

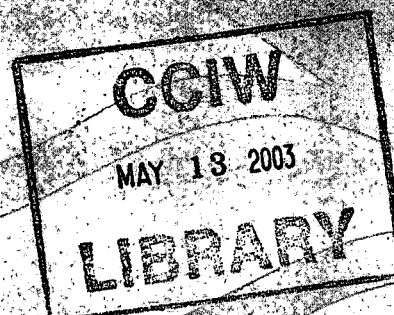
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**THE ROLE OF SEDIMENTS IN NUTRIENT
LOADINGS IN COOTES PARADISE**

T. Mayer, F. Rosa and M. Charlton

Technical Note No. AEP-TN03-002

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Report prepared for the Regional Municipality of Hamilton Wentworth

Technical Note No. AEP-TN03-002

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ACKNOWLEDGMENT

The authors gratefully acknowledge the dedicated assistance of Aaron Lawrence and the capable field assistance of Mike Mawhinney and Ken Hill. The field equipment was prepared and calibrated by Sergio Krickler and Bob Rowsell. The logistical support of the RBG staff, namely, Tys Theysmeijer is greatly appreciated. Professor Peter Lee of the Lakehead University in Thunder Bay kindly shared the information with us and provided access to sediment data. The financial support of the Regional Municipality of Hamilton Wentworth is greatly appreciated..

NWRI Research Summary

Plain language title

Investigation of nutrient loadings from sediments in a Great Lakes coastal marsh Cootes Paradise.

What is the problem and what do scientists already know about it?

High nutrient levels, and a prolific algal growth are major stresses, affecting the water quality in Cootes Paradise even after the installation of a fishway and carp barrier. While there was some reduction in nutrient loadings through the upgrades to Dundas sewage treatment plant (STP) and combined sewer overflow (CSO) events, the response of the marsh to restoration efforts has not been as good as anticipated. To better predict the results of restoration efforts, nutrient loadings from both external and internal sources have to be assessed and compared. While the loadings from the external sources such as Dundas STP and CSOs have been quantified, internal loadings from sediments are unknown.

Why did NWRI do this study?

To determine if further reduction in the external nutrient loadings would result in substantial improvement in the water quality in Cootes Paradise, the relative importance of nutrient sources, including internal loadings from sediments needs to be assessed. This requires a quantification of nutrient fluxes from sediments. Presently, there is little information on the amount of nutrient loadings from sediments in Cootes Paradise. The present study provides this information. Assessment of nutrient loadings from sediments will help to better predict the outcomes of the management actions and aid in development of reasonable expectations for the water quality of this Great Lakes coastal marsh.

What were the results?

The work has shown that there are large differences in nutrient fluxes from sediments attributable to sediment spatial heterogeneity. Nutrient fluxes were highest at the sites adjacent to point sources, where the sediment had the largest nutrient pool. Conversely, nutrient fluxes were lowest at the site with the smallest sediment nutrient pool. The sediment nutrient pool affected the concentrations of nutrients in porewater, that governed the nutrient fluxes from sediments.

How will these results be used?

The results will be used for decision making in the restoration efforts of Cootes Paradise, specifically provide the information if further costly reduction of external nutrient loadings would enhance the water quality in the marsh.

Who were our main partners in the study?

The Regional Municipality of Hamilton Wentworth
Royal Botanical Gardens

Publishing Information

This report was prepared for the VNR client, The Regional Municipality of Hamilton Wentworth and for the Royal Botanical Gardens. The full title of the report is "The role of sediments in nutrient loadings in Cootes Paradise".

Sommaire des recherches de l'INRE

Titre en langage simple et clair

Étude sur la charge en nutriments provenant des sédiments dans un marais côtier des Grands Lacs, à Cootes Paradise.

Quel est le problème et que savent déjà les scientifiques à ce sujet?

De fortes concentrations de nutriments et une abondante croissance algale représentent des contraintes majeures qui s'exercent sur la qualité de l'eau de Cootes Paradise, même après l'installation d'une passe à poissons et d'une barrière à carpes. Il y a eu une certaine réduction des charges de nutriments grâce aux améliorations apportées à la station d'épuration des eaux usées (STEU) de Dundas et aux déversoirs d'orage, mais les résultats des activités de remise en état du marais n'ont pas été aussi bons que prévus. Pour arriver à mieux prévoir les résultats des activités de restauration, il faudra évaluer et comparer les charges de nutriments provenant de sources tant externes qu'internes. Les charges issues des sources externes, comme la STEU de Dundas et les déversoirs d'orage, ont été quantifiées, mais on ignore quelles sont les charges provenant des sédiments.

Pourquoi cette étude de l'INRE?

Pour déterminer si des réductions additionnelles des charges de nutriments provenant de sources externes permettraient d'améliorer de façon sensible la qualité de l'eau de Cootes Paradise, il faudra évaluer l'importance relative des sources de nutriments, et notamment les charges internes provenant des sédiments. Cela requiert la quantification des flux de nutriments issus des sédiments. On ne possède actuellement que peu d'information sur la charge de nutriments provenant des sédiments à Cootes Paradise. La présente étude fournit cette information. L'évaluation des charges de nutriments provenant des sédiments aidera à mieux prévoir l'issue des activités de gestion et à concevoir des objectifs raisonnables en matière de qualité de l'eau pour ce marais côtier des Grands Lacs.

Quels ont été les résultats?

Les travaux ont montré qu'il existe de grandes différences dans les flux de nutriments provenant des sédiments, lesquelles sont attribuables à l'hétérogénéité spatiale de ces derniers. Les flux de nutriments étaient les plus élevés aux sites voisins de sources ponctuelles, où les sédiments contenaient les réserves les plus importantes de nutriments. Inversement, les flux de nutriments étaient les plus faibles aux sites dont les sédiments renfermaient le moins de réserves de nutriments. Les réserves de nutriments des sédiments influencent les concentrations de nutriments de l'eau interstitielle, qui régissent les flux de nutriments issus des sédiments.

Comment ces résultats seront-ils utilisés?

Ces résultats seront utilisés pour les prises de décision concernant les activités de remise en état de Cootes Paradise, grâce notamment aux données permettant de déterminer si des réductions additionnelles coûteuses des charges de nutriments provenant de sources externes pourraient améliorer la qualité de l'eau dans le marais.

Quels étaient nos principaux partenaires dans cette étude?

La municipalité régionale d'Hamilton Wentworth
Jardins botaniques royaux

Info-publication

Ce rapport a été préparé pour un client RAVC, la municipalité régionale d'Hamilton Wentworth et pour les Jardins botaniques royaux . Le titre complet du rapport est « The role of sediments in nutrient loadings in Cootes Paradise ».

EXECUTIVE SUMMARY

An investigation was carried out to determine the nutrient fluxes from sediments in Cootes Paradise, a coastal wetland adjacent to Hamilton Harbour, at the western tip of Lake Ontario. This information is essential for the assessment of the overall importance of nutrient sources and for decision making in the marsh restoration efforts. Three sites were selected for the investigation. The sites were located at the West Pond, which receives the effluent from the Dundas Sewage Treatment Plant (STP), near the mouth of the Chedoke Creek, and in the vicinity of the RBG boathouse. The results derived from the Fickian diffusion model indicate that there are substantial (nearly 20 fold) differences in diffusive P fluxes from sediments, resulting from large spatial variation in sediment porewater chemistry. Sites receiving outfalls of STP and Combined Sewer Overflows (CSOs) had the highest nutrient fluxes, with the estimates of phosphorus (P) fluxes highest ($5.3 \text{ mg/m}^2\cdot\text{d}$) at the West Pond site, followed by the site adjacent to the Chedoke Creek ($4.4 \text{ mg/m}^2\cdot\text{d}$). The lowest flux was estimated at the Boathouse site ($0.3 \text{ mg/m}^2\cdot\text{d}$) which is located in the main body of Cootes Paradise. The differences in nutrient fluxes appear to be attributable to spatial heterogeneity of bottom sediments. The West Pond site, which has the greatest phosphorus fluxes has the largest sediment phosphorus pool and exhibits the highest porewater P gradients, followed by the Chedoke Creek site. These two sites have also the highest $\text{NH}_3\text{-N}$ fluxes. The RBG Boathouse site, which has the lowest nutrient fluxes has the lowest sediment nutrient pool and the smallest nutrient gradients. The results suggest that sediment P geochemistry is important in regulating the P concentrations in porewater, which in turn is an important factor controlling the fluxes of P from sediments. The data also suggest that sediment may be an important source of nutrients in areas containing nutrient contaminated sediments and release of nutrients from these sediments may delay the recovery of the marsh even after the reduction of the external phosphorus loading.

RÉSUMÉ

Une étude a été effectuée afin de déterminer les flux de nutriments provenant des sédiments à Cootes Paradise, un marais côtier voisin du port d'Hamilton, à l'extrémité ouest du lac Ontario. Cette information est essentielle si on veut évaluer l'importance globale des sources de nutriments et prendre les bonnes décisions pour les mesures de restauration du marais. Trois sites ont été choisis pour l'étude. Ils sont situés à l'étang West, qui reçoit l'effluent provenant de la station d'épuration d'eaux usées de Dundas, près de l'embouchure du ruisseau Chedoke et au voisinage de la remise à bateaux des Jardins botaniques royaux. Les résultats obtenus à l'aide du modèle de diffusion Fickian montrent qu'il existe des différences importantes (presque un multiple de 20) entre les flux de diffusion de P à partir des sédiments, écarts attribuables à la grande variation spatiale de la chimie de l'eau interstitielle des sédiments. Les sites recevant l'exutoire de la STEU et le trop-plein des déversoirs d'orage présentent les flux les plus élevés de nutriments; ainsi, les estimations des flux de phosphore (P) donnent des valeurs maximales au site de l'étang Pond (5,3 mg/m² par jour), suivi du site voisin du ruisseau Chedoke (4,4 mg/m² par jour). Le flux le plus faible a été obtenu au site de la remise à bateaux (0,3 mg/m² par jour), qui est situé dans la partie principale de Cootes Paradise. Les différences dans les flux de nutriments semblent être causées par l'hétérogénéité des sédiments de fond. Le site de l'étang West, où les flux de phosphore sont les plus élevés possède les réserves sédimentaire les plus importantes de phosphore et présente les gradients de P interstitiel les plus élevés, suivi du site du ruisseau Chedoke. Ces deux sites présentent également les flux les plus élevés de N-NH₃. Le site de la remise à bateaux des Jardins botaniques royaux, où les flux de nutriments sont les plus faibles, possède également les réserves sédimentaires de nutriments les moins importantes ainsi que les gradients de nutriments les plus faibles. Les résultats semblent montrer que la géochimie sédimentaire du P est importante pour la régulation des concentrations de P dans l'eau interstitielle, qui à son tour est un important facteur pour la régulation des flux de P provenant des sédiments. Les données laissent enfin supposer que les sédiments peuvent être une importante source de nutriments dans des secteurs contenant des sédiments contaminés par les nutriments, la libération de ces derniers à partir des

sédiments risquant alors de retarder la remise en état du marais, même après la réduction de la charge de phosphore provenant de sources externes.

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THE ROLE OF SEDIMENTS IN NUTRIENT LOADINGS IN COOTES PARADISE

1. INTRODUCTION

Wetlands are important links between the terrestrial and aquatic ecosystems as they have an ability to attenuate nutrients and toxicants to receiving waters and provide a habitat for many species of fauna and flora. Many Great Lakes wetlands receive a broad variety of contaminant loads from various sources, including agricultural and urban runoff, municipal waste waters and effluents from Combined Sewer Overflows (CSOs). In spite of their nutrient attenuation capacity, excessive loadings of nutrients have disrupted their natural cycles, resulting in accelerated eutrophication. It has been suggested (Peverly 1982) that nutrient retention by wetlands depends on nutrient history and water movement through the system. There is, therefore, a need for better understanding of wetland processes which effect the assimilative capacity of wetlands.

Cootes Paradise Nature Sanctuary, a coastal wetland at the Western tip of Lake Ontario has once been a mesotrophic aquatic system (Chow-Fraser et al. 1998). The marsh has been considerably degraded due to the excessive sediment and nutrient inputs from Dundas Sewage Treatment Plant (STP), marsh tributaries and Combined Sewer Overflows (RBG 2001). Various strategies were initiated to improve the water quality in the marsh and restore the native vegetation. Exclusion of carp from the marsh was one of the initiatives undertaken, as it was suggested that resuspension of sediment and uprooting of plants by carp was largely responsible for the marsh degradation. Reduction in nutrient loadings from point sources through upgrades in Dundas STP and reduction in CSO events was another initiative in the restoration efforts. Although some improvement in water quality was evident, the response of marsh to the restoration efforts is variable. For instance, in 2001 the phosphorus concentration in the water column averaged at 210 µg/L (RBG 2001). This concentration is substantially higher than 70 µg/L, the target goal for phosphorus, set by the Hamilton Harbour Remedial Action Plan (RAP).

The ability of sediments to sequester phosphorus from the water column has long been recognized. However, whether sediments act as a P source or sink is determined by sediment composition and limnological conditions. Interchange between the dissolved and particulate P in

both water and sediments occurs through chemical and biological reactions. In sediments, the major processes which control the particulate/dissolved P equilibrium include adsorption/desorption, precipitation/dissolution, ligand exchange and enzymatic hydrolysis. The dominant transport mechanism from sediments to overlying water are diffusion, resuspension (by wind), bioturbation and gas ebullition.

Studies of shallow lakes (Phillips et al. 1994) have shown that sediment may be an important source of phosphorus to the overlying water, with the P release as high as 278 mg P/m².d. To determine the role of sediments to act as a source/sink of nutrients in Cootes Paradise, research on the role of sediments in nutrient cycling was initiated.

2. PROJECT OBJECTIVE

The aim of the project was to quantify the nutrient fluxes from sediment to overlying water, in order to allow for comparison of the loadings from sediments with those from external sources.

3. METHODS OF INVESTIGATION

Study Area

Cootes Paradise Nature Sanctuary is a 250 ha coastal wetland, adjacent to Hamilton Harbour, at the Western tip of Lake Ontario. The wetland has been classified by the Ministry of Natural Resources of Ontario as a Class I Wetland and an Area of Natural and Scientific Interest (ANSI). The marsh is 4 km long and its maximum width is 1 km (Painter et al. 1989). The surface area and the volume of the marsh vary according to the water level fluctuations. The mean depth of the marsh is 0.7 m (Chow-Fraser 1999). The water levels vary substantially, with the interannual mean water levels fluctuations up to 1 m over the past two decades (Chow-Fraser et al. 1998). Three main tributaries drain into Cootes Paradise (Figure 1). The largest one is the Spencer Creek, a 43.5 km watercourse, which drains 79% of the 290.9 km² watershed (Chow-Fraser 1999). Two smaller creeks Borer's Creek and Chedoke Creek drain 6.9 and 9.4%, respectively of the remaining watershed (Chow-Fraser 1999).

Three sites (Figure 1), representative of different sedimentary environments (Lee 2001) were selected for the study of nutrient fluxes from sediments. One of the sites, denoted as CC, was adjacent to the McMaster University plant enclosure, situated near the mouth of the Chedoke Creek which conveyed the effluent of the CSO and upstream Kaydrage Park Landfill site (RBG 2001). In 1997, a large CSO control tank became operational along the Chedoke Creek (RBG 2001). The second site, BH, was located near the Royal Botanical Garden (RBG) boathouse in the north-eastern corner of the main body of Cootes Paradise. Finally, the third site, WP, was located at the West Pond, which is a 9 ha receiving water body of the Dundas STP (RBG 2001). Water from the West Pond passes via Willow Line into the main body of Cootes Paradise. At each site, sediment porewater profiles were obtained by deployment of interstitial water (porewater) samplers and sediment cores and water column samples were collected. In addition, surficial sediments were collected from six sites (Figure 1) distributed over the entire area of Cootes Paradise.

Sampling and Analytical Procedures

Interstitial water was sampled using the acrylic porewater samplers (peepers [Figure 2]) fitted with the inert 0.45 μm polysulfone membrane (Gelman Scientific, Inc.). The peepers were filled with oxygen-free double distilled water (Azcue and Rosa 1996). Prior to deployment, the samplers were kept for several days in oxygen-free water maintained by bubbling with N_2 gas. Details concerning their preparation are given in Rosa and Azcue (1993) and Azcue and Rosa (1996). Subsample of water used for assembling and storage of peepers was kept as a procedural blank for analysis to monitor for any possible contamination. The P concentration of the procedural blank was 0.0105 mg/L. On July 25, 2001, several assembled samplers were placed in the sediments and allowed to equilibrate for a two week period at each of the three locations. Porewater samples were withdrawn from each cell immediately after retrieval using disposable syringes. They were transferred to plastic tubes which contained appropriate sample preservative and stored at 4⁰ C until analyses. Sampling was completed within 10 minutes of retrieval of peepers from the sediments. Separate sets of samples were used for nutrient, metal, and chloride analyses. The samples used for nutrient analyses were stored in vials containing 10 μl of 7% H_2SO_4 , and the samples used for metal analyses were preserved with 50 μl of ultrapure Seastar concentrated HNO_3 .

The porewater samples were analyzed for a wide range of parameters by the National Laboratory for Environmental Testing (NLET) in Burlington using Environment Canada Protocol (1979). An ascorbic acid technique was used to determine soluble reactive phosphorus (SRP), which includes mostly H_2PO_4^- and HPO_4^{2-} species, denoted further as $\text{PO}_4\text{-P}$. The O-tolidine method was used to determine ammonia-nitrogen ($\text{NH}_3\text{-N}$) from ionized (NH_4^+) and unionized (NH_3) species. Dissolved organic carbon (DOC) was determined using an Infrared Beckman Detector, Model 880. Chloride concentrations were determined using the thiocyanate colorimetric method. Metals (Fe, Mn, Ca, Mg, Na, K, Sr, Ba, Al) were measured with an inductively coupled Ar plasma emission spectrophotometer (ICAP-ES). Alkalinity of porewater samples was determined in the field using standardized H_2SO_4 and a Hach digital titrator. Oxidation-reduction potential (Eh) and pH was determined in porewater immediately after retrieval in the field. A glass combination electrode calibrated against standard buffers (4 and 7) was used for pH measurements and a Pt/Ag/AgCl combination electrode calibrated against standardized ($\text{KCl}/\text{K}_4\text{Fe}(\text{CN})_6/\text{K}_3\text{Fe}(\text{CN})_6$) solution was used for Eh measurements.

Water column samples were collected at each site at the time of peeper deployment and retrieval. The collected samples were transported to the laboratory in 2-L bottles in a cooler. The bottles were shaken and subsamples were taken for pH and conductivity measurements. Separate subsamples were taken for total suspended solids (TSS), total P (TP) and total Kjeldahl, nitrate + nitrite and ammonia nitrogen determinations. Additionally, two ~100 mL filtered samples were obtained using 0.45 μm filter paper for total filterable P (TFP) and filterable total Kjeldahl, nitrate + nitrite and ammonia nitrogen. The subsamples taken for TP and TFP analyses were acidified with 1 ml of 30% H_2SO_4 . In addition, the depth and the temperature of the water column were measured at the time of the peeper retrieval. Because of the drought conditions, there was approximately 15 cm drop in water level between the deployment and retrieval of peepers.

Sediment cores were also collected from all three sampling sites. The collected cores were transported to the National Water Research Institute, where they were refrigerated and sliced into 1-cm sections to a depth of 20 cm and into 2-cm sections further down. The sectioned sediments were frozen in polystyrene vials and subsequently freeze-dried for chemical analysis. Homogenized sediments were used for all analyses. The surficial sediments were collected using a miniponar dredge. The top 5 cms of sediment was collected into a polystyrene vial for

analysis from each site. The processing of collected sediment was described above. Water content and porosity of sediment was determined gravimetrically. Loss on ignition (LOI), a measure of the organic matter content, was determined gravimetrically after igniting the dry sediment at 550⁰ C in a muffle furnace for two hours. The resulting weight loss, expressed as a percentage of the dry material was taken to represent the loss due to ignition of organic material. Total phosphorus (TP) concentrations were determined on ignited sediments using a 16-hr 1 N HCl extraction. Forms of P, non-apatite inorganic phosphorus (NAI-P), apatite-P (AP) were determined by sequential extraction of Williams et al. (1976). Organic P (OP), which is considered to represent refractory organic P, was calculated by difference between the TP and the sum of the NAI-P and AP concentrations.

A Hydrolab datasonde was installed at the boathouse site about 10 cm from the sediment-water interface to monitor the diurnal fluctuation in oxygen concentration near the sediment surface. The datasonde was deployed and retrieved at the same time as peepers.

A rectangular acrylic box 50 cm x 25 cm x 20 cm with an open bottom was constructed according to Matisoff and Eaker (1992) and used as a flux box for direct flux measurements. The box which encloses 1,245 cm² of sediment surface and a volume of 9.5 liters was positioned in the sediment near the boathouse and was sampled every 4 hr over a 24-h period. However, because there was no replication in this experiment, results are not discussed in this report. The preliminary results, however, suggest that the use of this technique is viable in Cootes Paradise, therefore we propose to repeat this experiment.

4. RESULTS

Water Column

The physical parameters of the water column presented in Table 1 indicate hot summer conditions, which prevailed in the marsh at the time of our survey. Because there was no substantial change in conductivities and pH of water samples between July and August, average values are presented in Table 1.

Table 1. Physical parameters of the water column at the three sampling locations

Parameter	Site		
	CC	BH	WP
Depth (m)	0.4	0.4	0.15
Temperature (C)	25	28	26
Conductivity ($\mu\text{S}/\text{cm}$)	725	675	875
pH	8.2	8.4	8.2

The chemical parameters in the water column measured at the time of peeper deployment and retrieval are presented in Table 2.

Table 2. Chemical parameters in the water column measured at the time of the peeper deployment and retrieval

Parameter	CC		Site BH		WP	
	July*	August**	July*	August**	July*	August**
TSS (mg/L)	27.3	24.8	170.0	40.4	10.4	28.8
TP (mg/L)	0.185	0.178	0.153	0.122	0.273	0.228
TFP (mg/L)	0.0309	0.0246	0.0295	0.0310	0.145	0.071
TKN-F (mg/L)	0.545		0.561		0.72	8.30
NH ₃ -N (mg/L)	0.005	0.072	<0.005	<0.005	0.06	6.66
NO ₃ +NO ₂ (mg/L)	0.071	0.575	0.030	0.153	15.7	6.9

* time of peeper deployment

** time of peeper retrieval

As expected, the highest nutrient concentrations in the water column were observed in the West Pond (Table 2), where extremely high NH₃-N concentrations were measured in August. Under the hot summer conditions, much (9-14%) of the NH₃-N in the water column would have been present as toxic unionized ammonia (NH₃). In July, the NO₃+NO₂ concentrations reached 15.7 mg/L in West Pond, concentrations substantially higher than those measured at the other two sites. As shown in Table 2, TFP accounted on average for about 19% of the TP in the main water body of the marsh. The proportion of TFP was, however, substantially higher (average

42%) in the West Pond, where massive benthic algae mats were observed during the large part of the summer (RBG 2001).

The oxygen concentrations above the sediment-water interface measured by the Datasonde show a strong diurnal variation. (Figure 3). Although the oxygen concentrations were dropping steadily, at no time the concentrations dropped much below 4 mg/L. This indicates that at no time over a two week period anoxic conditions were present above the sediment-water interface. The oxic conditions above the sediment-water interface were likely sustained by frequent mixing of the water column caused by the wind action. As the site was located in the main body of water of shallow depth (0.4 m), the water column was highly exposed to the wind action.

Porewater

The porewater profiles of major dissolved constituents are shown in Figure 4. Although the concentrations of all dissolved constituents increase with depth, there are noticeable inter-site differences between the porewater profiles and also between the values of maxima. As seen from Figure 4, the highest porewater concentrations of phosphorus were measured at the West Pond (WP) site, where the maximum $\text{PO}_4\text{-P}$ concentrations reached about 7.5 mg/L. The site adjacent to the Chedoke Creek (CC) had the second highest P concentrations with maximum $\text{PO}_4\text{-P}$ values slightly exceeding 5 mg/L. The lowest P concentrations were measured at the Boathouse (BH) site, where the maximum $\text{PO}_4\text{-P}$ values hovered around 1 mg/L. The WP site, with the highest P concentration had the steepest porewater P gradient, followed by the CC site. Conversely, the BH site with the lowest porewater P concentration had the smallest P gradient. $\text{PO}_4\text{-P}$ is the form of dissolved P, which is most readily utilized by the aquatic biota in the water column.

A similar trend was also observed for the $\text{NH}_3\text{-N}$. The CC site had the highest $\text{NH}_3\text{-N}$ concentrations, followed by the WP site. Similarly as for P, the BH site had the lowest $\text{NH}_3\text{-N}$ concentrations. At the CC site, the porewater reached concentrations of nearly 65 mg/L of $\text{NH}_3\text{-N}$ at 40 cms below the sediment surface. The porewater profiles of Fe resembled those of $\text{NH}_3\text{-N}$ rather than those of $\text{PO}_4\text{-P}$.

There was a noticeable increase in porewater alkalinity with depth at the CC site, where the alkalinity increased from 169 mg/L CaCO_3 at 9 cm above the sediment-water interface to 897

mg/L CaCO_3 at 30 cm below the sediment surface. This alkalinity increase is likely due to denitrification, Fe reduction and CaCO_3 dissolution. As expected, the Eh was dropping from positive values (+40 mV, 3 cm above the sediment-water interface) to -140 mV at 14 cm below the surface. DOC concentrations increased with depth from 7 mg/L in the water column to 13 mg/L at 12 cm below the sediment surface and kept increasing to 30 mg/L DOC at 42 cm below the surface. The increase in the alkalinity and decrease in Eh with depth was also observed at the remaining two sites, BH and WP. However, the steady increase in the DOC concentrations with depth was lacking at these two sites. In general, the porewater DOC concentrations at the BH site were low (7-10 mg/L); higher DOC concentrations (14-17 mg/L) were measured at the WP site. Major anion composition in shallow porewater from two sites, CC and WP, is shown in Table 3.

Table 3. Major anion concentrations at the two sampling sites

Site	Cl mg/L	Parameter SO ₄ mg/L	SiO ₂ mg/L
CC	152	50.0	56.2
WP	222	7.6	15.5

Sediments

The LOI, water content and porosity of sediments from all three locations are shown in Figure 5. Sediments from WP had the highest porosity and the highest content of organic matter. As shown by the LOI values (Figure 5), a sharp increase in organic matter content, is observed at about 12-13 cms below the sediment surface at the WP site. The LOI increase is coupled with the marked drop in the TP concentrations (Figure 6) at this depth, largely because of an abrupt drop in NAI-P concentrations (Figure 7). Interestingly, the OP concentrations increase at this depth from ~300 mg/kg to ~500 mg/kg at 25 cm below the sediment surface (Figure 7). This increases the OP contribution to the TP from ~20 to ~50%. The P distribution and the LOI profile in this core suggest changes in the character of the deposited organic matter. Organic matter below 13 cm is more refractory and suggest the presence of vascular plant material rather

than phytoplankton and benthos. This suggests a presence of a bog, which was present in the area of the West Pond until the late 1960's to early 1970's. A similar trend associated with a disappearance of a bog, due to a fire, was observed at the Sanctuary Pond of the Point Pelee Marsh (Mayer et al. 1999). Assuming linear deposition rates and knowing the depth of recent sediments, the calculated rate of sediment deposition in the West Pond is ~ 0.4 cm/y. This is somewhat higher than 0.24 cm/y, the intermediate sediment accumulation rate estimated for Cootes Paradise by Prescott and Tsanis (1997). This is however not unexpected as the West Pond is the receiving water body for the Dundas STP and storm sewer.

The sediments from the West Pond (WP, Figures 6 and 7) had the highest TP concentrations, followed by the sediments from the CC site. The lowest TP concentrations (Figures 6 and 7) were measured at the BH site. The NAI-P, which includes the most readily soluble forms of P, accounted for 50 % of the TP in the top 12 cms of WP sediments (Figure 7), while below 13 cms this form of P contributed only 21% to the sediment TP content. The NAI-P distribution in this core is consistent with the earlier proposition, suggesting that a bog was once present at the West Pond location. The NAI-P constituted about 47% of the TP in sediment core collected at the CC site. The proportion of the TP in the NAI-P fraction (45%) was lower in the top 20 cms than that in deeper sediments, where the NAI-P accounted for more than 50 % of the TP. The sediments from BH site, with the lowest TP concentrations had the lowest proportion (22%) of TP in the NAI-P form (Figure 7). The results clearly show, that the sediments with the highest TP concentrations and greatest proportion of the NAI-P, have the largest dissolved P pool.

To investigate the spatial variability of phosphorus in sediments, TP concentrations in surficial sediments from six stations, were determined. The selection was based upon the data of Lee (2001) to represent different depositional environments, hence sediments with different geochemical characteristics. The total P contents of sediments varied from 891 to 1655 mg P/kg dry weight (Table 4). In addition to total P estimation, distribution of P among various fractions was also determined in these sediments and is presented in Table 4. The P apportionment shows that sediments which had the highest P content had also the greatest NAI-P component.

Table 4. Phosphorus forms in surficial sediments from six sampling stations distributed over the Cootes Paradise Marsh

Site	TP mg/kg	OP mg/kg	NAI-P mg/kg	Apatite-P mg/kg
CP 1	1299	207	558	534
CP 2	1655	383	801	471
CP 3	1003	228	260	515
CP 4	1190	293	412	485
CP5	957	169	242	546
CP6	891	122	170	600

5. DISCUSSION

A mass balance study of Cootes Paradise (Prescott and Tsanis 1997) suggested that reflux from sediments may be equivalent to as much as 57% of the total P loadings or 45 mg P/m².d. The reflux estimate of that study includes diffusion, wind resuspension and bioturbation. Similar phosphorus release rates were reported for Lake Sobygard, a shallow lake in Denmark by Sondergaard et al. (1990). Since Cootes Paradise is shallow and largely well mixed, anoxic conditions would not likely occur and anoxic release from sediments would not likely take place except for the areas with restricted water circulation. This includes areas such as West Pond, Westdale Cut and Chedoke Inlet. The transport of P from sediments into the overlying water would likely occur from readily exchangeable and highly mobile P in porewater through diffusion and resuspension (Bostrom et al. 1982). While the estimates of P reflux from sediments were derived from the mass balance calculation, no validation of this parameter was performed and the reflux of P from sediments of Cootes Paradise was identified as a data gap (Prescott and Tsanis 1997).

There are various methods to estimate the solute fluxes from sediments. Three of them, namely direct flux, diffusional flux and seepage flux measurements were employed by Matisoff and Eaker (1992) in their study of the Lake Erie coastal wetlands Old Woman Creek. Diffusional flux calculation assuming Fickian diffusion was used to estimate the nutrient fluxes from sediments in this study. The fluxes across the sediment-water interface were calculated

from the porewater data using solute gradient $(dC/dZ)_{Z=0}$ across the interface and the Fick's First Law:

$$F = - \phi D_s (dC/dZ)_{Z=0}$$

where, F is the diffusive flux of the porewater solute (mass/unit area .time), ϕ is the porosity of sediments, C is the solute concentration (mass of solute / unit of volume) and Z is the space co-ordinate. D_s is a diffusion coefficient (unit area / time) estimated from free ion diffusion coefficients using an empirical relationship $D_s = \phi^n D$, where n is a constant (n=2, Lerman 1979), and D is a diffusion coefficient of ion at infinite dilution obtained from Li and Gregory (1974). The following assumptions were made for calculations: 1) viscosity and coupling effects are negligible, 2) there is no solid phase precipitation or biological uptake of the dissolved species near sediment water interface, 3) concentration gradients are linear, so that $(dC/dZ)_{Z=0}$ is equal to $\Delta C/\Delta Z$ (Lerman 1979). The concentration gradients $(dC/dZ)_{Z=0}$ were found by fitting the porewater data to a linear regression equation $Y = A + BZ$, where Y is the concentration of the solute at the depth Z (Z=0 at the sediment-water interface), B is the calculated slope of the line (dC/dZ) and A is a constant calculated from the linear regression.

The calculated upward diffusive fluxes of P are shown in Table 5. The results show that

Table 5. Calculated diffusive fluxes (F) of phosphorus using Diffusion Coefficient $D_s=231.5\text{cm}^2/\text{y}$

Site	ϕ	F	F
		$\mu\text{g}/\text{cm}^2.\text{y}$	$\text{mg}/\text{m}^2.\text{d}$
CC	0.66	162.02	4.43
BH	0.69	9.75	0.27
WP	0.80	191.60	5.25

there are substantial (nearly 20 fold) differences in diffusive fluxes of P from sediments, resulting from large spatial variation in sediment porewater chemistry. The estimates of P fluxes are highest ($5.3 \text{ mg}/\text{m}^2.\text{d}$) at the West Pond site, followed by the site adjacent to the Chedoke

Creek ($4.4 \text{ mg/m}^2\cdot\text{d}$) and lowest at the Boathouse site ($0.3 \text{ mg/m}^2\cdot\text{d}$). The large differences observed in this study are plausible, as a broad spread of values ($0.27\text{-}270 \text{ mg/m}^2\cdot\text{d}$) were reported for the freshwater sediments by Lerman (1979). The estimated fluxes were highest for sediments containing highest concentrations of dissolved phosphorus, which appeared to be related to sediment P pool, particularly to the most labile form of sediment P, the NAI-P. It is, therefore, evident that the NAI-P is the source of the exchangeable P in sediment. This conclusion is consistent with the conclusion of Sondergaard et al.(1993), who found that most of P lost from sediment was derived from the NaOH fraction and some from the organically-bound fraction. The results suggest that sediment geochemistry, including forms of P and LOI (Figures 6 and 7), is an important factor, regulating the P concentrations in porewater.

Comparable calculations were carried out for the release of the $\text{NH}_3\text{-N}$. Fluxes 29.3 and $23.9 \text{ mg/m}^2\cdot\text{d}$ of $\text{NH}_3\text{-N}$ were calculated using $D_s=624.4 \text{ cm}^2/\text{y}$ for CC and WP sediments, respectively. No calculation was done for BH sediments, as there was a poor fit for the $\text{NH}_3\text{-N}$ concentrations, however, because of the small gradient of this parameter (Figure 4), the fluxes at this site are not expected to be high. The nutrient enriched sediments deposited in areas receiving the outfalls of the STP and CSOs are reservoirs of a large pool of nutrients which are rendered soluble during the early stages of diagenesis. Release of P from sediments with a history of high nutrient loadings such as those in West Pond has been suggested by Schindler et al. (1977).

The results of this investigation show that there are hot spots in Cootes Paradise, where sediment may be an important source of nutrients to the water column. For instance, calculation using the estimated flux indicates that West Pond sediments may contribute 0.47 kg/d of P to the water column, assuming similar composition of sediments throughout the West Pond. This compares with the Dundas STP phosphorus loading of 7.15 kg/day , calculated from the mean (May-September) effluent P concentration ($436 \text{ }\mu\text{g/L}$, RBG 2001) and average flow of $0.19 \text{ m}^3/\text{s}$ (RBG 2001). Although the Dundas STP has a certificate of approval (CA) to discharge effluent with P concentrations up to 0.500 mg/L , it is capable, under the optimal operating conditions, to remove P to concentrations as low as 0.250 mg/L . Assuming this concentration and an average daily flow of $0.21 \text{ m}^3/\text{s}$ (a value more realistic for all seasons), the average calculated loadings of P from the STP are about 4.5 kg/day . These loadings are lower than the loadings calculated for the four month summer period, which may reflect the worse case scenario. Assuming a mean

flux of $1 \text{ mg P/m}^2 \cdot \text{d}$ over the entire area (250 ha) of Cootes Paradise, the calculated internal loading of P from sediments is 2.5 kg/d . Although the net internal loading of P from sediment to the water column would be somewhat lower due to sedimentation, the results show that sediment is an important contributor of dissolved nutrients in Cootes Paradise. The internal loading from sediment is particularly important in the areas with the restricted water circulation such as West Pond, where an abundant growth of benthic algae was observed during the summer. The release of nutrients from sediments may be further exacerbated if periods of anoxia occur from time to time in these parts of the marsh. Enhanced release of P from sediments encourages the growth of benthic algae (Phillips et al. 1994), such as the one observed in West Pond.

While higher temperature in the summer enhances the diffusional fluxes, the above flux estimates may be conservative and probably underestimate the quantities of P released from sediments, as they consider diffusion under quiescent conditions only. Wind factor, which has not been taken into account, enhances release of phosphorus and other nutrients from sediments by stirring of sediment, thus reducing the distance at the sediment-water interface, over which phosphorus diffuses (Andersen 1974). Stirring of sediment by wind also exposes the sediments to chemical changes which may promote increased phosphorus release (Bostrom et al. 1982) and allows direct mixing of porewater and overlying water thereby increasing P concentration in the water column. There is also evidence (Sondergard et al. 1993, Phillips et al. 1994) that bioturbation enhances the phosphorus release from sediments.

Several studies (Phillips et al. 1994, Sondergard et al. 1993) have shown that phosphorus may be released from sediments long after the external loadings of P are reduced. Significant release of P from sediments apparently occurs (Phillips et al. 1994, Holdren and Armstrong 1986) if dissolved phosphorus in sediment exceeds the molar equivalent of dissolved iron. Our porewater data (Figure 4) indicate a substantial excess of dissolved P ($25 \text{ } \mu\text{mol/L}$) in comparison to molar Fe concentration ($5 \text{ } \mu\text{mol/L}$) at the sediment-water interface at the West Pond (WP) site and suggest a strong release of P from sediment. The porewater data ($36.8 \text{ } \mu\text{mol/L}$ P and $24.5 \text{ } \mu\text{mol/L}$ Fe, at the interface) suggest that the rate of P release would be somewhat lower at the Chedoke Creek (CC) site and no P release would occur at the Boathouse (BH) site, where the molar concentration of dissolved Fe exceeds that of P. Sediment release of phosphorus, thus

may hinder recovery of Cootes Paradise following any further reduction of nutrient loadings from the external sources and further delay the restoration efforts.

Since nutrient fluxes are highly dependent on the sediment nutrient pool, spatial differences in sediment geochemistry constitute an important factor in overall internal loadings of nutrients. An earlier sediment survey (Lee 2001) of Cootes Paradise has shown that there is a large spatial variation in sediment geochemistry and our results (Table 4 and Figures 6 and 7) confirm it. Thus, a large spatial grid needs to be investigated to address the spatial heterogeneity of sediments and provide meaningful estimates of fluxes for quantifying the potential loadings from sediments.

Furthermore, no information is available on the occurrence and fate of other contaminants entering the marsh from Dundas Wastewater Treatment Plant. Number of Priority Substances (PSL-1, 2), such as nonylphenol (NP) and its ethoxylates, have been identified in municipal effluents. Investigation of the occurrence of these substances in the marsh would provide beneficial information on current and historical trends of this class of contaminants in the marsh.

6. SUMMARY AND CONCLUSIONS

The study of Cootes Paradise has shown that there is a large spatial variation in nutrient fluxes from sediments. The fluxes are site specific and appear to be related to spatial heterogeneity of sediments. The estimates of P fluxes were highest ($5.3 \text{ mg P/m}^2\cdot\text{d}$) at the West Pond (WP) followed by the Chedoke Creek (CC, $4.4 \text{ mg P/m}^2\cdot\text{d}$) site. These sites receive the outfalls of STP and CSOs and their sediments are reservoirs of a large pool of nutrients. The estimate of the P flux was lowest at the Boathouse site, with the value of $0.3 \text{ mg P/m}^2\cdot\text{d}$. The P fluxes appear to be related to sediment phosphorus geochemistry which is an important factor in regulating the P concentration in porewater. The data indicate that the NAI-P is the source of exchangeable P in sediments. The sites with the highest sediment phosphorus concentrations (WP and CC) have the highest concentrations of P in the porewater and the steepest nutrient gradients. Consequently, this results in greatest P fluxes into the overlying water. A similar trend was observed for the $\text{NH}_3\text{-N}$, which showed the highest fluxes 29.3 and $23.9 \text{ mg/m}^2\cdot\text{d}$, respectively at the Chedoke Creek (CC) and West Pond (WP) sites. The results show that nutrient enriched sediments from contaminated areas may be an important source of nutrients to

overlying water in Cootes Paradise. Experience from other shallow lakes suggests that the release of nutrients from sediments may continue even after the reduction of the external phosphorus loading, delaying the recovery of the marsh, thus making the marsh more resistant to restoration.

7. RECOMMENDATIONS

The results of this investigation show a large variation in nutrient fluxes, due largely to spatial variation in sediment nutrient geochemistry. Presently, internal loadings can not be calculated as only fluxes from three sites were estimated. This is clearly insufficient spatial representation for the area as large as Cootes Paradise. To obtain meaningful estimates, additional porewater and sediment data need to be collected, particularly from open water areas, and relation between dissolved nutrients in porewater and sediment physico-chemical characteristics established. To delineate sediments with similar physico-chemical characteristics, geochemistry of surficial sediments from a large spatial grid has to be determined and mapped using a GIS approach. This will address the spatial heterogeneity of sediments and provide meaningful spatial representation from which internal loadings can be calculated. Any further investigation should include the Westdale Cut, to document the changes resulting from the Westdale CSO improvement.

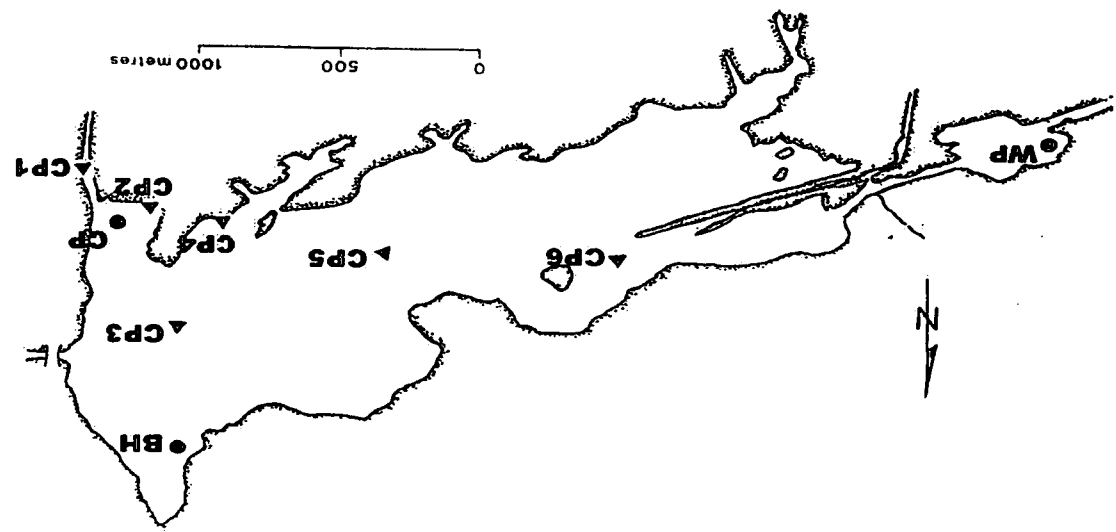
An investigation of the distribution of the faecal sterol tracer, coprostanol in the sediments of Cootes Paradise would provide a beneficial information on the fate and transport of the STP and CSO effluents in the marsh.

Additionally, distribution of nonylphenol ethoxylates (NPEs) and their degradation products, such as nonylphenol, in the marsh should be investigated to obtain the information on their occurrence in the marsh. These substances are known endocrine disrupting chemicals (EDCs) which enter the receiving waters from the STPs. Their occurrence and fate in the marsh is presently not known.

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● sediment cores
▲ surficial sediments

Figure 1. Map of Cootes Paradise, showing locations of the sampling sites

Sampler components

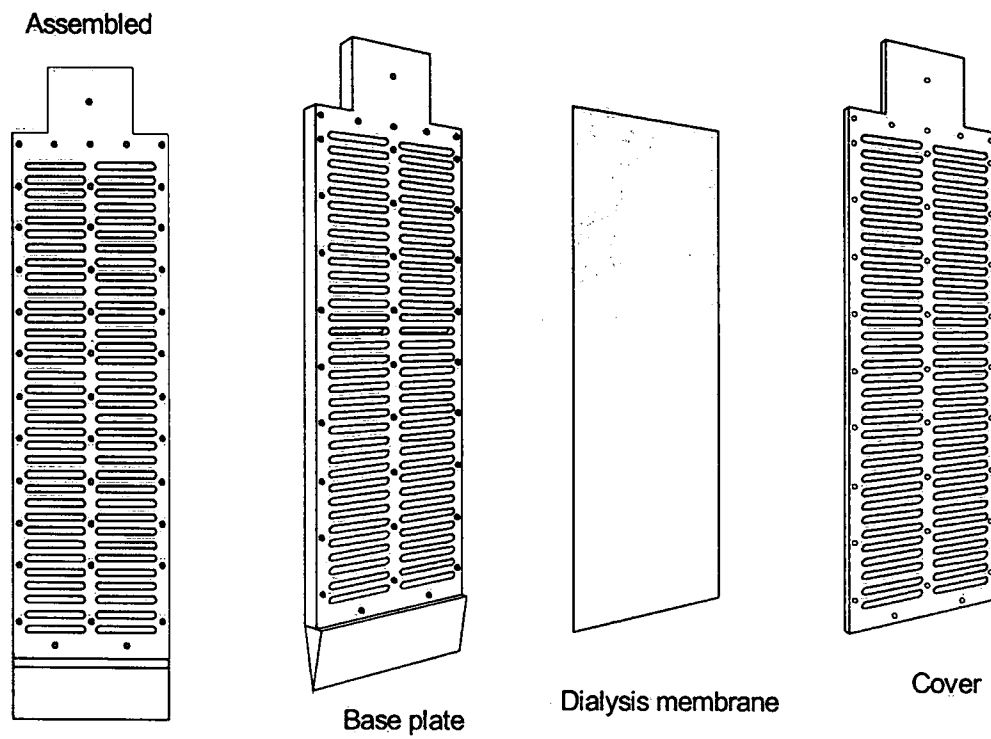


Figure 2. Drawing of the interstitial water sampler (peeper) used in the study

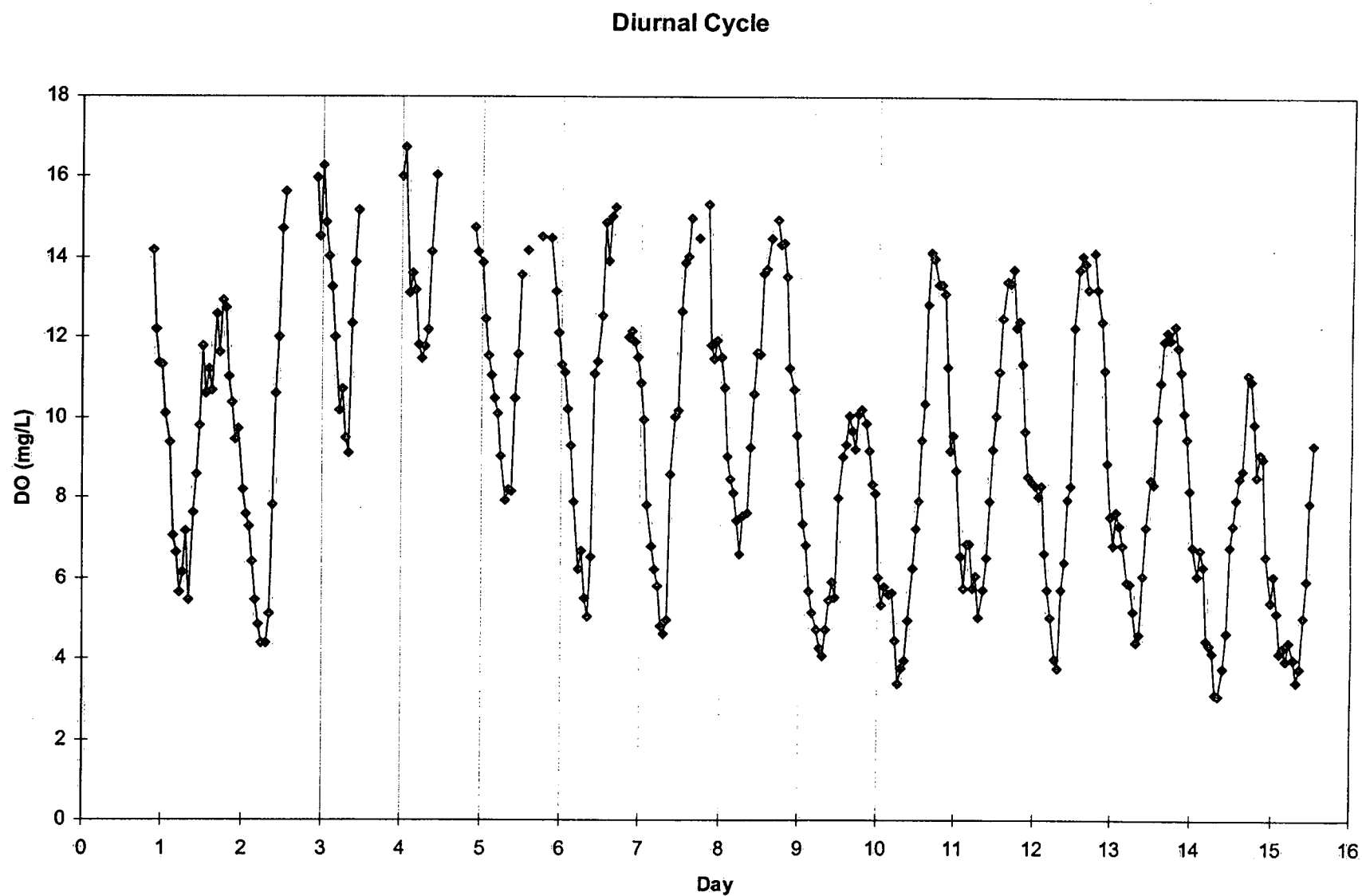


Figure 3. Diurnal oxygen cycle, as measured over the two week period (July 23 - August 7, 2001) at the RBG Boathouse site

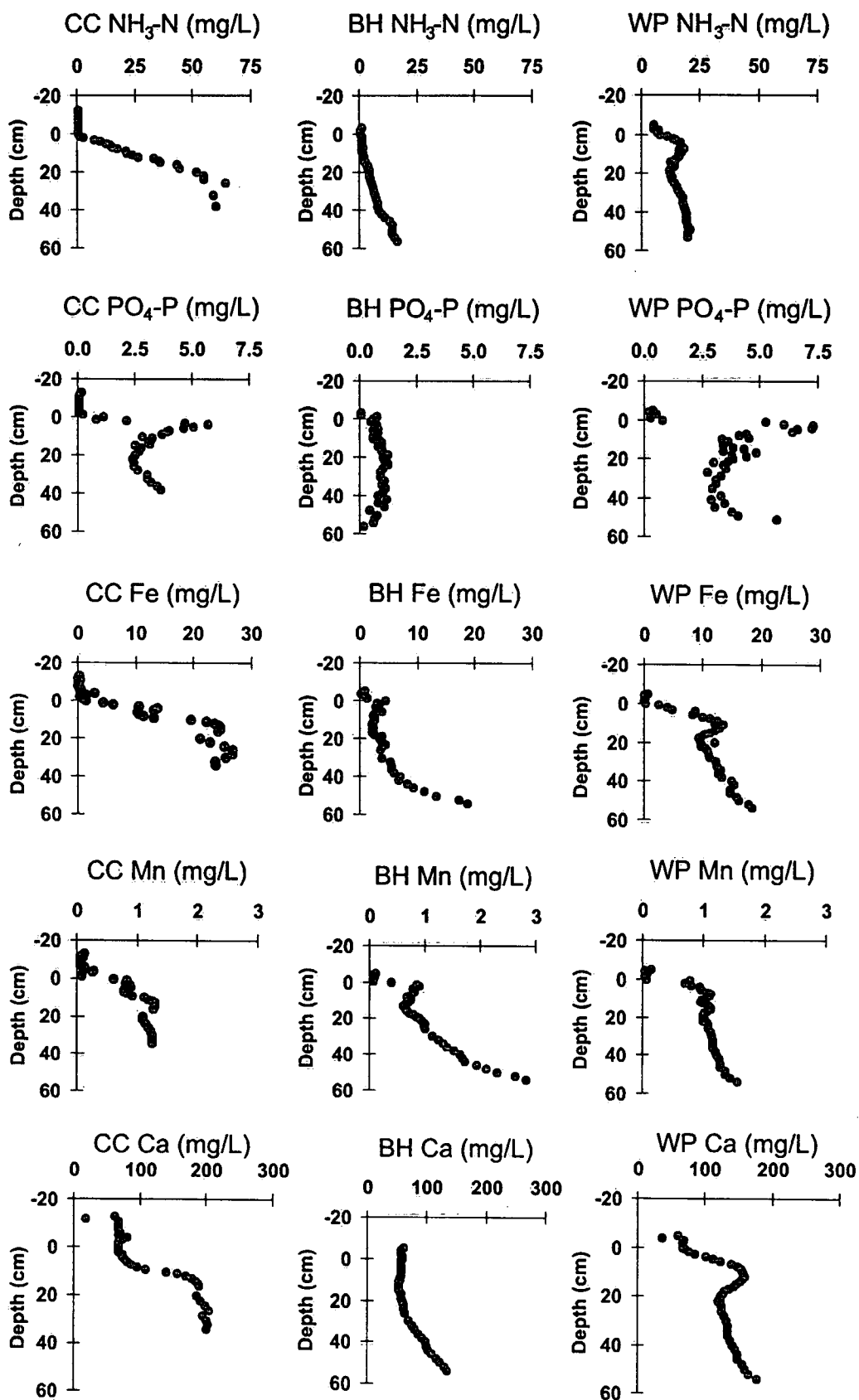


Figure 4. Porewater profiles for major dissolved constituents at the three study sites (CC, BH, and WP)

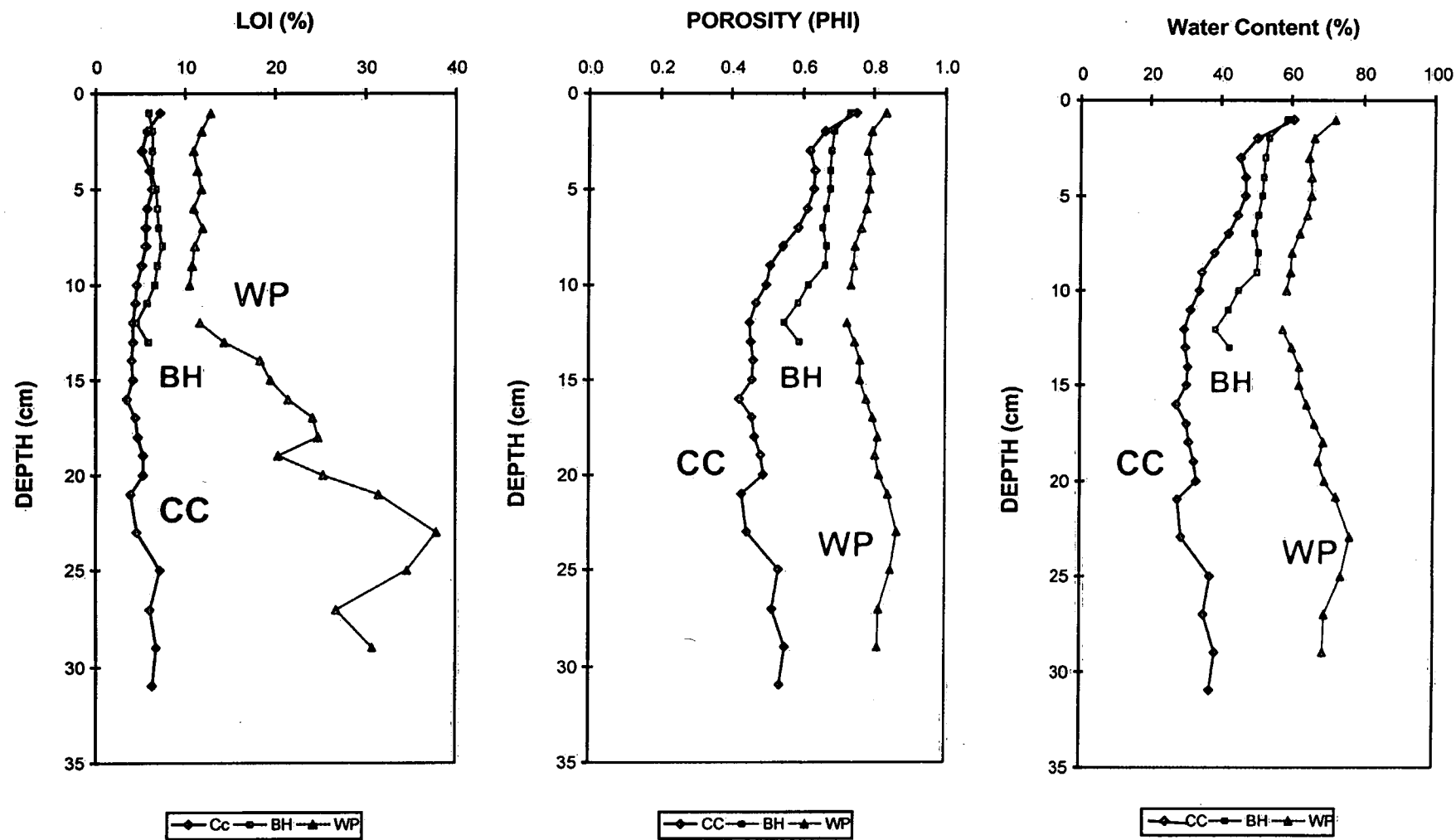


Figure 5. Loss on Ignition (LOI), Porosity and Water Content in sediment cores from CC, BH and WP sites

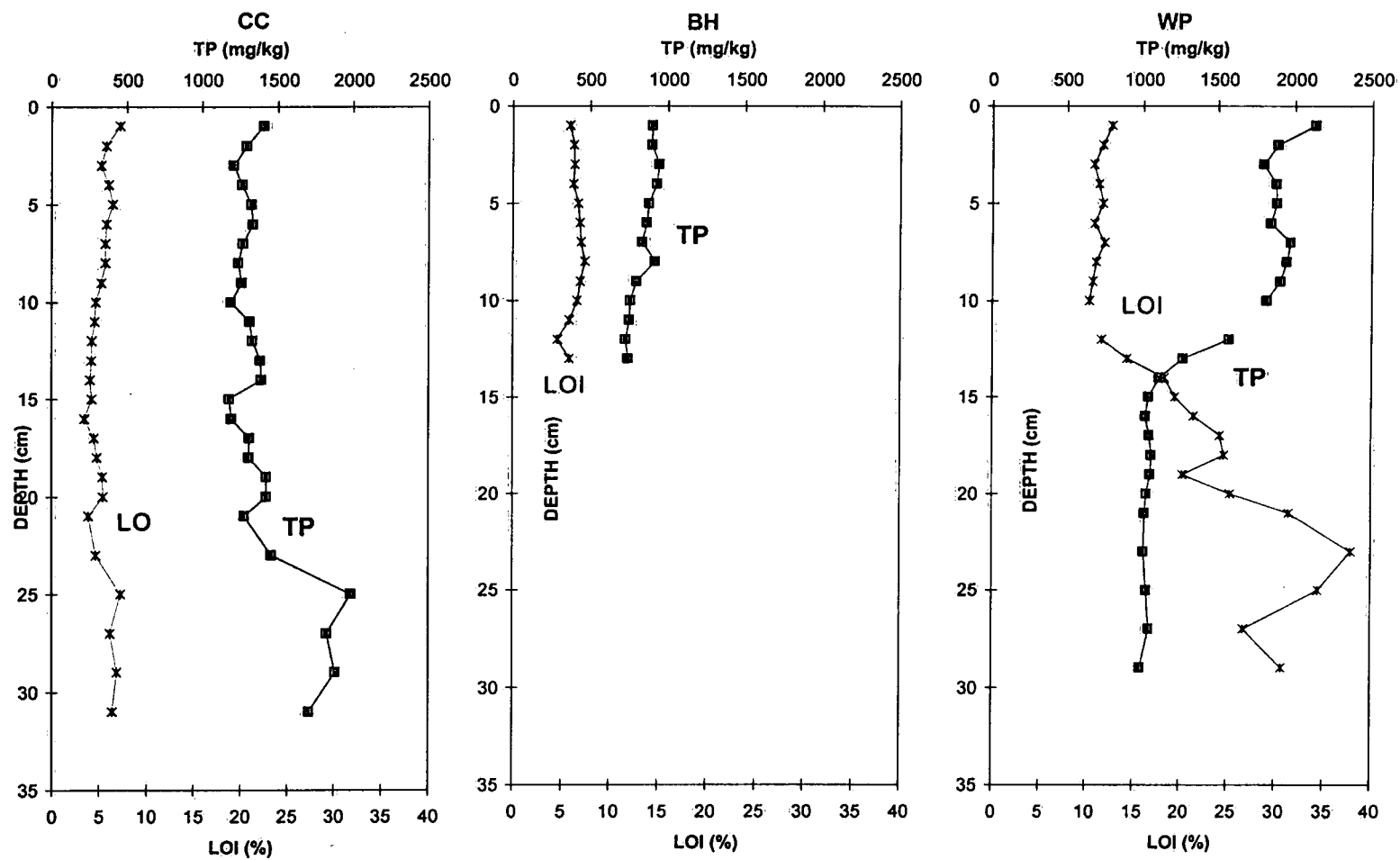


Figure 6. Loss on Ignition (LOI), and Total Phosphorus (TP) concentrations in sediment cores from CC, BH and WP sites

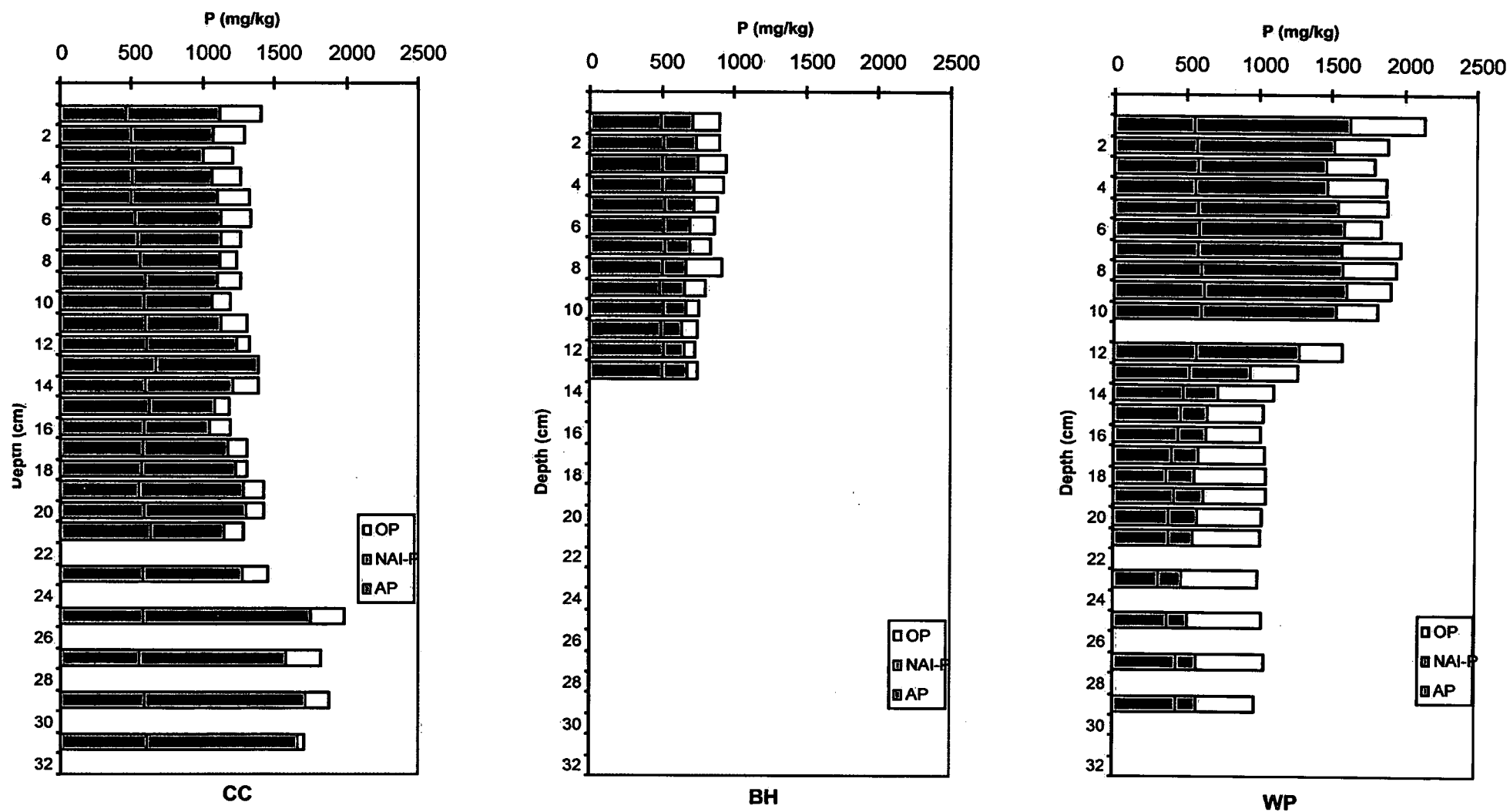


Figure 7. Phosphorus forms in sediment cores from CC, BH, and WP sites

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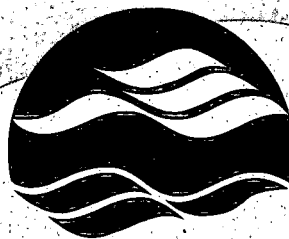
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