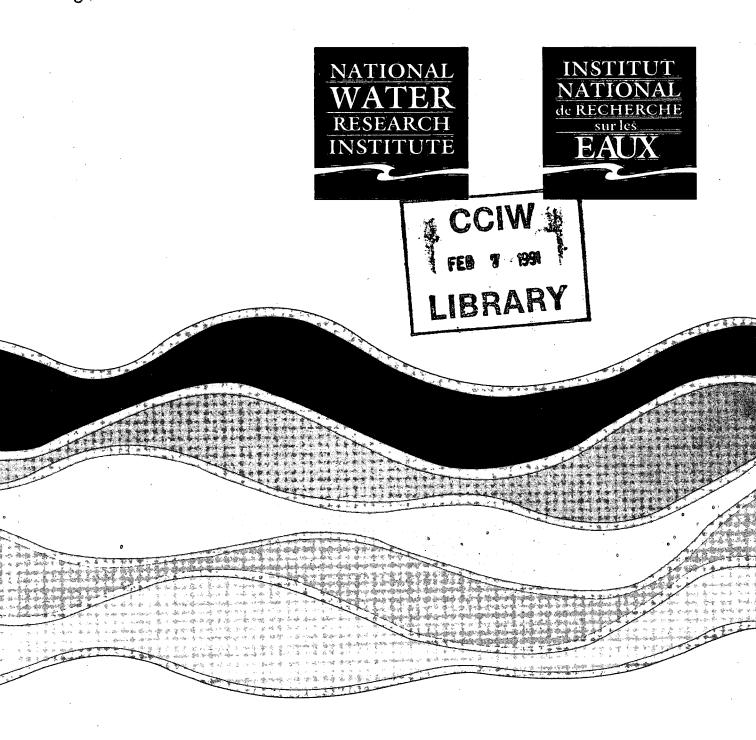
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TRENDS AND LOADINGS OF BIOAVAILABLE PARTICULATE PHOSPHORUS FROM THE NIAGARA RIVER

T. Mayer, K.W. Kuntz and A. Moller

NWRI CONTRIBUTION 90-156

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bу

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MANAGEMENT PERSPECTIVE

Knowledge of bioavailable phosphorus loadings is required to further refine the phosphorus abatement strategy in the Great Lakes Basin.

Presently, loading estimates are obtained using the total P concentrations, without adequate differentiation between loadings of available and unavailable P forms. This is the first study presenting the annual loadings of bioavailable P from the Niagara River, a major tributary to Lake Ontario, accounting for 83% of the tributary inflow. The results of this study show that particulate phosphorus accounts between 53 and 63% of the total phosphorus load from the Niagara River to Lake Ontario. Furthermore, the results suggest that about 48% of the total particulate P load is bioavailable and is of environmental significance. This important finding has implications for implementation of phosphorus control programs and for lake wide management plans which are being considered for Lake Ontario.

If faut connaître les apports de phosphore biodisponible pour raffiner encore plus la stratégie de réduction des concentrations de phosphore dans le bassin des Grands-lacs.

Actuellement, on évalue les apports à partir des concentrations de phosphore total, sans faire une distinction suffisante entre les apports des formes disponibles et non disponibles. Cette étude est la première faisant état des apports annuels de phosphore biodisponible à partir de la rivière Niagara, un tributaire important du lac Ontario responsable du 83 % du débit entrant. Les résultats de cette étude indiquent que le phosphore particulaire constitue de 53 à 63 % de la charge totale de phosphore rejetée dans le lac Ontario avec les eaux de la rivière Niagara. De plus, selon les résultats, environ 48 % de la charge totale de phosphore particulaire serait biodisponible et donc importante du point de vue environnemental. Ces résultats auront des effets sur la mise en oeuvre des programmes de réduction des concentrations de phosphore, ainsi que sur les plans de gestion globale que nous envisageons actuellement pour le lac Ontario.

TRENDS AND LOADINGS OF BIOAVAILABLE PARTICULATE PHOSPHORUS FROM THE NIAGARA RIVER

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ABSTRACT

The forms and concentrations of phosphorus were determined in suspended sediments of the Niagara River for the purpose of assessing the annual loads of bioavailable and total particulate Ρ. The bioavailable phosphorus (BAP) in suspended sediments accounted for about 44% of the total particulate P. Concentrations of BAP and total P (TP) were significantly higher in the summer than in the winter, due to the presence of material of biogenic origin entering the river from Lake Erie. Apatite-P which is generally considered to be biologically inert in aquatic environments accounted for about 26% of the total particulate P. The calculated annual loadings of particulate BAP and TP in 1987 were 1.01x106 and 2.18x106 kg/year, respectively. calculated BAP and TP loadings from the sediments were 1.18x10° and 2.38x10° kg/year, respectively. The results indicate that only about 48% of the total particulate P load is in the form which is of environmental significance. This has important

implications for implementation of phosphorus control programs and for the lake wide management plans considered now for Lake Ontario.

ADDITIONAL INDEX WORDS: Total phosphorus, apatite-P, suspended sediments.

Running Title: Loadings of particulate phosphorus from Niagara River.

Nous avons déterminé les formes et les concentrations de phosphore dans les sédiments en suspension dans la rivière Niagara, en vue d'évaluer les quantités de phosphore particulaire biodisponible et total qui y sont déversées annuellement. Le phosphore biodisponible (PB) dans les sédiments en suspension constituait environ 44 % du phosphore particulaire total. Les concentrations de PB et de phosphore total (PT) étaient beaucoup plus élevées durant l'été que durant l'hiver, en raison de la présence de matières d'origine biogénique qui pénétraient dans la rivière à partir du lac Érié. phosphore de l'apatite, que l'on considère généralement inerte du de vue biologique dans les environnements aquatiques. constituait environ 26 % du phosphore particulaire total. Les valeurs calculées des apports de PB et de PT particulaires pour l'année 1987 étaient de 1,01 x 10^6 et 2,18 x 10^6 kg/an respectivement. l'année 1988, les valeurs calculées des apports de PB et de PT à partir des sédiments étaient de 1.18×10^6 et 2.38×10^6 kg/an respectivement. Les résultats indiquent que seule 48 % environ de la charge totale de phosphore particulaire existe sous une forme importante du point de vue environnemental. Ces résultats auront des effets importants sur la mise en oeuvre des programmes de réduction des concentrations de phosphore et sur les plans de gestion globale que nous envisageons actuellement pour le lac Ontario.

AUTRES MOTS CLÉS: Phosphore total, phosphore de l'apatite, sédiments en suspension

Titre courant: Apports de phosphore particulaire à partir de la rivière Niagara

INTRODUCTION

Implementation of present phosphorus abatement programs is based on control of total P in water. This includes the dissolved fraction which is most readily available for utilization by biota as well as the particulate fraction which can account for a major portion of the total P in water. The availability of particulate P for biological utilization varies depending on the mode of P incorporation within the solid particles. Ample evidence exists (Golterman 1976; Peters 1981; Sonzogni et al. 1982; Williams et al. 1976a; 1976b; 1980) that some forms of particulate P entering the lakes have limited effect on lake productivity.

The Niagara River is the major tributary to Lake Ontario, accounting for about 83% of the tributary inflow (Post et al., 1987; NRTC, 1984) and 50% of the total sediment load to Lake Ontario (Kemp and Harper, 1976; Post et al., 1987; NRTC, 1984; Kuntz and Biberhofer, 1986). Generally, loading estimates are obtained using total P concentrations without adequate differentiation between loadings of available and unavailable P forms. Hence, these are the first loading estimates of bioavailable P from the Niagara River to Lake Ontario.

Recognizing the importance of P loadings from the Niagara River to the water quality of Lake Ontario, the significance of the sediment-associated tributary P load (Ongley and Blachford, 1982) and differences in availability of the particulate P forms,

the estimates of bioavailable particulate P loadings become of interest.

The objectives of this report are: (1) to provide estimates of bioavailable P in suspended sediments collected from the Niagara River; (2) determine the temporal and spatial trends in the particulate P load; and (3) calculate the annual bioavailable and total particulate P load from the Niagara River to Lake Ontario.

MATERIALS AND METHODS

Sample collection

Samples of suspended sediments were collected at two locations on the Niagara River in 1987 and 1988. The two locations chosen were Niagara-on-the-Lake and Fort Erie, both of them in Ontario. The sampling site at Niagara-on-the-Lake (NOTL), is located on the former property of the Regional Municipality of Niagara Water Treatment Plant, one mile upstream from Lake Ontario, and is considered representative of the water flowing into Lake Ontario (Chan, 1977; Kuntz and Biberhofer, 1986; Green, 1988). The sampling site at Fort Erie (FE), was chosen as representative of the Lake Erie outflow (Kuntz and Biberhofer, 1986). Previous surveys of both areas indicated minimal cross-stream variability. Intakes at both stations were located in the main stream of the current. A detailed description of the sampling system can be found in Kuntz et al. (1982) and in the Niagara River Sampling Protocol documents

(1986; 1988). Discharge data and suspended sediments concentrations from 1987 and 1988 were used for load calculations.

Chemical analysis

The suspended solids, collected from a Westfalia continuousflow centrifuge, were frozen and subsequently freeze-dried. Biologically available P (BAP) in suspended particulate solids was estimated using the procedure of Williams et al. (1980), employing 0.1 N NaOH/1.0 N NaCl extracting reagent. The strong correlation between P estimated by this procedure and BAP estimated by bioassay makes this form of P a good surrogate measure of bioavalable P (Golterman et al., 1969; Dorich et al., 1980; Williams et al., 1980; DePinto et al., 1981; Young et al., 1985). Concentrations of total P (TP), non-apatite inorganic P (NAI-P) and apatite-P were determined by the extraction procedure of Williams et al. (1976) and Mayer and Williams (1981). Organic P was determined by difference between the total P concentration and the sum of the NAI-P and apatite-P concentrations. Organic C was determined by the Hewlett Packard Model 185 CHN analyzer.

RESULTS AND DISCUSSION

The mean values of P concentrations in suspended sediments are given in Table 1. Summer and winter average values of BAP,

NAI-P, apatite-P and TP are presented separately for each sampling site and for the whole data set for each year.

As expected, the BAP accounts for most of the NAI-P (95.0% and 86.5%, respectively, on an annual basis, in 1987 and 1988), and for only about 42.3% and 45.4%, of the total P, respectively (Table 2). A highly significant correlation (p<0.001) was found between BAP and NAI-P, and BAP and TP (Fig. 1, and Fig. 2). The BAP determined by the NaOH extraction is thought to be the most labile portion of the NAI-P which can be taken up by algae under aerobic and anaerobic conditions over the short term (Logan et al. 1979 a). The NAI-P includes orthophosphate adsorbed on Feand Al- oxides, Fe- and Al-P minerals, and Ca-P minerals other than apatite. In addition to these inorganic P forms, labile organic P, from algal tissue, is also included in this fraction. It has been shown (Psenner et al., 1984; Mayer, 1985) that extraction used to determine the NAI-P in our extraction scheme renders P incorporated in algal tissue soluble. Logan et al. (1979 a; 1979 b) considered the NAI-P to be a measure of maximum available P, i.e. P that would be available over a long period of time under anaerobic conditions.

The seasonal differences in concentrations of BAP, NAI-P and TP are readily apparent (Table 1). Statistical analysis (Student's T-test) reveals highly significant differences (p<0.001) between the summer and winter BAP, NAI-P and TP concentrations, with these concentrations being higher in the summer than in the winter (Table 1). The higher concentrations

of the BAP, NAI-P, TP and organic C (Kuntz, unpublished data) in the summer suggest the presence of material of biogenic origin, entering the river from productive waters of the Eastern basin of Lake Erie. A similar temporal trend in these parameters was found in suspended sediments from the nearshore area of Lake Erie (Mayer and Manning, 1989). In a few cases in the summer, the presence of suspended solids of biogenic origin (with high org. C concentrations, ~8%) resulted in overestimation of the NAI-P on account of the organic P. This was evident by lower than expected organic P concentrations and consequently high (1038) organic C/P ratios. The mean org. C/P ratios in 1987 and in 1988 were 153 (FE), 151 (NOTL) and 157 (FE), 123 (NOTL), respectively. Little annual variability in these ratios is observed, however for both years, org. C/P ratios are slightly higher at FE than at NOTL.

Data was examined for statistical dependence between the discharge and BAP and TP concentrations. No statistical dependence was found between the particulate BAP concentrations and disharge (R=0.111 in 1987; R=0.343 in 1988) and particulate TP concentrations and discharge (R=0.119 in 1987; R=0.376 in 1988), indicating that P concentration in suspended sediments is independent on the flow of the Niagara River. However, the particulate P concentration appears to be more dependent on the conditions in the eastern basin of Lake Erie, the source of the Niagara River.

As seen in Table 2, a relatively large fraction (~25.9%) of the total particulate P is in the form of apatite-P. This form of P is comprised of orthophosphate present in the crystal lattices of apatite grains and is derived mainly from erosion and resuspension of benthic sediments. Apatite-P has been generally considered biologicaly inert in aquatic environments. No correlation was found between the apatite-P and the total P concentrations (Fig. 3), suggesting that the NAI-P accounts for most of the variation in the total particulate P concentration. Little annual variability is observed in apatite-P concentrations (Table 3), however, seasonality is readily apparent (Table 1). The average winter apatite-P concentration is significantly (p< 0.001) higher at FE than the summer concentration (Table 1). The differences between the summer and winter apatite-P concentrations are somewhat less pronounced at NOTL (Table 1). The higher winter apatite-P concentrations are obviously a result of increased erosion of the Lake Erie shoreline and resuspension of benthic sediments in Lake Erie, consequences of the rough weather conditions and seasonal mixing.

The consistently higher apatite-P concentrations at FE than at NOTL indicate that there are spatial differences in distribution of particulate P forms in suspended sediments. Apatite being associated with heavier particles of detrital origin would settle out more rapidly from the water column than the remaining particles; perhaps in the nearshore depositional areas of the Lower Niagara River, where current velocity is

reduced (NRTC, 1984) or more likely in the power reservoirs (Kauss and Post, 1987).

No consistent trend is evident in spatial distribution of other particulate P forms. In 1987 the concentrations of BAP, NAI-P and TP were higher at NOTL than at FE, whereas in 1988 the opposite was observed. This may be due to the fact that settling of the coarser inorganic particles is accompanied by input of P from point (industrial and municipal) and diffuse sources, tributaries and shoreline erosion along the strech of the Niagara River.

The respective annual loadings of bioavailable particulate P and total particulate P were calculated using the daily flow data, daily suspended solids, BAP and TP concentrations from the NOTL site for the respective years. Since no statistical dependence was found between the discharge and the BAP and discharge and TP concentrations mean daily values of discharge, BAP, TP and suspended sediments concentrations were calculated. Using these values the mean daily loadings, L, (kg/day) of the particulate BAP and TP were calculated using the following formulas:

$$L = C_{(a)} \times C_{(BAP)} \times Q \times 2.447 \times 10^{-6}$$
 (1)

$$L = C_{(a)} \times C_{(TP)} \times Q \times 2.447 \times 10^{-6}$$
 (2)

where $c_{(a)}$ are suspended sediments concentrations in water (in mg/L), $c_{(BAP)}$ and $c_{(TP)}$ are bioavailable and total P concentrations in suspended sediments (in mg/kg), respectively, and Q is the mean daily discharge (in cubic feet per second, CFS). The mean

daily discharge and suspended sediments concentration used in loading calculations in 1987 were 238,402 CFS, 7.6 mg/L, respectively, and in 1988 209,320 CFS, and 9.2 mg/L, respectively.

The calculated mean daily loadings of the particulate BAP and TP in 1987 are 2.77x103 and 5.96x103 kg/day, respectively. The mean daily loadings of particulate BAP and TP in 1988 are 3.24x103 and 6.53x103 kg/day. To obtain the respective annual loadings the calculated mean daily loadings were multiplied by 365.25. The calculated annual loadings of particulate BAP and TP in 1987 were 1.01x106 and 2.18x106 kg/year, respectively. 1988 the calculated BAP and TP loadings were 1.18x10 and 2.38x106 kg/year, respectively. The calculated loadings reveal that there is very little annual variability in loadings of particulate P forms. A comparison of the annual particulate P load with the annual total P water load (4.45x106 kg/year in 1987, 3.44x10° kg/year in 1988, Kuntz, unpublished data), calculated from TP concentrations in water, reveals that between 53.5 and 63.3% of the total P loading is in the particulate form. The data further reveal that only about 48% of the particulate P load is bioavailable and is of concern. represents about 26-30% of the total P load. This finding is of importance for implementation of abatement programs and for lake wide management plans which are being considered for Lake Ontario.

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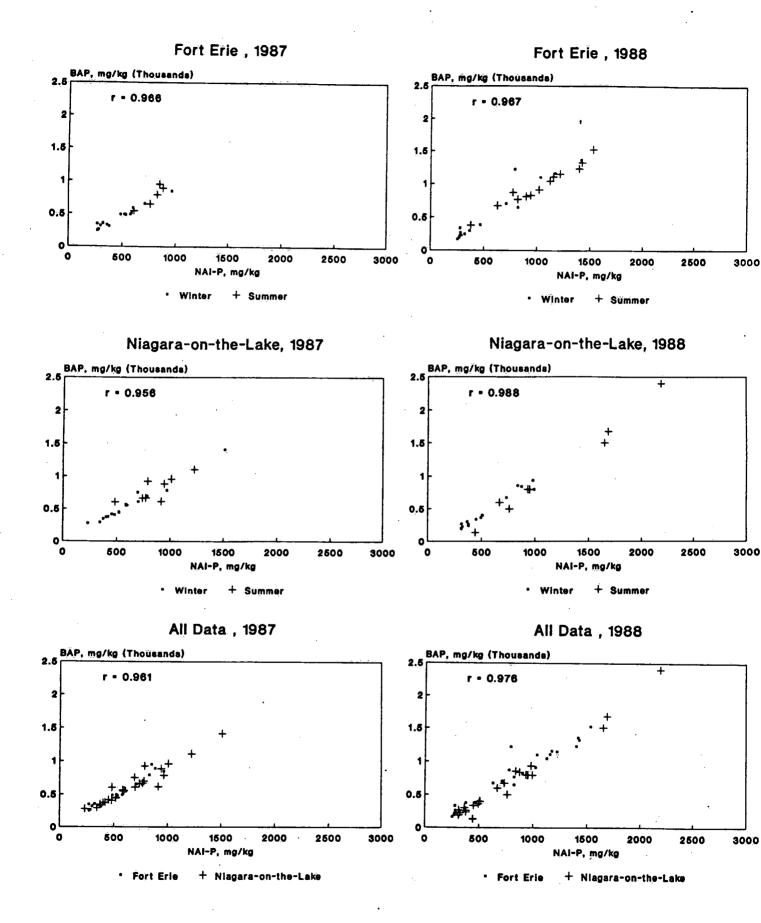


Fig. 1.

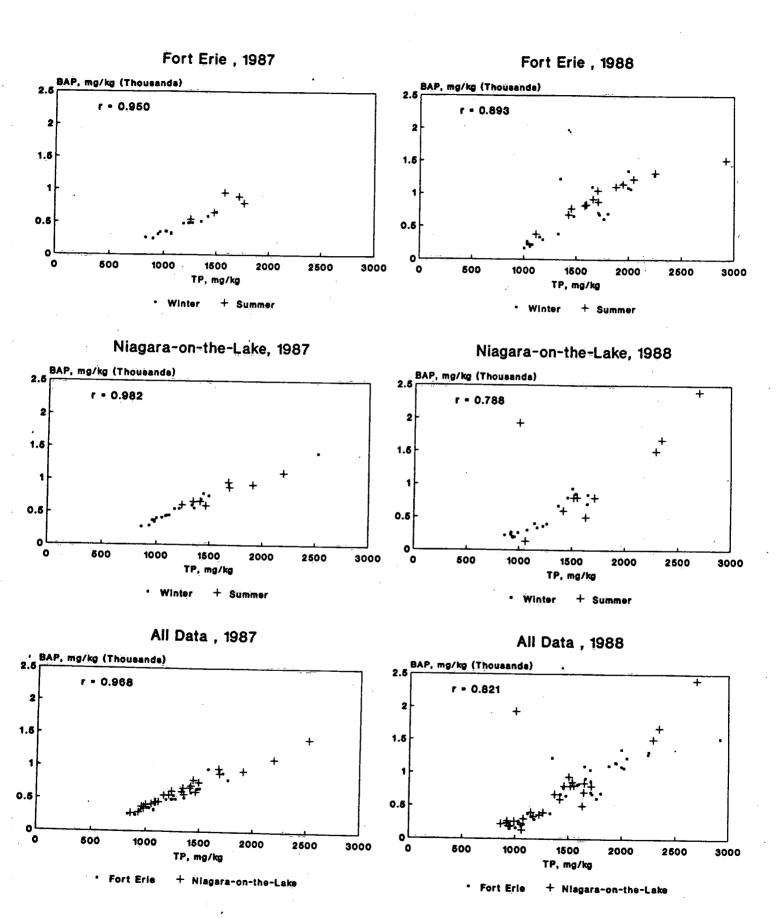


Fig. 2.

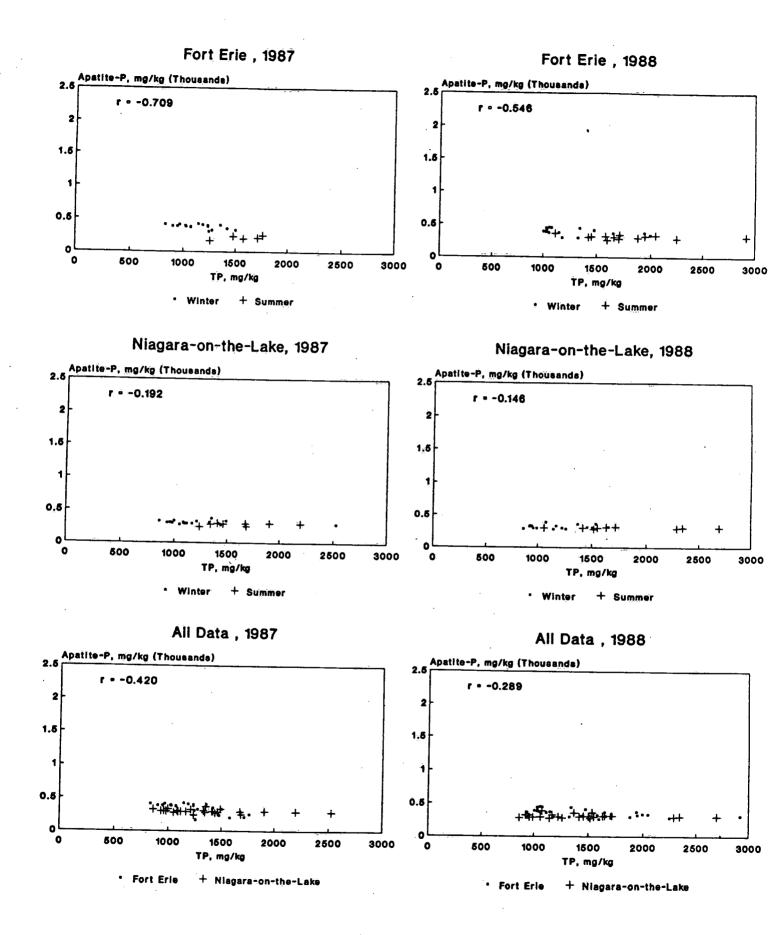


Fig. 3.

Mean summer and winter concentrations of phosphorus in suspended sediments from the Niagara River. Presented in the table are also values of standard deviations and number of cases (n). TABLE 1

| | Sum BAP | Win BAP | Sum | Win | Sum | Win AnatiterD | Sum | Win |
|--------------------------|------------|------------|-----------------------|---------|---------|------------------|-----------------|--------------|
| • | (mg/kg) | (mg/kg) | g/kg) (mg/kg) (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) | (mg/kg) (mg/kg) | (mg/kg) |
| Fort Erie 1987 | | | | | | | | |
| Average | 764 | 445 | 784 | 467 | 216 | 373 | 1558 | 1141 |
| Std dev | 151 | 150 | 96 | 177 | l N | 41 | 200 | 181 |
| ជ | വ | 17 | വ | 18 | S | 18 | S S | 17 |
| Niagara-on-the-Lake 1987 | | | • | | | | | |
| Average | 803 | 542 | 856 | 592 | 281 | 3.07 | 1614 | 1220 |
| Std dev | 176 | 256 | 204 | 278 | | 23 | 2 | 1 (2) |
| u . | ω | 18 | ∞ | 18 | œ | 18 | 8 | 18 |
| All Data 1987 | | | | | | | | |
| Average | 788 | | 829 | ~~ | 256 | 340 | 1593 | α |
| Std dev | 168 | 217 | 175 | 241 | 39 | 47 | 2 | 2 6 |
| ď | 13 | 35 | 13 | 36 | 13 | 36 | 13 | 35 |
| Fort Erie 1988 | | | - | | | | | |
| Average | 940 | 611 | 1024 | 565 | 312 | 383 | 1790 | 1482 |
| Std dev | 297 | 401 | 317 | 3.65 | 26 | | . 4 | 40 |
| c | 14 | 26 | 13 | 1.6 | 13 | 16 | 13 | 22 |
| Niagara-on-the-Lake 1988 | | | | | | | | |
| Average | 1115 | 9 | 1136 | 534 | 299 | 317 | 1723 | σ |
| Std dev | 685 | 251 | 541 | 239 | 10 | 50. | 529 | , כ |
| E | 10 | 19 | თ | 17 | თ | 17 | 10 | 18 |
| All Data 1988 | | | - | | | | | |
| Average | 1013 | 548 | 1070 | 549 | 306 | 349 | 1761 | 13:54 |
| Std dev | 505 | 3.54 | 427 | 3.07 | 22 | 51 | 476 | 373 |
| E | 24 | 45 | 22 | 33 | 22 | 33 | 23 | 40 |

TABLE 2
Distribution of particulate P among different fractions.

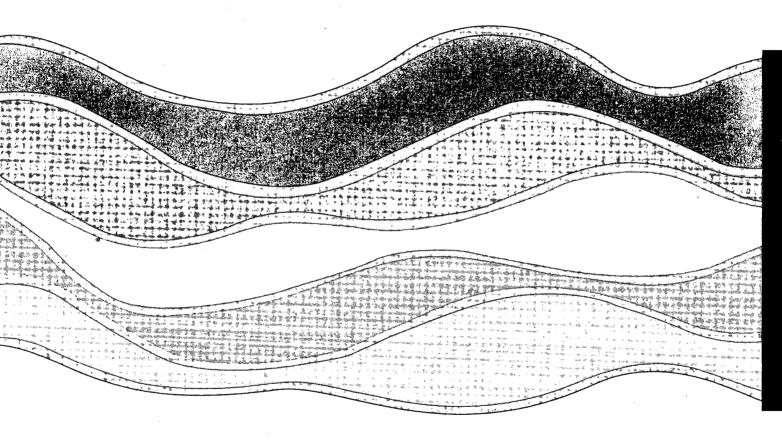
| | BAP as \$ of NAIP | BAP as % of TP | Apatite-P as % of TP | Org-P as % of TP |
|-------------------------------|-------------------|----------------|----------------------|------------------|
| Niagara-on-the-Lake (1987) | 93.4 | 44.9 | 24.0 | 27.1 |
| Fort Erie (1987) | 96.8 | 39.2 | 29.7 | 2.9 .8 |
| All Data (1987) | . 95.0 | 42.3 | 26.6 | 28.3 |
| Niagara-on-the-Lake (1988) | 7.9.5 | 46.2 | 24.6 | 26.1 |
| Fort Erie (1988) | 92.9 | 44.8 | 25.4 | 27.6 |
| All Data (1988) | 86.5 | 45.4 | 25.0 | 26.9 |

Average annual concentrations of P forms in suspended sediments from Niagara River. Presented in the are also values of standard deviations and number of cases (n). TABLE 3

| BAP(mg/kg) 87 1988 |
|-----------------------|
| 687 673 |
| |
| |
| 726 536 |
| 400 2 |
| |
| |
| 468 2 |
| 69 49 |



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