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Potential Contribution of Nutrients and Polycyclic Aromatic Hydrocarbons from the Creeks of Cootes Paradise Marsh

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During the summer of 1994, we compared the physical and nutrient characteristics of the three main tributaries of Cootes Paradise: Spencer, Chedoke and Borer's creeks. On all sampling occasions, concentrations of CHL α and nutrients were always lowest in Borer's Creek and highest in Chedoke Creek. There were generally 10-fold higher CHL α concentrations and 2 to 10 times higher levels of nitrogen and phosphorus in Chedoke Creek compared with Spencer Creek. Despite this, the light environment did not differ significantly between Spencer and Chedoke creeks because the low algal biomass in Spencer Creek was balanced by a relatively high loading of inorganic sediments from the watershed. Laboratory experiments indicated that sediments from Chedoke Creek released up to 10 µg/g of soluble phosphorus per gram (dry weight) of sediment, compared with only 2 µg/g from Spencer Creek. By contrast, sediment samples from Spencer Creek contained levels of polycyclic aromatic hydrocarbon that were as high as or higher than those from Chedoke Creek, and much higher than those found in Borer's Creek. The distribution of normalized PAH concentrations suggests a common source of PAHs in all three tributaries, most likely automobile exhaust, since there were high concentrations of fluoranthene and pyrene, both of which are derivatives of engine combustion.

Key words: **polycyclic aromatic hydrocarbons (PAHs), phosphorus, creeks, Cootes Paradise, urban wetland, sediment release**

Introduction

The sediment of aquatic systems can either act as a sink or a source of nutrients and contaminants in the overlying waters (Schindler et al. 1987; Ostrofsky et al. 1989; Kairesalo 1994). It acts as a sink when particles settle out in slow-flowing water, but acts as a source in shallow creeks and rivers, where the sediment can become easily resuspended through wind and wave action, and from activities of bottom-feeding animals (e.g., benthivorous fish; Haines 1973). One example of such a pollutant is phosphorus, the primary nutrient responsible for cultural eutrophication of lakes and rivers in North America (Schindler et al. 1978; Bothwell 1985). When phosphorus is present in its soluble form, it is quickly assimilated into the phytoplankton and/or carried downstream to the receiving water, and thus contributes to the deterioration of water quality in both the stream and lake or wetland.

Another pollutant that causes problems is the family of organic contaminant known as polycyclic aromatic hydrocarbons (PAHs). The Environmental Protection Agency has designated 16 PAHs (Appendix) as priority pollutants and has outlined restrictions on their point-source emissions into the environment (Menzie et. al. 1992). These compounds are created by the incomplete combustion of wood and fossil fuels, and enter the aquatic foodweb through roadway runoff or atmospheric deposition. Once in the aquatic environment, they are either assimilated by the biota or are adsorbed to particles (including algae and detrital particles) which are subsequently ingested by primary consumers in the water column or in the benthos. Since these compounds are lipophilic, they can also bioaccumulate in the foodweb (Baker et al. 1991) and lead to higher incidence of diseases such as skin and liver neoplasm in the fish community. In addition, short term bioassays (Ames microsome of *Salmonella typhimurium*) indicate that PAH-contaminated sediments are associated with mutagenic compounds (Marvin et al. 1994).

In urban areas where there are high inputs from diffuse sources (e.g., lawn fertilizers and automobile exhaust), the sediments of creeks and rivers can potentially contribute a large amount of both phosphorus and PAHs to receiving waters, depending on the type of land uses in the watershed (i.e., urban, rural, agricultural or forested) and their proximity to major roadways. The risk of exposure to PAH contamination may also depend on the rate of PAH incorporation into the foodweb, which may in turn depend on the trophic status of the tributary. Increased productivity tends to be associated with higher concentrations of organic suspended particles to which the contaminant can bind, and to which the organisms can subsequently ingest. Therefore, a study that simultaneously examines inputs of both pollutants would be more beneficial than one that addresses each pollutant separately, as is customary in previous investigations (e.g., Benner and Gordon 1989; Chambers et al. 1992).

In this study, we examine the potential contribution of phosphorus and PAHs from the sediments of three tributaries of Cootes Paradise Marsh, a degraded wetland that lies west of Hamilton Harbour, which is being restored as part of the Hamilton Harbour Remedial Action Plan (HHRAP). We will first describe seasonal changes in the water quality of the three creeks during 1994, and relate these to the potential release of phosphorus from sediment samples. We will also measure the sediment concentration of 16 of the PAHs identified by the Environmental Protection Agency as priority pollutants. This information, together with data on overall creek productivity and substrate characteristics, will be used to determine the relative impact of various anthropogenic activities on the water quality of Cootes Paradise Marsh.

Description of Study Sites

Cootes Paradise Marsh is a 250-hectare Class I wetland located at the western end of Hamilton Harbour in Hamilton, Ontario. This wetland is bounded on the east side by Highway 403 and on the southwest end by Cootes Drive in the town of Dundas (Fig. 1). Over the past six decades, vegetation in the marsh has declined from a cover of over 90% in the 1920s to less than 10% in the 1990s. The loss of marsh vegetation has been attributed to increased nutrient and sediment loads and the presence of a very large population of the common carp, *Cyprinus carpio* (HHRAP Stage 1 Report 1992). Eutrophication of the marsh has been attributed to inputs from urban, rural and agricultural activities in the watershed, while high turbidity levels have been attributed to increased sediment load from creeks that are kept in suspension by wind and wave action and to the feeding and spawning activities of carp (HHRAP Stage 2 Report 1992; Chow-Fraser, unpublished data). High turbidities have led to low light availability, which in turn have presumably limited the growth of both emergent and submergent vegetation in the marsh (Painter et al. 1989). Therefore, a major component of the restoration is to reduce the inputs of both nutrients and sediments from the tributaries of Cootes Paradise Marsh.

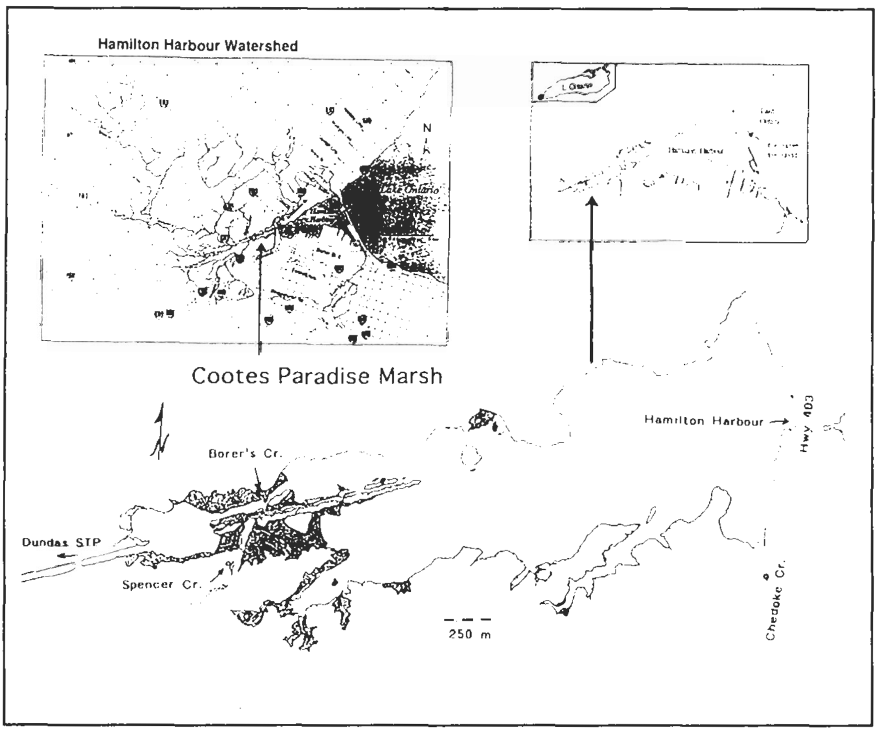

Fig. 1. Map of study sites. Asterisks indicate the approximate location of the sampling stations on Chedoke, Spencer and Borer's creeks.

The three main tributaries of Cootes Paradise Marsh are Spencer Creek, which drains into the marsh from the southwest end, Borer's Creek, which empties into the marsh north of the Desjardins Canal, and Chedoke Creek, which flows into Cootes from the southeastern end (Fig. 1). We took a series of water-quality measurements (e.g., turbidity and nutrient concentrations) along Spencer and Chedoke creeks in the summer of 1994 to verify that data collected at the stations used in this study are representative of creek flow and not back flow from Cootes Paradise (Chow-Fraser, unpublished data). The water quality of these three tributaries has not been monitored simultaneously, and no study has yet been conducted to examine the relationship (if any) between the sediment and water quality of these creeks. As a reference site, we chose a tributary of Spencer Creek (approximately 50 km upstream), named Spring Creek, which is a fast-flowing, cold-water and relatively undisturbed stream (see inset in Fig. 1). The characteristics of the sediment collected at all four creeks are presented in Table 1. Discharge data available for Spencer Creek and Chedoke Creek indicate that both streams contribute substantially to the water budget of Cootes Paradise whereas Borer's Creek is only an intermittent stream that contributes small amounts of water during spring and after rainfalls (Chow-Fraser, unpublished data).

Table 1. Summary of land use in drainage basin and physical attributes of the four creeks in this study

Attribute	Spencer	Chedoke	Borer's	Spring
Size of drainage basin (km^2)[a]	70[b]	25	19	10
Land use in drainage basin[a]	urban & agricultural	urban	rural & agricultural	rural & wooded
Range in water depth (cm)[c]	135 to 190	45 to 95	10 to 40	25 to 40
Range in stream flow (m/s)[a]	0.65 to 1.7	0.083 to 1.5	0.9 to 8.5	5.2
Sediment composition[d]	20% sand 75% silt 5% clay	70% sand 30% silt	45% sand 10% silt 45% gravel	100% sand
% water in sediment[c]	60%	32%	43%	19%

[a]Data for land use, size of watershed and streamflow were obtained from Hamilton Region Conservation Authority, unpub. data; data for sediment composition were taken from D. Smith, unpub. ms.

[b]Only 70 km^2 is being considered in this study even though the total drainage area is 291, of which 75% drains into two reservoirs.

[c]Values measured during the course of this study.

[d]Obtained from D. Smith, unpub. ms, a report submitted to the Fish and Wildlife Habitat Restoration Committee of the HHRAP.

Materials and Methods

Physical and Chemical Characteristics of the Creek

The release of phosphorus from the sediment is thought to be affected by a combination of physical and chemical processes, including water temperature and pH, as well as the nitrate concentration in sediments (Holdren and Armstrong 1980). In this study, the physical and chemical parameters of the water were obtained with a H20 Hydrolab and Scout monitor and include dissolved oxygen concentration (DO), pH, temperature (°C), and specific conductance (µS/cm). Although we monitored Chedoke and Spencer creeks biweekly from May to September 1994, the intermittent flow of Borer's Creek only permitted irregular measurements (approximately monthly from July to October). Water turbidity was measured with a Hach turbidimeter, and incident light was measured at 10-cm intervals from the surface to 1% of the surface irradiance with a Li-Cor light meter equipped with submersible spherical sensor. Secchi depth transparencies were also recorded on each sampling occasion with a 20-cm black/white disk.

We also collected water for determination of concentrations of total phosphorus (TP), soluble reactive phosphorus (SRP), total dissolved phosphorus (TDP), total kjeldahl nitrogen (TKN), total ammonia nitrogen (TAN), total nitrate nitrogen (TNN), total alkalinity (TA), chlorophyll *a* (CHL *a*), and total suspended solids (TSS). Samples for nutrients were collected with acid-washed bottles and processed with a Hach DR2000 spectrophotometer with EPA approved methods (Hach Water Analysis Handbook, Loveland, Colorado). TAN and TA determinations were made immediately upon return to the laboratory, while other samples were filtered as required and kept frozen for later analyses. Filters for CHL a were extracted in 90% acetone for 24 h after the lawns were disrupted with a glass rod. The final concentrations of CHL a were determined spectrophotometrically and corrected for phaeophytin, using standard methods. Samples for TSS determinations were filtered onto preweighed GF/C filters and porcelain crucibles, dried at 100°C for 24 h, transferred to a desiccator for 1 hour, and weighed to the nearest 0.0001 mg. Filters were then ignited at 550°C for 2 h, transferred to desiccator and reweighed for determination of total inorganic suspended solids (TISS). Total organic solids (TOSS) was calculated as the difference between TSS and TISS. Total nitrogen (TN) was calculated as the sum of TKN and TNN.

Sediment Samples for PAH Concentrations and Nutrient Release

Monthly sediment samples were collected for determination of PAH concentrations and nutrient release from all four creeks. Samples from the three tributaries of Cootes were collected 100 m upstream from where the creeks emptied into the marsh. Sediment samples were collected midpoint between stream banks with an Ekman Grab sampler (usually the surface 5 cm of sediment). They were strained to remove most of the water, placed in plastic Ziploc bags, and kept in the dark at 5°C until they were analyzed.

To determine the water content of sediment samples, 50 g wet weight of sediment was placed in three preweighed tissue culture dishes and put in a dehydrator for 24 hours at 51°C. Samples were reweighed to determine the fraction of water in the sediment. A time series test over 36 hours showed that a drying period of 24 hours was sufficient to achieve a constant weight (to three decimal places). To determine the potential release of phosphorus from sediments collected in October, we spread a thin layer of wet sediment (10.0 g) in the bottom of acid-washed glass jars (120-mL capacity) and added 100 mL of deionized water (7 jars per site). We covered the jars with foil, swirled them to gently mix the water and sediment, and punched two holes in the foil to permit limited air diffusion. They were incubated for 14 days at 5, 10, 15, 20 and 25°C in dark growth chambers. Every second day, one jar from each site and incubation temperature was filtered through a GF/C filter and analyzed in triplicate for SRP. Phosphorus concentrations measured in the water were calculated as µg phosphorus released per gram dry weight of sediment and expressed as "release" since the initial SRP of the water was zero. Jars intended for further incubation were gently swirled and left in the growth chamber.

We calculated the phosphorus "release rate" (µg/g dry weight/d) from sediment samples as follows:

$$release\ rate = \frac{release_{max}}{d_{max} \bullet WC}$$

where $release_{max}$ is the total amount of SRP released into overlying water (µg/10 g wet weight of sediment) that corresponds to d_{max}; d_{max} is the day on which peak release is recorded; and WC is the conversion of wet weight to dry weight (ww; dw). Although this "release rate" may be analogous to the sediment P release rate in situ, it should not be interpreted as such without a direct comparison of field and laboratory data.

July and October sediment samples were analyzed for the 16 priority PAHs identified by the EPA. Samples of sediment (35 g) were dried in air then in a desiccator over $CaCl_2$ for 24 hours. These samples were extracted with dichloromethane using an ultrasonication procedure described previously by Marvin et al. (1994). A non-polar fraction was prepared and analysed by gas chromatography-mass spectrometry (GC-MS) using the separation and chromatographic protocols described by Marvin et al. (1994). The GC-MS analyses were performed in the selected-ion monitoring mode. Authentic standards were available for all compounds reported and the amounts detected were equal to or greater than 40 times the detection limit. At these level the error in the quantification of peaks is about $\pm$5%.

The Ames bioassay experiments were conducted in *Salmonella typhimurium* strain YG 1024, a strain related to TA 98 which contains extra copies of the gene encoding for O-acetyltransferase. A standard mutagen (2-aminofluorene) and negative controls were run with each set of bioassays. Full details of this methodology can be found in the report by Marvin et al. (1994).

All statistical analyses were performed with the SAS Jmp (SAS Institute Inc. 1982) software package. Means are presented with standard errors wherever appropriate.

Results and Discussion

Seasonal Variation in Physical and Nutrient Characteristics

The physical characteristics of Spencer and Chedoke creeks varied considerably throughout the 1994 growing season (Fig. 2). In general, the station in Chedoke Creek was approximately 25 cm shallower than the station in Spencer Creek (Fig. 2a and Table 1), with consistently warmer temperatures (from 2 to 5°C warmer [Fig. 2b and Table 2]), higher pH (by up to 0.4 units higher [Fig. 2c and Table 2]), and higher conductivity (up to 300 µS/cm higher [Fig. 2d and Table 2]). Water at these two stations was well oxygenated in May, but dropped to moderately low levels, approaching 4 mg/L by the end of June. DO concentrations in Spencer Creek remained between 6 and 7 mg/L for the balance of the summer whereas those in Chedoke Creek became supersaturated in late July and then dropped to low levels again by the end of August (Fig. 2e). Except for DO concentrations, seasonal means for all other physical variables were significantly different between creeks (Table 2).

A common indicator of the overall productivity of aquatic ecosystems is the Secchi depth transparency of the water body (e.g., Horne and Goldman 1994). This is based on the assumption that light levels in the water column are controlled by the concentration of algal particles. In turbid waters such as the study creeks, however, Secchi depth is not a reliable measure of primary productivity. For example, Secchi depths for Spencer Creek decreased consistently throughout the summer (Fig. 3b), indicating that algal productivity should have been increasing; however, CHL a concentrations were in fact decreasing through time (Fig. 3d). The lower Secchi values probably reflected increased turbidities in Spencer Creek in July and August (Fig. 3a) when a relatively large concentration of inorganic suspended solids were present in the water column. By comparison, the Secchi measurements corresponding to Chedoke Creek did not vary a great deal (Fig. 3b), even though concomitant measurements of CHL a and suspended solids were highly variable (Fig. 3d,e). Thus, the light environment in the creeks was probably controlled by the presence of both organic and inorganic particles in Chedoke Creek whereas light extinction was primarily driven

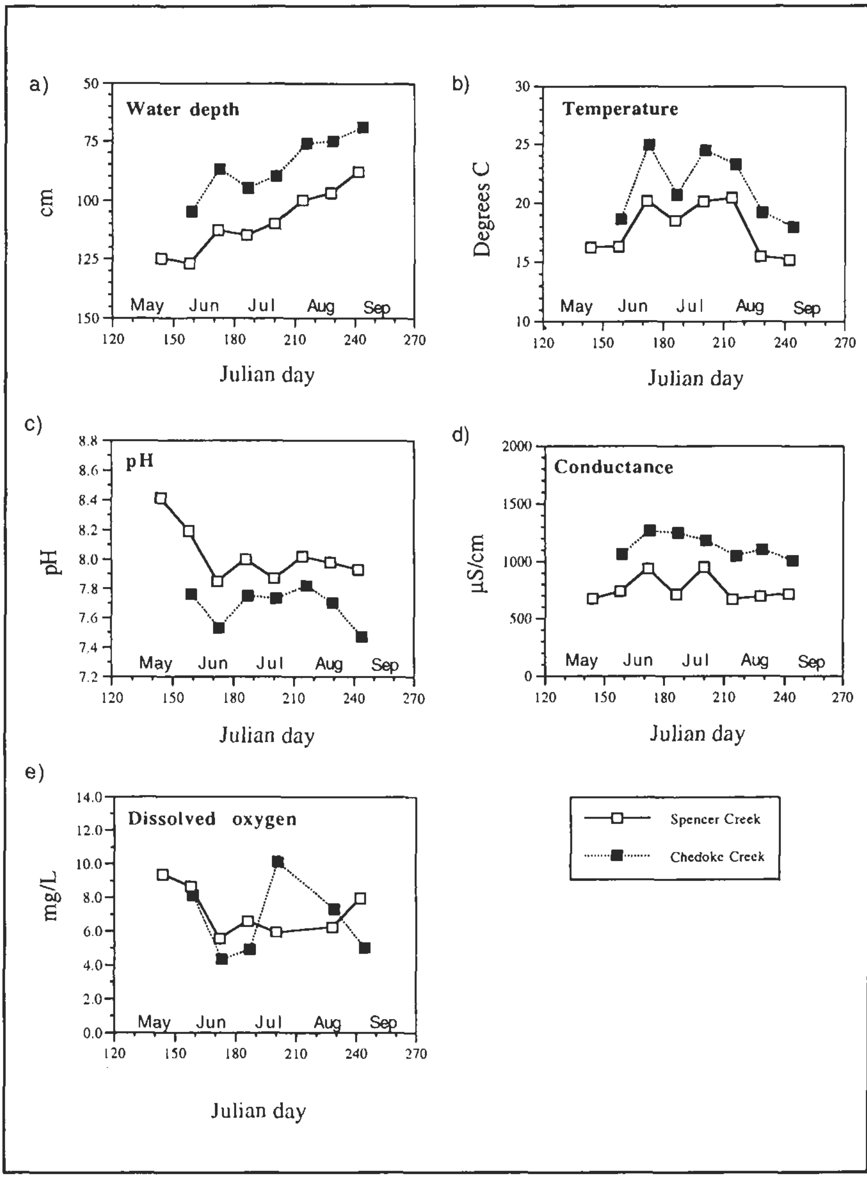

Fig. 2. A comparison of seasonal changes in (a) water depth, (b) ambient water temperature, (c) pH, (d) specific conductance and (e) dissolved oxygen concentration in Spencer Creek and Chedoke Creek during 1994.

by the presence of inorganic sediments in Spencer Creek. This situation resulted in statistically similar light conditions (indicated by Secchi depth, light extinction and water turbidities [Table 2]) in both creeks even though the source of the attenuating particles were quite different.

Table 2. Summary of mean (May to September) physical and nutrient characteristics of Spencer and Chedoke Creek

Parameter	Spencer[a]	Chedoke[b]	P-value[c]
Secchi depth (cm)	51.9 (18.86)	32.76 (2.53)	N.S.
Turbidity (FTU)	41.1 (7.14)	33.3 (2.50)	N.S.
Light extinction coefficient	3.95 (0.38)	4.01 (0.16)	N.S.
CHL a (μg/L)	4.3 (1.34)	39.5 (11.99)	0.008
TSS (mg/L)	55.9 (7.75)	47.5 (4.85)	N.S.
TISS (mg/L)	49.3 (7.45)	38.3 (4.28)	N.S.
TOSS (mg/L)	6.6 (0.47)	10.6 (1.23)	0.006
Water depth (cm)	109 (4.8)	88 (4.6)	0.008
Temperature (°C)	17.8 (0.80)	21.3 (1.09)	0.02
DO (mg/L)	7.3 (0.55)	6.6 (0.93)	N.S.
pH[d]	8.03	7.62	0.0001
Specific Conductance (μS/cm)	761 (41.1)	1133 (38.2)	0.001
TP (μg/L)	64 (7.5)	325 (17.3)	0.001
TDP (μg/L)	26 (4.9)	178 (34.1)	0.0003
SRP (μg/L)	18 (5.2)	167 (36.2)	0.0007
TKN (mg/L)	2.29 (0.139)	2.84 (0.187)	0.03
TAN (mg/L)	0.14 (0.011)	>0.55	0.0001
TNN (mg/L)	0.55 (0.066)	1.53 (0.074)	0.0001
TN (mg/L)	2.83 (0.144)	4.37 (0.189)	0.0001

[a]Sample size is 8.
[b]Sample size is 7.
[c]P-value refers to the probability that means are significantly different (alpha=0.05) as determined by a t-test. See text for explanation of abbreviations.
[d]Value reported is the meadian pH.

A better indicator of stream productivity is the nutrient status of the creeks; accordingly, Chedoke Creek is clearly the more productive of the two. The higher concentration of both phosphorus and nitrogen (Table 2 and Fig. 4a to e) as well as the warmer and shallower nature of the creek (Fig. 2a,b) promoted the formation of algal blooms (Fig. 3d). This is supported by the appearance of supersaturated oxygen conditions in July (usually a result of high photosynthesis) coincident with high algal biomass, and the subsequent decomposition of the algae and concomitant depression in DO concentrations by late August (Fig. 2e). There is also a suggestion that Chedoke Creek is contributing disproportionately to the eutrophication of Cootes Paradise since roughly half of the 325 μg/L of TP from this creek is soluble and can be easily carried downstream into the marsh where it is readily assimilated (Table 2).

Nutrient Release from Sediments

To compare the potential contribution of SRP from sediments to the overlying waters in the three main tributaries of Cootes Paradise Marsh, we performed a series of 14-day nutrient-release experiments at 5, 10, 15, 20 and 25°C— temperatures that represent the range normally encountered in the

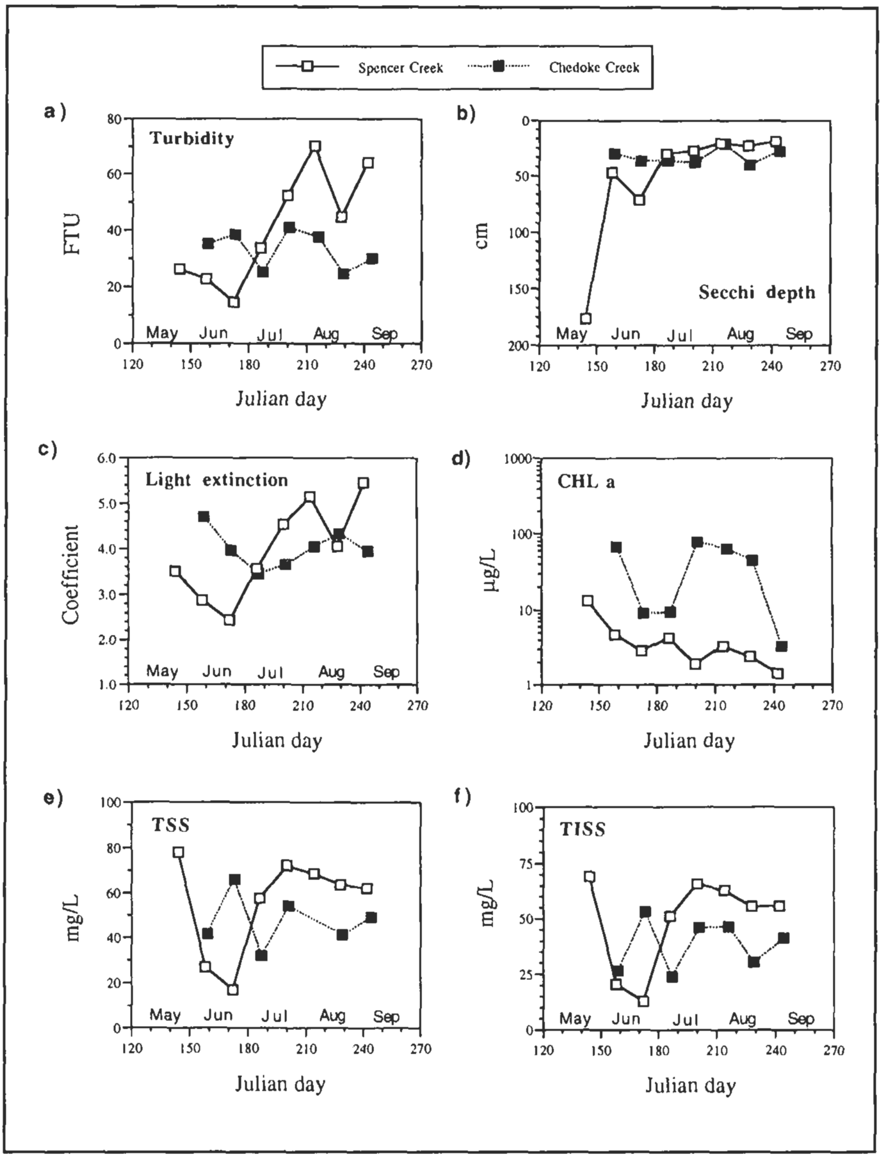

Fig. 3. A comparison of seasonal changes in (a) water turbidity, (b) Secchi depth transparency, (c) light extinction coefficients, (d) CHL a concentration, (e) concentration of total suspended solids (TSS) and (f) concentration of total inorganic suspended solids (TISS) in Spencer Creek and Chedoke Creek during 1994.

field during the ice-free season (April to November). Sediment from Spring Creek, an unproductive fast-flowing stream in the Spencer Creek watershed, was used to provide reference values for the experimental protocol. In all temperature treatments, negligible amounts of SRP were

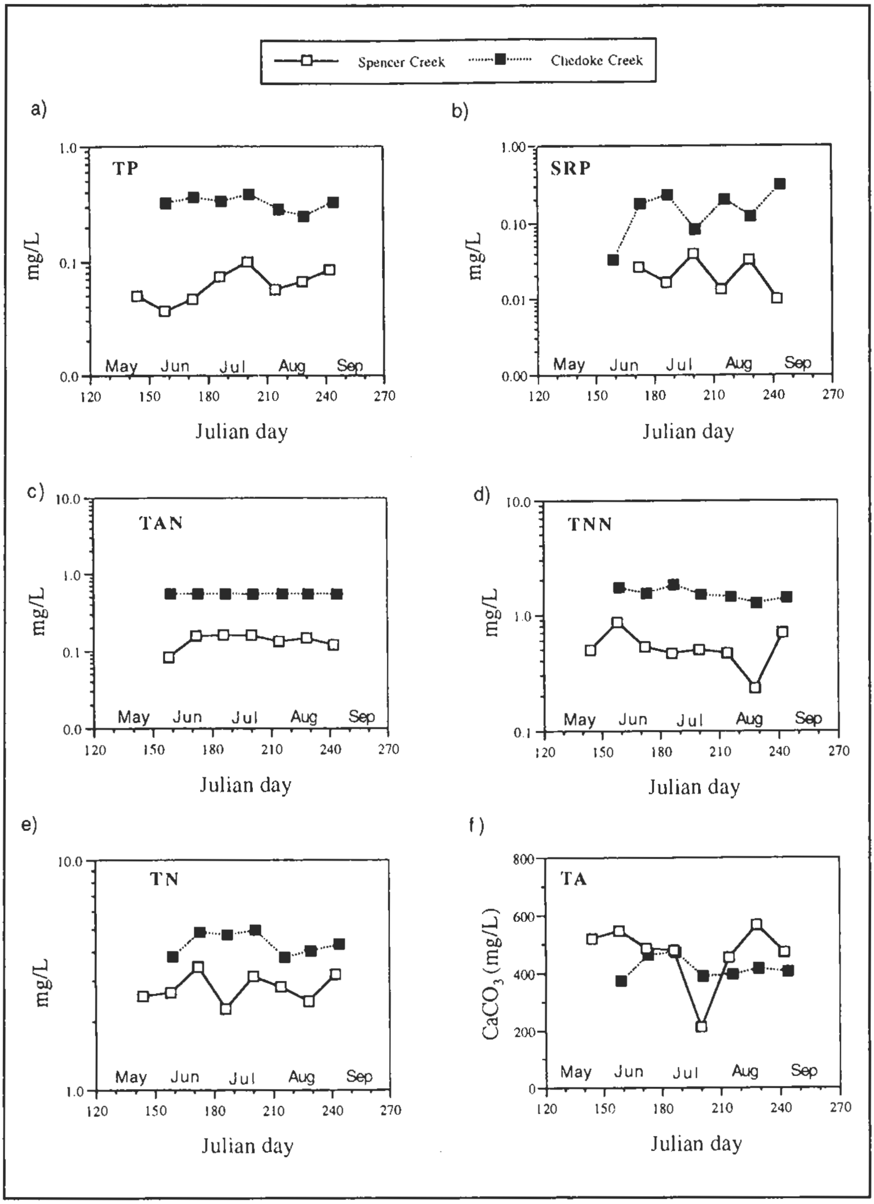

Fig. 4. A comparison of seasonal changes in concentration of (a) total phosphorus (TP), (b) soluble reactive phosphorus (SRP), (c) total ammonia nitrogen (TAN), (d) total nitrate nitrogen (TNN), (e) total nitrogen (TN) and (f) total alkalinity (TA) in Spencer Creek and Chedoke Creek during 1994.

released from sediments of Spring Creek (Fig. 5a to d). Because of the pristine nature of this site and the relatively low release, in addition to

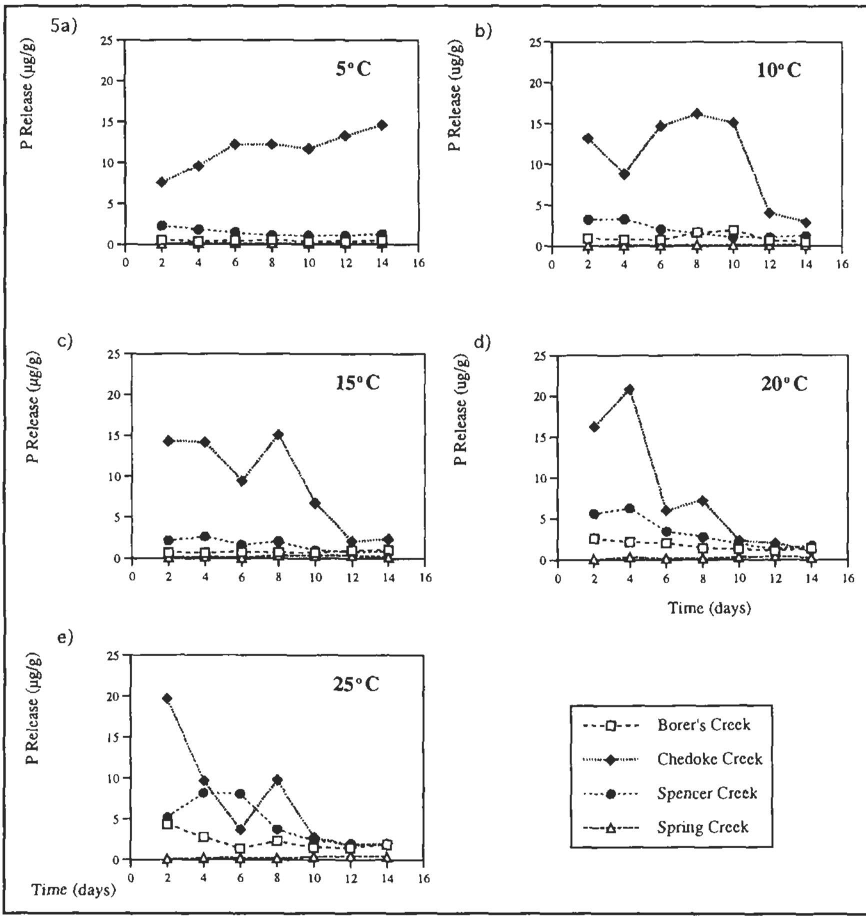

Fig. 5. Release of phosphorus (µg of SRP/g dw) from sediments of the four study creeks incubated over 14 days at temperatures ranging from 5°C to 25°C. Sediments were collected in October 1994.

previous studies, we feel confident that this technique yields reliable data regarding nutrient release from sediments (Phillips et. al. 1994). At temperatures below 20°C, there were consistently greatest phosphorus release from Chedoke Creek, moderately high release from Spencer Creek, and relatively small release from Borer's Creek (Fig. 5 a to d). At 25°C, however, release of SRP from Spencer Creek exceeded the amount released from Chedoke on day 6 even though this trend was reversed on day 8 (Fig. 5e). This suggests that there were two episodes of phosphorus release associated with the Chedoke sediment over the 14 days, a trend that is also supported by data from the 10, 15 and 20°C treatments. Ostrofsky (1987) also found that two or more episodes of phosphorus release occurred during the incubation period, and attributed this to bacteria colonies which tie up the soluble phosphorus.

We compared phosphorus "release rates" (standardized to daily rate of release per unit dry weight; see Materials and Methods section) from sediments of the three main tributaries and found that in all cases, release rates increased with temperature (Fig. 6). This suggests that the remineralization processes (which are mediated by bacterial activity) were temperature-dependent. This positive effect of temperature may explain why there are higher TP concentrations in Chedoke Creek relative to Spencer Creek since the former is several degrees warmer (Fig. 2b; Table 2), and may thus facilitate higher phosphorus remineralization from the sediments.

Seasonal Variation in Levels of PAH in sediment

Absolute and normalized concentrations of the 16 priority PAHs in sediments of the four study creeks were used to indicate the general level of contamination as well as possible sources of contaminants. With regards to sediments of Spencer and Chedoke creeks, total PAH levels and the number of revertants from the Ames bioassays increased from July to October (Table 3), although the increase for Spencer Creek was only marginal. Concentrations of PAH in the sediments of Borer's Creek were generally low, even in October; however, the mutagenic activity associated with the sediment sample collected in July was relatively high. Since there is no relationship between total PAH and mutagenic activity, it would require further study to isolate the compound(s) which caused the high mutagenic activity.

The normalized concentrations of PAH compounds to benzo[a]pyrene were compiled for each site and sample to provide a comparison of the different sources of PAHs in each creek (Fig. 7). The similar pattern in the normalized concentrations for all three tributaries suggest to us that the sources of PAHs are similar, and that they may originate from road runoff since both the absolute levels and normalized ratios of fluoranthene (Flanth) and pyrene (Pyr) (derivatives of automobile exhaust) were high. By contrast, the total PAH concentrations from Spring Creek were much lower and its normalized concentrations did not resemble those of the other creeks, indicating that the PAHs probably came from a different source. Results from the bioassays indicated that the PAH fraction found in Spencer and Chedoke creeks contained the highest mutative ability, and that these sediments pose the greatest potential risk to the aquatic biota.

General Discussion

The majority of parameters considered in this study indicate that Chedoke Creek is contributing most to the degradation of Cootes Paradise Marsh both directly and indirectly. The presence of relatively high levels of PAH in the sediments are consistent with the contention

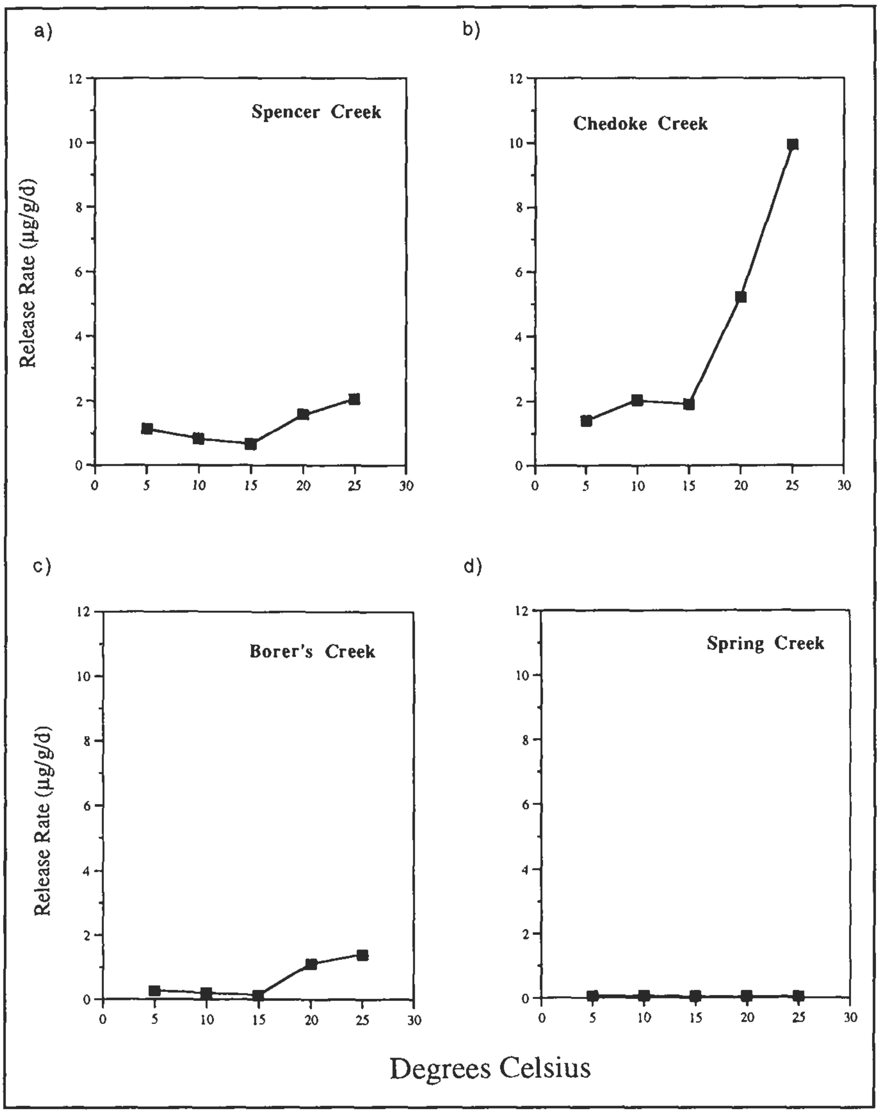

Fig. 6. Standardized phosphorus release rate (µg of SRP/g dw/d) as a function of temperature corresponding to sediment samples from (a) Spencer Creek, (b) Chedoke Creek, (c) Borer's Creek and (d) Spring Creek collected in October 1994.

that road runoff from Highway 403 contains residual asphalt and engine exhaust (Tables 2 and 3). On the other hand, high nutrient inputs, especially ammonia and soluble reactive phosphorus, are probably linked to combined sewer overflows (CSOs) that discharge untreated sewage and surface runoff during storm events. As part of the Hamilton Harbour Remedial Action Plan, retention tanks are being built to contain

Table 3. Summary of levels of PAH and mutagenic responses in *S. typhimurium* strain YG 1024 (-S9) in the sediments of four study creeks during 1994

	Total PAH (ng/g)		Revertants g^{-1} sediment[a]	
Creek	July	October	July	October
Spencer	1439	1635	67 (± 4)	2080 (± 50)
Chedoke	578	1796	212 (± 16)	2670 (± 80)
Borer's	52	223	970 (± 46)	275 (± 32)
Spring	5	18	252 (± 4)	n/a[b]

[a]Values (± standard deviation) were determined by the slope of the linear portion of the dose response data (7 doses per sample).
[b]n/a indicates that no data are available.

effluent from these overflows so that they will no longer be discharged directly into the marsh. Future monitoring of Chedoke Creek should therefore bear out the expected improvements.

The potential contribution of phosphorus from the sediments of Cootes Paradise may be substantial and it deserves further investigation. Results from our phosphorus release experiments suggest that high nutrient levels in the water column may be the result of phosphorus release from the sediment since direct inputs into the water column have decreased. Ryding (1985) found that phosphorus released from sediments constituted a major fraction of the phosphorus found in the water and that their inputs delayed the recovery of shallow eutrophic aquatic systems by up to 5 years, even after the external inputs were reduced. Results of the phosphorus release experiment illustrate that this problem may be occurring in Chedoke Creek. We suggest that sediments within Cootes Paradise may also release phosphorus, especially when sediment temperatures increase and the level of dissolved oxygen decline (Phillips et. al. 1994). In addition to this, during periods of high flow, creek sediments may also be resuspended and transported into the marsh in addition to inputs from the CSOs. In the absence of aquatic vegetation, the suspended nutrients and particles may flow directly into Hamilton Harbour without first being filtered or assimilated.

The release rates of phosphorus from the sediment of Chedoke Creek were consistently higher than those of all other creeks, regardless of the temperature (Fig. 6b). Phillips ét al. (1994) found that iron content of the sediment was a major factor limiting phosphorus release. Visual examination of the sediment samples indicated that iron oxides leached out of both Spencer and Chedoke Creek samples, although the putrid smell of samples from Chedoke Creek suggests that sulfate levels may also have been high. Since sulfate will combine with iron to form iron sulfide, the combination of iron and sulfate in the Chedoke sediment may

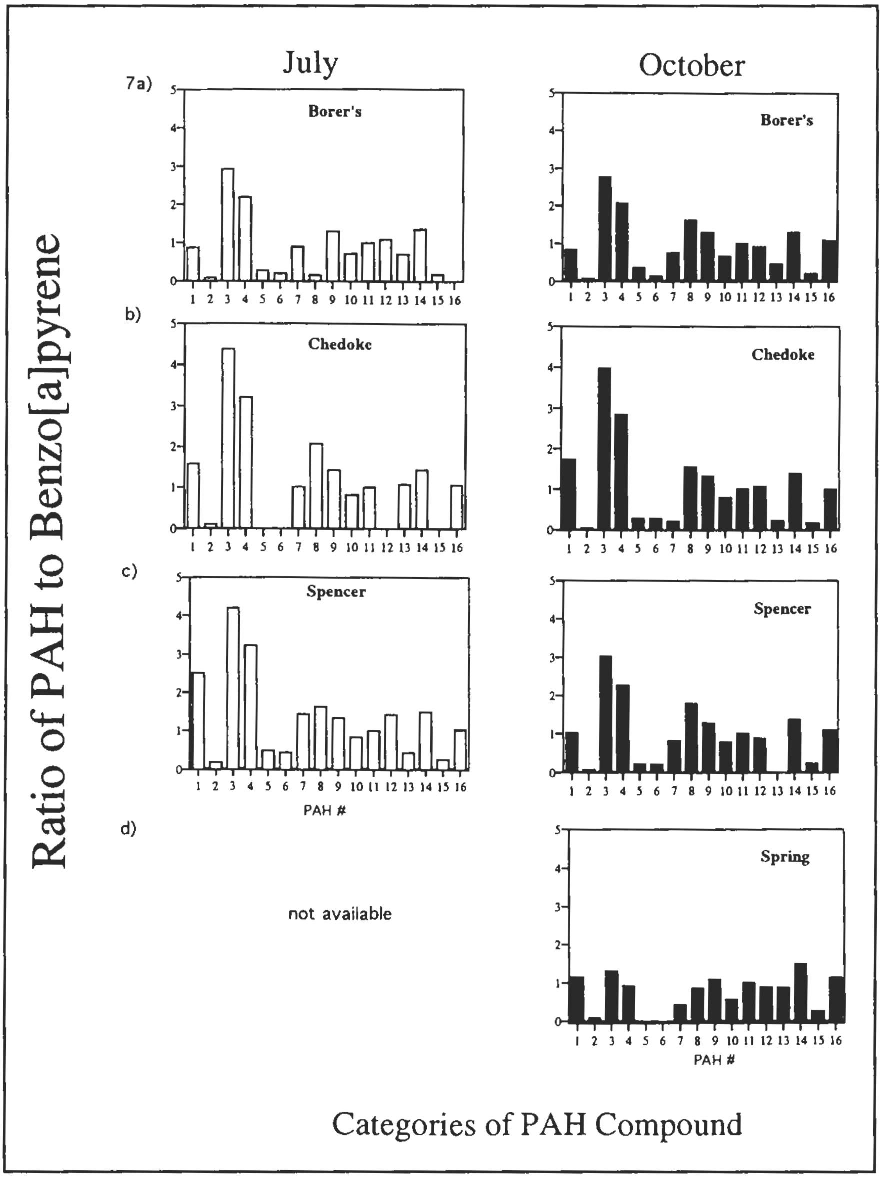

Fig. 7. Normalized concentrations of PAH compounds to benzo[a]pyrene for sediments collected from (a) Borer's Creek, (b) Chedoke Creek, (c) Spencer Creek and (d) Spring Creek in July and October 1994. See Appendix for key to the 16 categories of PAH compounds.

not have influenced phosphorus release whereas iron alone may have inhibited phosphorus release from the samples of Spencer Creek (De Groot 1991).

Compared to PAH levels present at Randle Reef in Hamilton Harbour, the levels in the sediments in Chedoke and Spencer Creeks are not high. However the mutagenic activity in the sediments of these two creeks was found to be equal, if not greater, than most of the areas sampled in the Harbour. This suggests that even though the PAH levels are low, their mutagenic activity is high enough to pose a risk to the organisms that live in the creeks, and possibly the marsh, and may bioaccumulate in the fish and bird communities. Furthermore, the normalized concentrations illustrate that the source of PAH in the tributaries of Cootes Paradise is likely the result of road runoff, suggesting that the inputs will continue to persist, and vary, according to road use. The levels in the marsh are unknown but may pose similar risks due to inputs from the creeks, runoff and groundwater. Further studies should therefore focus on the pathway of PAH bioaccumulation in the aquatic foodweb so that the potential risk from PAH contamination can be properly evaluated.

Acknowledgments

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Appendix

Key to list of priority polycyclic aromatic hydrocarbons (PAHs):

(1) phenanthrene (**Phen**)
(2) anthracene (**Anth**)
(3) fluoranthene (**Flanth**)
(4) pyrene (**Pyr**)
(5) benzo[a]fluorene (**B[a]F**)
(6) benzo[b]fluorene (**B[b]F**)
(7) benz[a]anthracene (**B[a]A**)
(8) chrysene (**Chry**)
(9) benzo[b/j/k]fluoranthene (**B[b/j/k]F**)
(10) benzo[e]pyrene (**B[e]P**)
(11) benzo[a]pyrene (**B[a]P**)
(12) perylene (**Peryl**)
(13) indeno[1,2,3-cd]pyrene (**I[1,2,3-cd]P**)
(14) dibenz[ac]anthracene (**DB[ac/ah]A**)
(15) picene
(16) benzo[ghi]perylene (**B[ghi]P**)

References

Baker, J.E., S.J. Eisenreich, B.J. Eadle. 1991. Sediment trap fluxes and benthic recycling of organic carbon, polycyclic aromatic hydrocarbons, and polychlorobiphenol congeners in Lake Superior Env. Sci. Technol. **25**:500–508.

Benner, B.A., Jr. and G.E. Gordon. 1989. Mobile sources of atmospheric polycyclic aromatic hydrocarbons: a roadway tunnel study. Env. Sci. Technol. **23**:1269–1278.

Bothwell, M.L. 1985. Phosphorus limitation of lotic periphyton growth rates: an intersite comparison using continuous-flow troughs (Thompson River system, British Columbia). Limnol. Oceanogr. **30**:527–542.

Chambers, P.A., E.E. Prepas and K. Gibson. 1992. Temporal and spatial dynamics in riverbed chemistry: the influence of flow and sediment composition. Can. J. Fish. Aquat. Sci. **49**:2128–2140.

Chow-Fraser, P., D.O. Trew, D. Findlay and M. Stainton. 1994. A test of hypotheses to explain the sigmoidal relationship between total phosphorus and chlorophyll-a concentrations in Canadian lakes. Can. J. Fish. Aquat. Sci. **51**:2052–2065.

DeGroot, C.J. 1991. The influence of FeS on the inorganic phosphate system in sediments. Analyst **108**:1235–1239.

Haines, T. 1973. Effects of nutrient enrichment and a rough fish population (carp) on a game fish population (smallmouth bass). Trans. Am. Fish. Soc. **102**:346–354.

Hamilton Harbour Remedial Action Plan. 1992. Stage 1 Report. Environmental options and problem definition. 247 p.

Hamilton Harbour Remedial Action Plan. 1992. Stage 2 Report. Goals, options and recommendations. 329 p.

Holdren, G.C. and D.E. Armstrong. 1980. Factors affecting phosphorus release from intact lake sediment cores. Env. Sci. Technol. **14**:79–86.

Horne, A.J. and C.R. Goldman. 1994. Limnology, 2nd ed. McGraw Hill, Inc., Toronto. 576 p.

Kairesalo, T. and T. Matilaninen. 1994. Phosphorus fluctuation in water and deposition into sediment within an emergent macrophyte stand. Hydrobiologia **275/276**:285–292.

Marvin, C.H., B.E. McCarry and D.W. Bryant. 1994. Determination and genotoxicity of polycyclic aromatic hydrocarbons isolated from *Dreissina polymorpha* (zebra mussels) sampled from Hamilton Harbour. J. Great Lakes Res. **20**:523–530.

Menzie, C.A., B.B. Potocki and J. Santodonato. 1992. Exposure to carcinogenic PAHs in the environment. Env. Sci. Tech. **26**:1278–1284.

Ostrofsky, M.L., D.A. Osborne and T.J. Zebulske. 1989. Relationship between anaerobic sediment phosphorus release rates and sedimentary phosphorus species. Can. J. Fish. Aquat. Sci. **46**:416–419.

Painter, D.S., K.J. McCabe and W.L. Simser. 1989. Past and present limnological conditions in Cootes Paradise affecting aquatic vegetation. Royal Botanical Gardens Technical Bulletin No. 13.

Phillips, G., R. Jackson, C. Bennett and A. Chilvers. 1994. The importance of sediment phosphorus release in the restoration of very shallow lakes (The Norfolk Broads, England) and implications for biomanipulation. Hydrobiologia **275/276**:445–456.

Ryding, S.O. 1985. Chemical and microbiological processes as regulators of the exchange of substances between sediments and water in shallow eutrophic lakes. Int. Rev. ges. Hydrobiologia **79**:657–702.

Schindler, D.W., E.J. Fee and T. Ruszcynski. 1978. Phosphorus input and its consequences for phytoplankton standing crop and production in the Experimental Lakes Area and in similar lakes. J. Fish. Res. Board Can. **35**: 190–196.

Schindler, D.W., R.H. Hesslein, and M.A. Turner. 1987. Exchange of nutrients between sediments and water after 15 years of experimental eutrophication. Can. J. Fish. Aquat. Sci. **44 Suppl 1**:26–33.