and habitat for many species of fish, waterfowl and mammals. It is only recently that their socio-economic values have been realized. One of the finest surviving marshes on the lower Great Lakes is located within the boundaries of Point Pelee National Park, Ontario. The Point Pelee Marsh is a highly productive diverse floral community with a large variety of wildlife. The marsh complex consists of extensive cattail mats and several shallow ponds.

Earlier studies (McCrea, 1993) reported elevated concentrations of phosphorus (P) and ammonia in several open-water ponds of the marsh, raising concerns over the health of this fragile aquatic ecosystem. The sources of nutrients to the marsh, however, have not been clearly identified. A study was, therefore, initiated to determine the role of benthic sediments in nutrient dynamics in the marsh.

The important role of sediments in regulating nutrient concentrations in overlying water has long been recognized. Under favorable conditions they act as a sink for P and other nutrients. However, under certain conditions they may become a nutrient source long after the loadings from external sources cease. The sediment-water interface, in particular, can be important in controlling the nutrient chemistry of the water column, as it is the layer of sediments at the interface that controls the exchange of nutrients between sediments and overlying water. Interchange between the sediment and water nutrient compartments takes place under the influence of various

processes. This includes physical (gravitational settling, resuspension), geochemical (adsorption/desorption, dissolution/precipitation, flocculation) and biochemical processes (Matisoff and Eaker, 1992).

The objective of this study is to investigate the role of sediments in internal cycling of P and to identify principal processes governing the nutrient dynamics in some of the hyper-eutrophic ponds, at the Point Pelee Marsh. Specifically, the objective is to determine the inventories and spatial variability of P in benthic sediments from the most effected pond and to determine the chemistry of interstitial water (referred herein also as porewater) which can influence the distribution and dynamics of dissolved nutrients in the pond. Composition of interstitial water is used to determine the mineral phases controlling the solubility of P in sediments.

Sanctuary Pond which is the most effected pond in the complex was selected for the present study. This pond exhibited the highest nutrients concentrations, commonly exceeding the guidelines for the protection of the aquatic life (McCrea, 1993).

MATERIALS AND METHODS

Study area

The Point Pelee Marsh is the largest Canadian wetland in western Lake Erie. It is located at a massive triangular spit of land, on the north shore of Lake Erie, that marks the division of the lake's western and central basins (Fig. 1). The marsh is protected from the lake by two barrier beaches, comprised largely of sand. Sanctuary Pond is situated in the north-west corner of the park (Fig. 1). It has a surface area of approximately 48.5 hectares and is connected to the other ponds in the marsh through a series of shallow ponds and channels.

Two sites (Fig. 1) were selected for investigation carried out at the end of July 1994. Site 1- Middle was located approximately 100 m east of the pond lookout, roughly in the centre of the longitudinal axis, while site 2 - Corner was located in the

north-west corner of the pond, about 200 m east of the park gate. There are a number of active tile beds in the western barrier bar that potentially may be contributing to the nutrient loads to the Sanctuary Pond. In addition, historical information indicates to the presence of cottages in this area of the Park. Potential input of groundwater, contaminated with discharges from tile beds and vault style toilets from these cottages, was suspected. At the time of sampling, water depth was about 1 m at both sites.

Sample collection and analysis

Interstitial water (porewater) concentrations profiles were obtained from deployment of modified *in situ* samplers developed by Hesslein (1976). The acrylic compartment porewater samplers fitted with a biologically inert polysulfone membrane (0.45 μm Gelman HT-450), and prepared according to Rosa and Azcue (1993), were placed in the sediments and allowed to equilibrate for two weeks. Sampling was completed within 10 min. of retrieval of samplers from the sediments. Porewater samples were withdrawn from each cell with a syringe, transferred to preacidified plastic tubes and kept at 4°C until analyses. Separate sets of samples were analyzed for dissolved reactive P (DRP), ammonia-N ($\text{NH}_3\text{-N}$) and metals. Analyses for N and P were conducted using an autoanalyzer (Environment Canada Protocol, 1979). DRP was determined using an ascorbic acid technique. Measured DRP concentrations were compared with the $\text{PO}_4\text{-P}$ concentrations measured on the fresh unacidified samples. No difference was found between the DRP and $\text{PO}_4\text{-P}$ concentrations, using the same method, indicating that all dissolved reactive P in the porewater was essentially present in the form of orthophosphate ($\text{PO}_4\text{-P}$). Ammonium-N was determined by a O-tolidine method and metals (Fe, Mn, Ca, Mg, Na, K, Al, Ba and Sr) were measured with an inductively coupled Ar plasma emission spectrometer (ICAP). Reactive silica (RSiO_2) was also determined spectrophotometrically using ammonium molybdate method in which the oxalic acid is used to eliminate the phosphate interference. All methods are described in the Environment Canada Protocol (1979). Selected samples were

analyzed for dissolved inorganic carbon (DIC), dissolved organic carbon (DOC) and alkalinity. Alkalinity was determined in the field using standardized H_2SO_4 and a Hach digital titrator.

Water samples were also collected at both sites from the mid-column at the time of deployment of porewater samplers. Temperature, pH, turbidity and conductivity were recorded at the time of sample collection. The collected samples were analyzed for total suspended solids (TSS) concentrations, total P (TP), total dissolved P (TDP), total Kjeldahl nitrogen (TKN), nitrate+nitrite-N ($\text{NO}_3+\text{NO}_2\text{-N}$), ammonia-N ($\text{NH}_3\text{-N}$) and chlorophyll *a* according to the Environment Canada Protocol (1979).

Two sediment cores were collected at each site and sectioned soon after retrieval. One core from each site was used for direct pH and oxidation-reduction potential (Eh) measurements. Metrohm portable pH meter and glass combination electrode, calibrated against standard buffers (4 and 7), were used for pH measurements. The same meter, in mV mode, and a Pt/Ag/AgCl combination electrode, calibrated against the standardized solution (ZoBell, 1946), was used for the redox potential (Eh) measurements. The sections from the second cores were frozen upon arrival to laboratory and subsequently freeze-dried. Homogenized dry sediments were used for analyses. Total and organic C (OC) content of the sediments was determined with a LECO-12 Carbon Determinator using a two temperature (575°C , 1371°C) dry combustion method. For comparison, the organic content of the sediments was also determined as loss on ignition (LOI), measured gravimetrically after igniting the-dry sediments at 550°C in a muffle furnace for two hours. Total P (TP) concentrations were determined on ignited sediments using a 16-hr 1N HCl extraction. Forms of P, non-apatite inorganic P (NAI-P), and apatite-P (AP) were determined by sequential extraction as described by Williams et al. (1976) and Mayer and Williams (1981). Organic P (OP) was determined by difference between the TP and the sum of the NAI-P and AP concentrations.

RESULTS AND DISCUSSION

Water column

The water quality data (Table 1) reveal a high turbidity and high nutrient concentrations in the water column. High chlorophyll levels (Table 1) suggest that primary productivity, in addition to silt, contributes significantly to decreased water clarity. Resuspension of sediments by the wind and wave energy and, more importantly, by feeding and spawning activity of carps are principal factors in the reduced water clarity.

Concentrations of total Kjeldahl nitrogen (TKN), a combined measure of organic N and $\text{NH}_3\text{-N}$, in the water column were high (Table 1), indicating extensive biological input. Similarly, P concentrations in the water column were high, with TP values exceeding Ontario Provincial Guidelines (0.020 mg/L P) for the avoidance of nuisance algae. Most of the TP (~85%) in the water column was in the particulate form (Table 1), presumably incorporated in the algal tissue and within the particles of resuspended sediments.

Elevated concentrations (>0.1 mg/L) of $\text{NH}_3\text{-N}$ in the water column (Table 1) indicate organic pollution, resulting likely from exchange between the sediments and overlying water. At the pH (9.1-9.2) and temperature (21°C) of the water column, measured ammonia-N (Table 1) concentrations exceeded the threshold levels stipulated by the U.S. EPA Guidelines. The U.S. EPA (1985) found ammonia to be toxic to many freshwater organisms, including invertebrates and fish. Un-ionized ammonia (NH_3) has been demonstrated to be the principal toxic form of ammonia. Its concentration in the water column is largely governed by pH and temperature. As the temperature and pH increase, the proportion of un-ionized NH_3 in aqueous ammonia solution rises.

Sediments

Sediment density measured as specific gravity by automated pycnometer (Micromeritics, 1992) was 1.9376 g/cm^3 (Turner, unpublished data). The top few centimeters of sediments consisted of fine soft floc. A distinct transition in the texture of sediment was observed between 39–43 cm in the core from the middle of the pond and at about 32 cm in the core from the site close to the park gate. Sediment below these horizons was darker and more consolidated. The geochemical data (organic C, AP and OP, Fig. 2 and Table 2), however indicated the transition in the sediment type at 27 cm at the corner site and below 34 cm in sediment core from the middle of the pond, suggesting transition in the sediments before it is detectable from their visual appearance. The texture and geochemical characteristics of sediments suggest that sediments below the marked horizons were deposited in different sedimentary environments. The high values of OC (Table 2) suggest deposition of highly refractory organic material, probably in a bog type sedimentary environment. Historical records (McCrea, 1993) show that the Sanctuary Pond was formed as a result of an extensive burn of a *Carex* meadow *circa* in 1937. Prior to this, a bog occupied the area of the Sanctuary Pond (G. Moulard, pers. communication).

Water content of the sediments decreased with depth from 97% at the surface to 89% at the 10-cm depth. High levels of organic matter were typical at both sites, with organic matter constituting nearly 50% of bulk sediment above the transition horizons and ~85% below them. The LOI/OC ratio in the upper sediments approached the value of two, and about 1.6 in the deeper sediments.

The pH observed in the sediment declined from 7.5 and 7 at the sediment-water interface at site 1 - Middle and site 2-Corner, respectively to values 6.5. A similar decline in pH was observed by Wersin et al. (1991) in freshwater carbonate sediments.

Wersin et al. (1991) suggested production of CO_2 and other acids, by intense mineralization of organic matter, as possible mechanisms responsible for the pH change.

The sediment P profiles showed little difference between the two sites. At both sites, there was a marginal decline in total phosphorus (TP) from the sediment-water interface downward (Fig. 2), largely due to decreasing organic phosphorus (OP) concentrations with depth. OP accounted for ~50% of the TP in the upper sediments (Fig. 2) and for most (60-86%) of the TP in the bottom part of the core. In the upper sediments of both cores, a decrease in OP concentrations with depth was accompanied by an increase in non-apatite inorganic P (NAI-P) concentrations. The two parameters were inversely correlated at 5% significance level ($p=0.05$), suggesting mineralization of OP. The NAI-P, which incorporates the DRP in the porewater, increases from about 30% of the sediment TP at the top of the cores to over 40% of the TP at the transition boundary (Fig. 2). This fraction of P also includes orthophosphate adsorbed on Fe and Al-oxides, Fe and Al-P minerals such as vivianite and variscite and Ca-P minerals other than crystalline apatite (Williams et al., 1976a, 1980). At both sites, the apatite-P concentrations were steady (Fig. 2) to the transition boundaries, where their concentrations dropped from ~200 mg/kg of dry sediment to <50 mg/kg of dry sediment. Apatite-P, which includes P bound in crystal lattices of apatite grains, accounts for just under 20% of the TP in the top 30 cm of the sediments. The deeper sediments had a much lower percentage (3-5%) of TP in this form. Apatite-P, present in the sedimentary material in the Great Lakes Basin is largely of detrital origin (Williams et al., 1976a, 1976b). The low concentrations of apatite-P in the deeper sediments of Sanctuary Pond suggest that these sediments were deposited in sedimentary environments supplying less watershed material containing this P form than the overlying sediments. The observed distribution of P forms is also consistent with the presence of a former bog in the area of the Sanctuary Pond.

The molar C:P ratios (Table 2) in the top 15 cm were high (575:1), suggesting that land plants (Bowen, 1966; Delwiche and Likens, 1977; Deevey, 1973) are the main source of the organic matter in the sediments. The increase in the C:P ratios with depth indicates higher loss rate for P during the decomposition of organic matter than for C, with values reaching 1030-2360 below the transition horizons (Table 2).

Porewater

The porewater profiles as well as the concentrations of dissolved constituents ($\text{PO}_4\text{-P}$, $\text{NH}_3\text{-N}$, Fe, Mn, Ca, Mg) were similar for both investigated sites (Figs. 3 and 4), showing little spatial difference in porewater chemistry. Steep vertical concentration gradients of $\text{PO}_4\text{-P}$, $\text{NH}_3\text{-N}$, Fe, Mn and Ca were observed in the interstitial water below the sediment-water interface at both sites. The concentrations of these species increase sharply just below the sediment-water interface and drop to much lower values at the depths corresponding to sedimentary sequences below the transition horizons. The low concentrations of dissolved constituents in the deeper porewater are consistent with the presence of bog type sediments in the lower sedimentary sequences. The concentrations of $\text{PO}_4\text{-P}$ increased with depth to slightly over $120\ \mu\text{mol P/L}$ at both sites and the concentrations of the $\text{NH}_3\text{-N}$ increased to over $1.5\ \text{mmol/L}$ (Fig. 3 and 4). These values are substantially higher than the values reported for Lake Erie sediments ($\sim 56\ \mu\text{mol P/L}$, $0.27\ \text{mmol NH}_3\text{-N/L}$, Rosa and Azcue, 1993) or other carbonate (Wersin et al., 1991) or shield lake sediments (Carignan and Lean, 1991), but they are comparable with those reported for a wetland receiving hyper-eutrophic lake water (D'Angelo and Reddy, 1994) and hyper-eutrophic lakes (Moore et al., 1991). The $\text{PO}_4\text{-P}$ correlated significantly ($p=0.05$) with the NAI-P concentrations in sediments, confirming that porewater P constitutes a part of the sediment NAI-P. Calculations indicate that porewater P constitutes less than 1% of the sediment P. This proportion is in agreement with the results obtained from the study of lake bottom sediments by Bostrom et al. (1982).

High concentrations of $\text{PO}_4\text{-P}$ and $\text{NH}_3\text{-N}$ in porewater result likely from anaerobic decomposition of organic matter which yields the high concentrations of these constituents in the porewater. As organisms senesce, die, and decompose in sediments, ammonium is produced by ammonifying bacteria (Buchanan and Gibbons, 1974). Ammonium release to the porewater is a function of the C:N ratio (Heath, 1992).

At a high C:N ratio ammonium is utilized for amino acids production and growth of

organisms, whereas at a low C:N ratio ammonium is released to porewater (Heath, 1992). The concentrations of dissolved $\text{PO}_4\text{-P}$, produced by the microbial degradation of organic matter, typically are controlled by precipitation of phosphate minerals (Nriagu and Dell, 1974; Golterman, 1982; Emerson and Widmer, 1978).

At both sites, Ca concentrations increase with increasing depth, from $\sim 1000 \mu\text{mol/L}$ in the water column to $\sim 3000 \mu\text{mol/L}$. Likewise, Mg concentrations increase with depth at both sites from $350 \mu\text{mol/L}$ at the sediment-water interface to values $\sim 750 \mu\text{mol/L}$. Increases in Ca and Mg concentrations with depth (Figs. 3 and 4) are attributed to production of CO_2 resulting from the degradation of organic matter and dissolution of carbonate minerals (Emerson, 1976). Fe and Mn concentrations follow a similar trend to that of $\text{PO}_4\text{-P}$ and $\text{NH}_3\text{-N}$ (Figs. 3 and 4). The observation that $\text{PO}_4\text{-P}$, $\text{NH}_3\text{-N}$, Fe and Mn follow the same depth trends in this study suggests that they are related. All these species are released into the porewater by reductive dissolution of sediments. The porewater Si concentrations (not shown) also show an increase with increasing depth, probably due to the dissolution of diatoms.

The alkalinities of pore water samples corresponding to sediments above the transition horizons were substantially higher than those below them. Zero alkalinities were measured in deep pore water samples, which is consistent with the premise of an early bog existence.

Mineral equilibria

Precipitation/dissolution reactions usually control concentrations of dissolved constituents in interstitial waters (Berner, 1980; Stumm and Morgan 1970). The formation of mineral phases results in removal and storage of the dissolved species in sediments (Matissof et al., 1980). Conversely, their dissolution releases the dissolved species into the interstitial water. The precipitation/dissolution of the mineral phase from solution is a function of 1) the saturation state and 2) reaction kinetics (Emerson and Widmer, 1978; Matissof et al., 1980; Wersin et al., 1991). The degree of

porewater saturation with respect to authigenic mineral phases is measured by a saturation index. The geochemical speciation program MINTEQA2, vs.3.11 (Allison et al., 1992) was used to calculate the ion activity products and saturation indices of phosphate minerals, potentially controlling the solubility of P in the sediment porewater.

Input consisted of the measured concentrations of ΣPO_4 and major cations, i.e. Fe, Ca, Mg, Na, K, Al, Mn, Ba, Sr and RSiO_2 . As the DRP concentrations were essentially equivalent to $\text{PO}_4\text{-P}$ concentrations, DRP values were used for $\Sigma\text{PO}_4\text{-P}$. Because we only had few direct alkalinity measurements, we used calculated alkalinity in the model.

Carbonate alkalinity was calculated using the electroneutrality equation $m\text{HCO}_3^- = 2m\text{Ca}^{2+} + 2m\text{Mg}^{2+}$ and the values were entered into the program as mg/L CaCO_3 .

Non-carbonate alkalinity was calculated by MINTEQA2, and was found to be insignificant in comparison with the carbonate alkalinity (lower by four orders of magnitude). Since direct pH measurement in sediments is subject to considerable error due to degassing of CO_2 , electrode interaction with DOC and sediment compaction, calculated pH values were used in our computation. The calculated pH values compare well (within 0.0-0.3 pH units) with the measured values. A temperature of 18°C was used for calculations, as this was the temperature measured in the field.

Measured Eh values input was averaged over the specific depth interval.

The saturation index (SI) was used to determine whether the reactions of phosphate dissolution/precipitation are at equilibrium. SI is defined by Troup (1974) as

$$SI = \frac{I}{n} \log\left(\frac{IAP}{K_{sp}}\right)$$

where IAP is the ion activity product, K_{sp} is the solubility constant, and n is the stoichiometric coefficient of the cation in the solid phase considered. A value of $SI > 0$ indicates that the porewater is supersaturated with respect to the phosphate mineral considered. Values $SI = 0$ and < 0 indicate that porewater is saturated and

undersaturated, respectively with respect to a solid phase considered. Saturation indices for calcite (CaCO_3), siderite (FeCO_3) and PO_4 minerals were calculated based on the thermodynamic data given in Table 3. The calculated SI values are plotted in Fig. 5.

The results indicate that the saturation indices for all considered minerals are similar for both sites (Fig. 5). The interstitial waters were near equilibrium, or slightly supersaturated with respect to calcite, suggesting that calcite precipitation/dissolution is controlling the concentrations of Ca and CO_3 in solution. At site #1 - Middle, the overlying water is undersaturated with respect to siderite (Fig. 5), but at both sites, sediment porewater is supersaturated with respect to siderite. Of the phosphate minerals, interstitial waters at both sites are highly supersaturated with respect to hydroxyapatite (SI ~1-6, Fig. 5), suggesting that apatite should be precipitating from solution. Hydroxyapatite ($\text{Ca}_5(\text{PO}_4)_3\text{OH}$) is a common detrital mineral phase in Lake Erie and its supersaturation and presence in sediment does not imply authigenic formation (Williams et al., 1976a, 1976b; Matisoff et al., 1980). Furthermore, its nucleation kinetics is such that the presence of other species can interfere with its growth (Martens and Harris, 1970; Stumm and Morgan, 1970; Stumm and Leckie, 1971). Moore et al. (1991) suggested that the presence of organic acids and Mg^{2+} may inhibit apatite formation and more soluble Ca- PO_4 minerals (such as tricalcium phosphate, $\text{Ca}_3(\text{PO}_4)_2$) may be forming. High organic matter content of the investigated sediments (50-85%), may favor precipitation of this phase from the interstitial water. Gregory et al. (1976), however, showed that pure $\text{Ca}_3(\text{PO}_4)_2$ phase formed only at high temperatures (1000°C). Fixen et al. (1983) found soils to have near-equilibrium concentrations of Ca and PO_4 with respect to $\text{Ca}_3(\text{PO}_4)_2$, but they stated that the similar mineral, whitlockite ($\text{Ca}_{18}(\text{Mg,Fe})\text{H}_2(\text{PO}_4)_{14}$) may be forming in soils. Saturation indices of tricalcium phosphate as well as other Ca- PO_4 minerals (brushite, monetite and octacalcium phosphate) are negative (Fig. 5), but approach zero as the concentrations of PO_4 and Ca in interstitial water increase. Of other phosphate minerals, vivianite would be expected to precipitate from the interstitial water (Fig. 5), however a recent

study of Wersin et al. (1991) showed no indication of vivianite precipitates using electron microscope techniques. Likewise, these investigators found no indication of siderite, using the same electron microscope techniques, even though the thermodynamic calculations favor precipitation of this phase from the interstitial waters.

One possible explanation of the Wersin's et al. (1991) study may be that the mass of vivianite and siderite is too low to be detected by the electron microscope techniques. These techniques do not detect small amounts of accumulated mass. Another explanation may be kinetic factors. Although thermodynamic conditions favor precipitation of vivianite and siderite, similarly as for apatite, precipitation of these phases may be inhibited, and other kinetically-favored solid phases may be precipitating from the interstitial waters (Mucci, 1988; Jakobsen and Postma, 1989; Wersin et al., 1989). The supersaturation of porewaters with respect to pure mineral phases (e.g. vivianite, hydroxyapatite) may be explained by the fact that the thermodynamic calculations use solubility constants determined on pure phases in the laboratory. Sediment porewaters are complex mixtures and precipitated authigenic mineral phases are likely to be chemically mixed with their solubilities being different from those of pure phases (Suess et al., 1979). Alternatively, supersaturation with respect to vivianite and siderite may also be explained by overestimation of Fe available for inorganic precipitation. It is possible that a large percentage of Fe in the porewater is organically bound and not available for inorganic precipitation. This would result in overestimation of Fe available for precipitation.

Similarly, geochemical modeling suggests that the porewaters are slightly supersaturated with respect to the Al- phosphate mineral, variscite at depths roughly between 3 and 30 cm below the sediment-water interface (Fig. 5). The amount of variscite precipitating from solution is dependent on the concentrations of Al in the interstitial water. Aluminum is not a redox sensitive species and it is not likely to be produced by reductive dissolution reactions. As the pH of sediments is close to neutral, dissolution of Al silicates and Al oxyhydroxides, releasing Al into porewater, would be very slow (Horowitz, 1991). However, it is possible that a large percentage of

Al, similarly as Fe, in porewater is organically bound and not available for inorganic precipitation.

Nutrient transport

In many aquatic systems, the main transport of dissolved substances across the sediment-water interface occurs by molecular diffusion (Carignan and Lean, 1991; Klump and Martens, 1981, 1987; Sherman et al., 1994). In shallow lakes, the prevailing mechanism for transport of nutrients into the overlying water is resuspension of benthic sediments (Blom et al., 1994; Koncsos and Somlyódy, 1994; Sondergaard et al., 1992; Young et al., 1994). In Sanctuary Pond, advective transport, resulting from turbulent conditions induced by feeding and spawning carp, wind/wave action and gas ebullition, is likely the principal mechanism for sediment-water nutrient exchange. Carps are numerous at the Sanctuary Pond and gas ebullition in the highly organic-rich sediments was observed. Furthermore, the shallow nature and the proximity of the pond to Lake Erie makes the physical turbation due to the wind/wave action important. Because of the susceptibility of floc sediment to resuspension (D'Angelo and Reddy, 1994) the above factors can cause substantial resuspension of benthic sediments and consequently, mixing of nutrient-rich porewater with the overlying water. Because the pond is shallow, the sediments are in the euphotic zone and nutrients originating from the sediments are readily available for biological utilization, resulting in prolific algal growth in the pond. The situation here is similar to that observed by Painter et al. (1989) at Cootes Paradise, a freshwater wetland located at the western end of Hamilton Harbour in Lake Ontario.

Implications for water quality

High concentrations of nutrients ($\text{NH}_3\text{-N}$ and DRP) in sediment porewater were observed at the Sanctuary Pond, at Point Pelee National Park. The concentrations are

comparable to those reported for wetlands receiving hyper-eutrophic lake water and hyper-eutrophic lakes. The sediment geochemistry and porewater chemistry revealed that the pond is well mixed and there are no spatial or stratigraphic differences between the two sampling sites in the levels of available nutrients in the sediments. The surrounding ponds, which connect to the Sanctuary Pond, all have substantially lower concentrations of nutrients in the water column (McCrea, 1993) and, therefore, would unlikely contribute to nutrient loads to the Sanctuary Pond. Although studies (Crowe and Ptacek, 1997, Ptacek and Crowe, 1997) carried out in other areas of the park reveal a widespread contamination of groundwater from the park's septic systems and measurable impacts (Mayer et al., 1997) of contaminated groundwater discharge on the nearshore zone of some open-water ponds, the lack of spatial differences in sediment P and porewater nutrient concentrations suggests that current nutrients contribution from contaminated groundwater to Sanctuary Pond may be a small component of the current nutrient budget. Alternatively, nutrient contribution from groundwater, if any, may be quickly incorporated into the nutrient pool by the highly active mixing processes occurring in the pond.

The high concentrations of nutrients in sediment porewater, the lack of spatial differences in sediment and porewater nutrient concentrations and the absence of known external sources of nutrients, suggest that sediments may be significant contributors of nutrients to Sanctuary Pond. The levels of nutrients in porewater are sufficiently high and mixing of sediments is sufficiently intense to introduce substantial quantities of nutrients to the water column. At Sanctuary Pond, release of nutrients from sediments, rather than input from the external sources, is contributing to nutrient pool in the water column, resulting in poor water quality in the pond.

CONCLUSIONS

The results of the present study show that the organic matter decomposition is an important mechanism responsible for high concentrations of dissolved nutrients in

porewater of Sanctuary Pond sediments. The levels of DRP in porewater, produced by mineralization of the organic matter, are likely governed by phosphate mineral equilibria. At both sites sediment porewater is highly supersaturated with respect to Ca, Fe, mineral phases, hydroxyapatite, vivianite, respectively, and slightly supersaturated with respect to Al mineral phase, variscite. There are no differences in the porewater profiles, nor in the levels of dissolved constituents between the two investigated sites. Nutrients, released through decomposition process in benthic sediments, are available for subsequent release to the water column. Various transport mechanisms are responsible for nutrients regeneration in the Sanctuary Pond. Of those, physical mixing of sediments caused by carps and to a lesser extent by gas ebullition are the main mechanisms responsible for transport of nutrients from sediments to the water column. Hence, at the Sanctuary Pond, high concentrations of nutrients in sediment porewater and resuspension of bottom sediments, primarily by carps foraging for food, are most likely responsible for the high nutrient levels in the water column and, subsequently, for hyper-eutrophic conditions. Therefore, at Sanctuary Pond release of nutrients from the sediments rather than the external sources are responsible for excessive nutrient inputs to the water column and subsequent deterioration of water quality in the pond.

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Table 1. Surface water quality at the Sanctuary Pond

Parameter	Site #1 - Middle	Site #2 - Corner
pH	9.1	9.2
TSS (mg/L)	52.5	50.0
Turbidity (NTU)	49	54
TP (mg/L)	.234	.231
TFP (mg/L)	.037	.034
Chlorophyl a (ug/L)	76.5	80.1
TKN (mg/L)	5.46	5.25
NO ₃ +NO ₂ -N (mg/L)	.028	.018
NO ₂ -N (mg/L)	.016	.014
NH ₃ -N (mg/L)	.132	.134

* Temperature of water column 21°C at both sampling sites

Table 2. Total and Organic C concentrations in sediments and molar C/P ratios

Site #1 - Middle				Site # 2 - Corner			
Depth (cm)	Total C %	Organic C %	molar C/P	Depth (cm)	Total C %	Organic C %	molar C/P
0-1	23.5	23.0	477	0-1	25.2	24.3	560
1-2	26.9	26.3	563	1-2	26.9	26.0	566
2-3	25.9	25.5	566	2-3	24.2	23.5	550
3-4	24.7	24.6	537	3-4	26.1	25.3	586
4-5	23.2	22.8	494	4-5	26.6	25.8	585
5-6	24.8	24.0	568	5-6	27.5	26.6	547
6-7	24.0	23.2	521	6-7	24.4	23.1	526
7-8	25.8	26.0	542	7-8	24.8	24.0	529
8-9	25.9	24.9	574	8-9	25.6	24.5	541
9-10	26.2	25.8	615	9-10	25.8	25.1	548
10-11	27.3	26.7	609	10-11	24.5	25.7	556
11-12	26.3	26.3	616	11-12	26.9	25.9	588
12-13	23.6	23.0	530	12-13	30.9	29.5	707
13-14	28.7	28.0	636	13-14	30.0	28.7	691
14-15	28.4	27.8	660	14-15	28.9	27.7	682
15-16	28.3	27.8	726	15-16			
16-17	27.4	26.3	815	16-17			
17-18	28.5	27.3	737	17-18			
18-19	29.0	28.8	678	18-19			
19-20	28.6	27.9	703	19-20	31.6	30.8	773
20-22	28.9	29.3	699	20-22	27.9	27.7	687
22-24	37.9	37.5	1024	22-24			
24-26	33.4	31.8	823	24-26	25.1	24.7	601
26-28	30.1	29.7	782	26-28	34.1	33.6	887
28-30	38.9	38.0	1032	28-30	45.2	44.9	1948
30-32	48.3	47.7	1456	30-32	50.0	49.8	1545
32-34	56.6	56.2	2041	32-34	49.1	48.4	1500
34-36	53.0	52.8	1996	34-36	46.7	46.3	1539
36-38	55.6	55.1	2359				
38-40	54.3	54.1	1994				

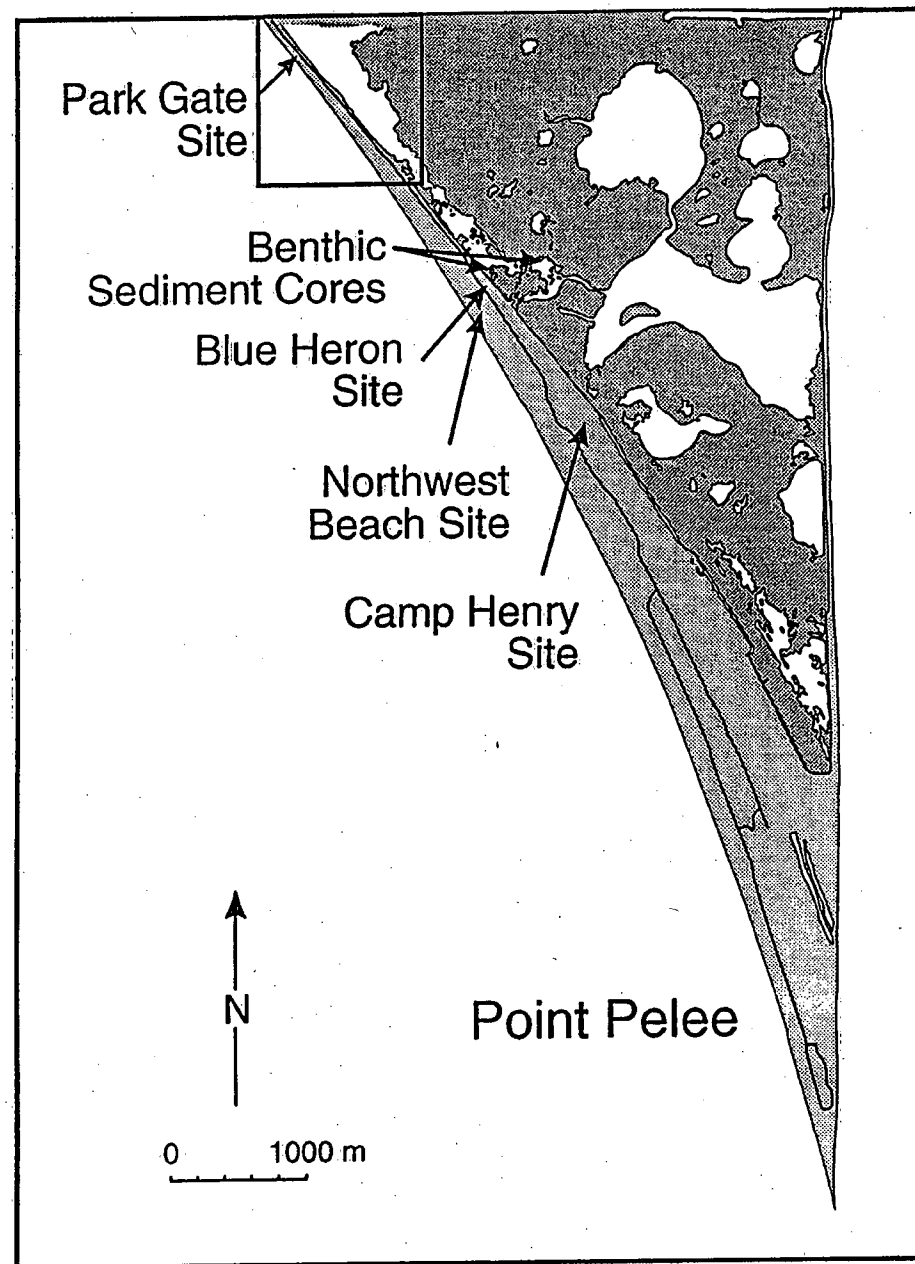
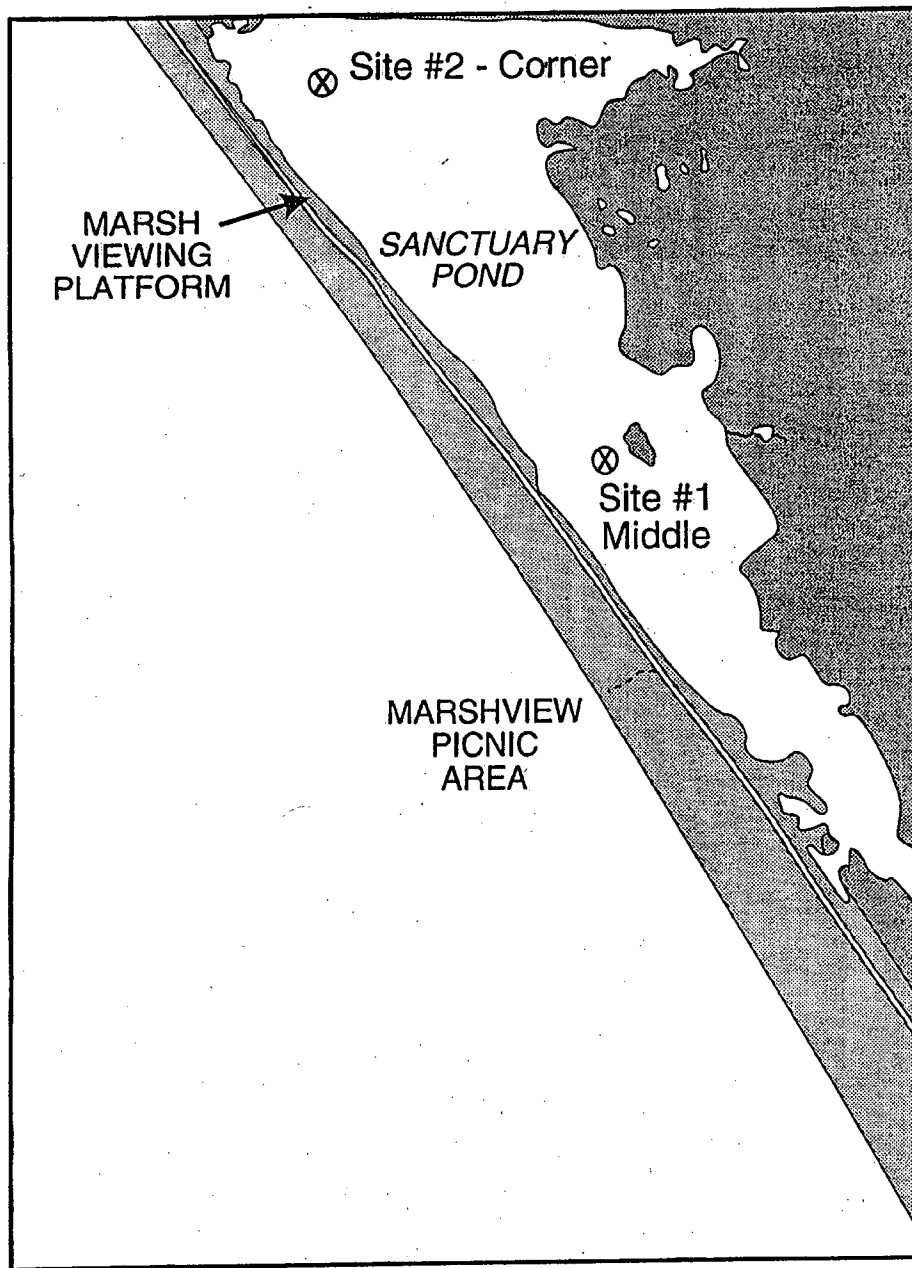
Table 3. Thermodynamic data used for MINTEQA2 calculations

Mineral	Reaction	Log Ksp	Reference
Calcite	$\text{CaCO}_3 = \text{Ca}^{2+} + \text{CO}_3^{2-}$	-8.4750	MINTEQA2 database
Siderite	$\text{FeCO}_3 = \text{Fe}^{2+} + \text{CO}_3^{2-}$	-10.550	MINTEQA2 database
Hydroxyapatite	$\text{Ca}_5(\text{PO}_4)_3\text{OH} + \text{H}^+ = 5\text{Ca}^{2+} + 3\text{PO}_4^{3-} + \text{H}_2\text{O}$	-44.199	MINTEQA2 database
Vivianite	$\text{Fe}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O} = 3\text{Fe}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O}$	-36.00	MINTEQA2 database
Strengite	$\text{FePO}_4 \cdot 2\text{H}_2\text{O} = \text{Fe}^{2+} + 2\text{PO}_4^{3-} + 8\text{H}_2\text{O}$	-26.40	MINTEQA2 database
Variscite	$\text{AlPO}_4 \cdot 2\text{H}_2\text{O} = \text{Al}^{3+} + \text{PO}_4^{3-} + 2\text{H}_2\text{O}$	-21.00	Stumm and Morgan (1981)*
Octacalcium Phosphate	$\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O} = 8\text{Ca}^{2+} + 2\text{H}^+ + 6\text{PO}_4^{3-} + 5\text{H}_2\text{O}$	-93.96	Lindsay and Vlek (1977)*
Brushite	$\text{CaHPO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} + 2\text{H}_2\text{PO}_4^{2-} + 2\text{H}_2\text{O}$	-6.60	Lindsay and Vlek (1977)*
Monetite	$\text{CaHPO}_4 = \text{Ca}^{2+} + \text{HPO}_4^{2-}$	-6.90	Lindsay and Vlek (1977)*
Tricalcium Phosphate	$\text{Ca}_3(\text{PO}_4)_2 = 3\text{Ca}^{2+} + 2\text{PO}_4^{3-}$	-28.92	Lindsay and Vlek (1977)*
	$\text{HPO}_4^{2-} = \text{H}^+ + \text{PO}_4^{3-}$	-12.35	Lindsay and Vlek (1977)*
	$\text{H}_2\text{PO}_4^- = 2\text{H}^+ + \text{PO}_4^{3-}$	-19.56	Lindsay and Vlek (1977)*

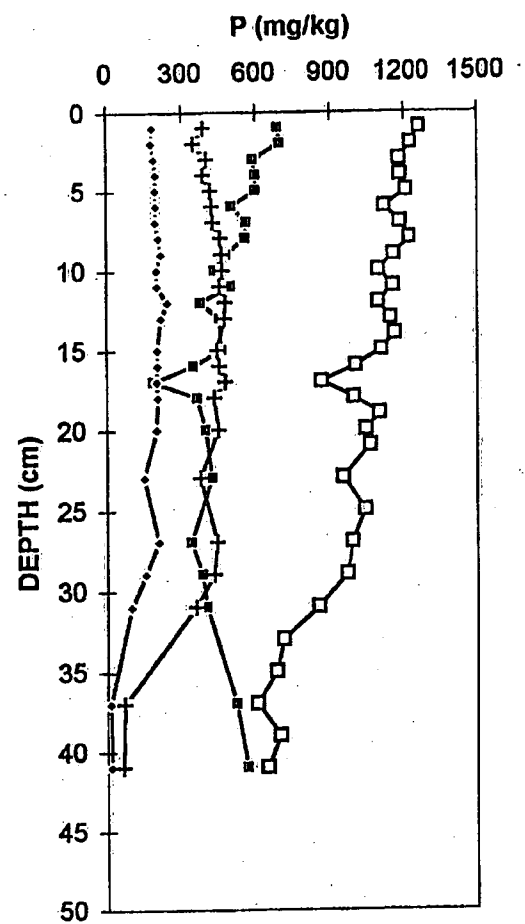
*Log Ksp values were compared to those listed in Nriagu and Dell (1984) and were found to be compatible

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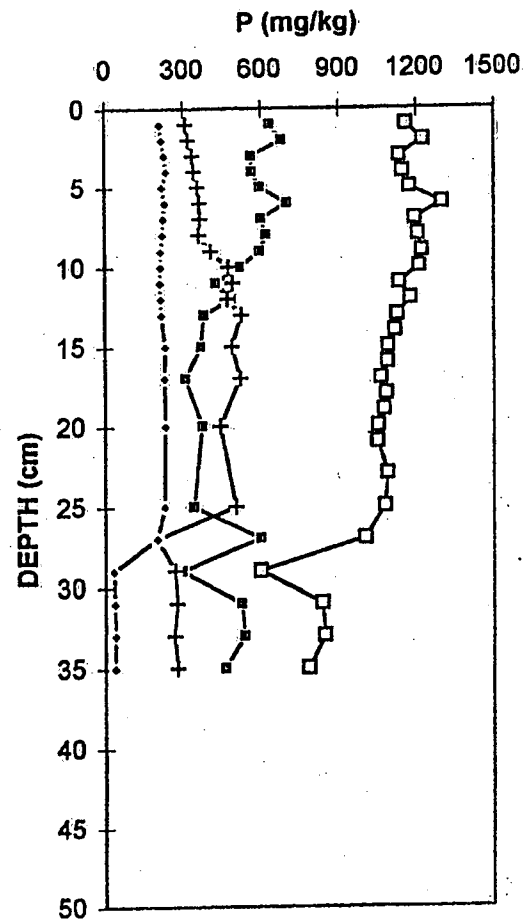


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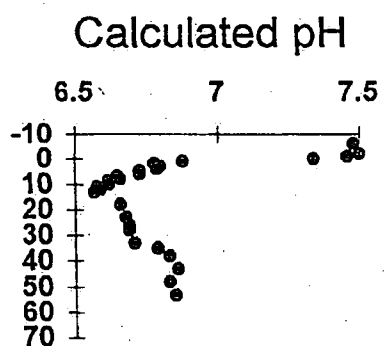
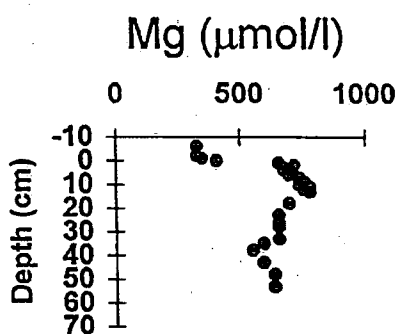
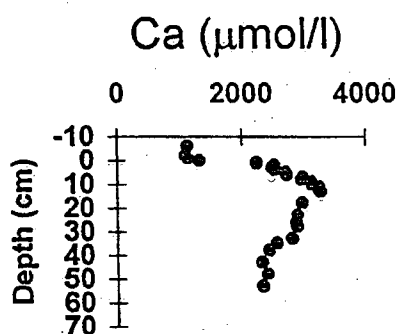
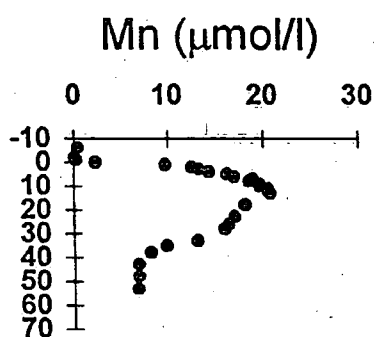
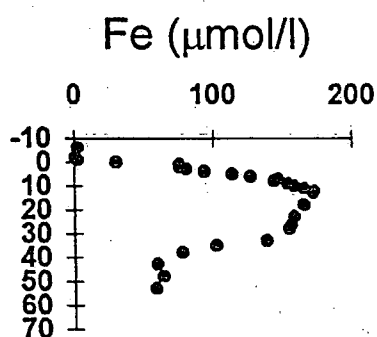
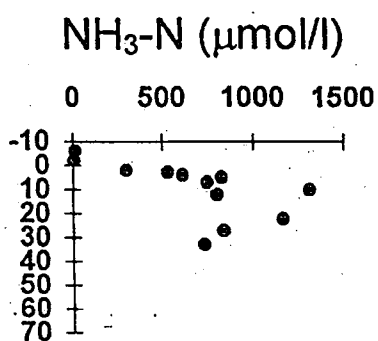
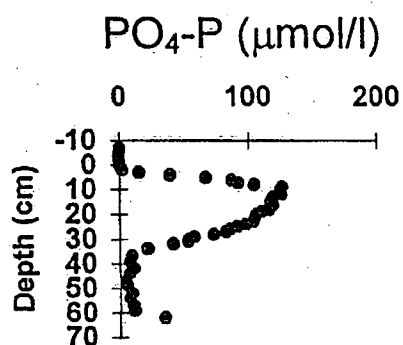
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—+— NAI-P

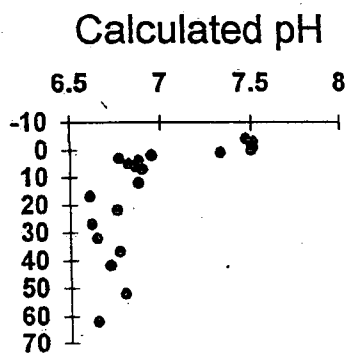
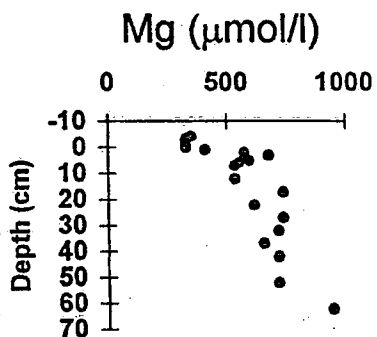
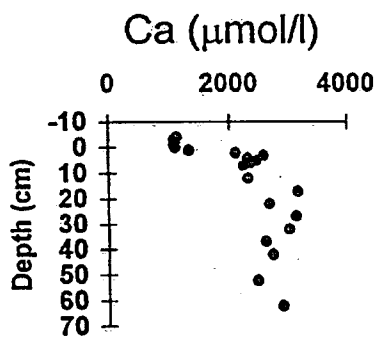
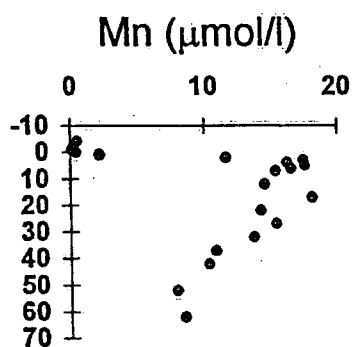
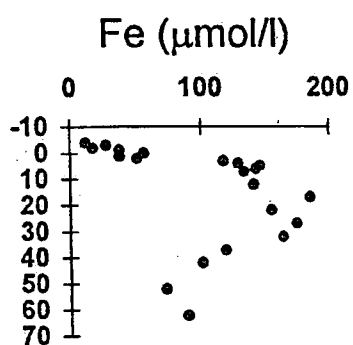
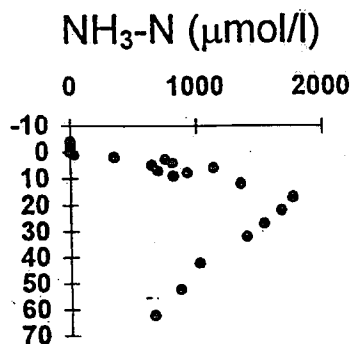
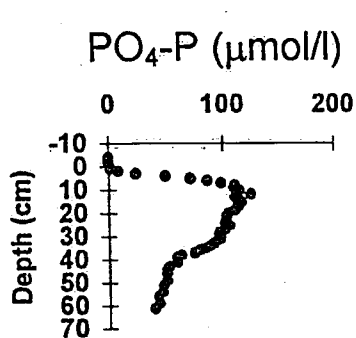
SITE #2 - CORNER



—■— OP
—♦— Apatite-P

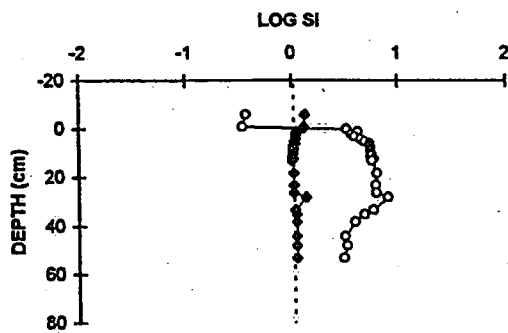
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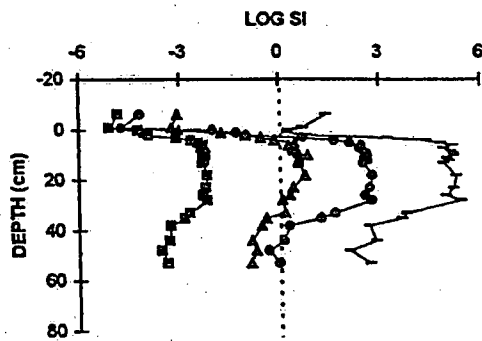
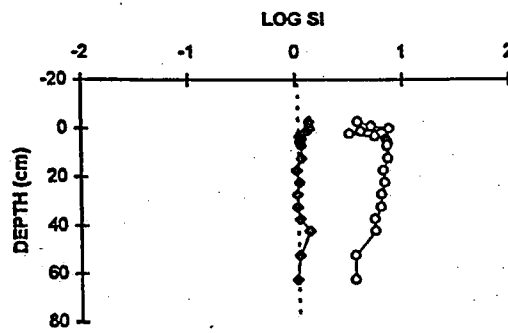
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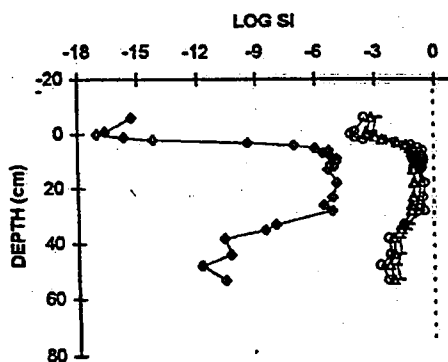
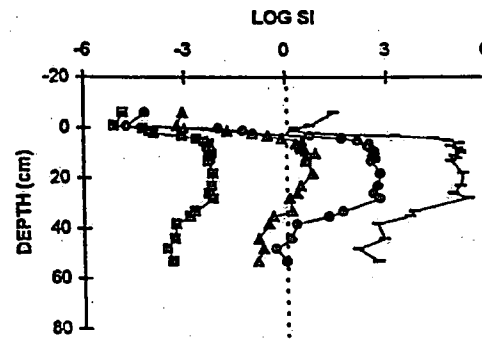


—●— Calcite —○— Siderite

SITE 2 (CORNER)

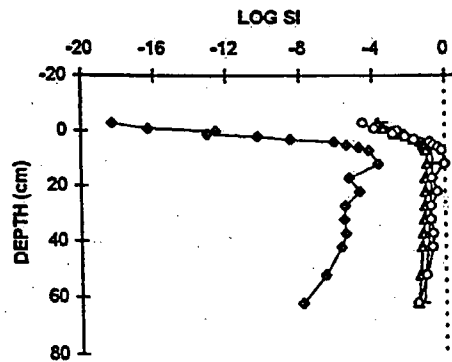


—●— Hydroxyapatite —▲— Variscite
—■— Strengite —◆— Vivianite



—●— Octacalcium Phosphate —▲— Brushite
—■— Monetite —◆— Tricalcium Phosphate

(a)



(b)

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