Limnol. Oceanogr., 30(3), 1985, 543–553

Factors controlling phosphorus limitation in stream sediments[1]

R. L. Klotz
Department of Biological Sciences, State University of New York, Cortland 13045

Abstract

Factors influencing the phosphorus limitation of benthic microorganisms were determined for four streams (two agricultural and two forested) in central New York State over an annual cycle. Phosphorus limitation was measured biweekly as specific alkaline phosphatase activity (APA) of sediment samples. Analysis of variance showed the forested streams (sites 2 and 4) to have significantly different sediment APA from the agricultural streams (sites 1 and 3), the higher APA for the forested sites indicating greater phosphorus limitation. Stream total reactive phosphorus concentrations showed no relationship with watershed type, with mean annual values of 10.5 and 6.0 μg liter^{-1} for agricultural sites 1 and 3 and 4.1 and 9.6 for forested sites 2 and 4. With all sites grouped together, sediment APA had a low correlation with stream water phosphate ($r = 0.184$, $n = 73$). Phosphorus sorption isotherms showed sediments from agricultural streams to have higher phosphate sorption indices than forested sites and to sorb rapidly large amounts of phosphorus. This resulted in higher available phosphorus content for the agricultural sediments and lower sediment APA.

Although nutrient limitation has been studied extensively in lakes, only recently has similar research been done on lotic ecosystems. Phosphorus was shown to be limiting to both decomposers and primary producers in a second-order woodland stream in Tennessee by the technique of nutrient spiking (Elwood et al. 1981). Stockner and Shortreed (1978), using a similar approach with constructed stream channels, found phosphorus limiting to primary producers in the coastal rainforest ecosystem on Vancouver Island, British Columbia. Nitrogen was found to limit primary producers in hot desert free-flowing streams of the southwestern United States (Grimm et al. 1981). Nitrogen also limited leaf litter decomposition in a laboratory study by Hynes and Kaushik (1969), a finding supported by in situ studies in two North Carolina streams by Meyer and Johnson (1983). Using a different method for measuring decomposition, Egglishaw (1972) found that the loss in tensile strength of cotton duck (94% dry weight cellulose) in Scottish rivers was positively correlated with nitrate concentration. Others have found no effect of phosphorus or nitrogen enrichment on stream periphyton (Patrick 1966; Wuhrmann and Eichenberger 1975; Rodgers 1977).

Elucidation of the mechanisms for nutrient limitation of stream organisms should explain why streams differ in their nutrient limitation; however, these mechanisms are not completely understood. The flowing water environment can provide a continual supply of a nutrient to stream organisms, the rate of supply to epilithic organisms being controlled by the rate of diffusion through a laminar boundary layer around the cells (Whitford 1960). The river velocity and nutrient concentration influence the diffusion rate. For phosphorus, the concentration in stream water is to a large extent controlled by the sediments through sorption-desorption processes (Meyer 1979; Mayer and Gloss 1980; Hill 1982). Factors such as sediment particle size, iron, aluminum, and organic content (Syers et al. 1973; Meyer 1979; Hill 1982) influence phosphorus sorption by river sediments. This sorption capacity affects phosphorus availability to epilithic organisms through regulation of stream phosphorus concentration and thus affects the concentration gradient across the boundary layer. The extent to which this sorption capacity influences the availability of phosphorus to sediment organisms has not been studied, although Meyer (1978) suggested that it might be extremely important.

I have investigated the mechanisms for phosphorus limitation of sediment microorganisms in four streams in central New York State. Two of the streams drain pre-

[1] This research was supported by a grant from the SUNY Cortland Faculty Research Program.

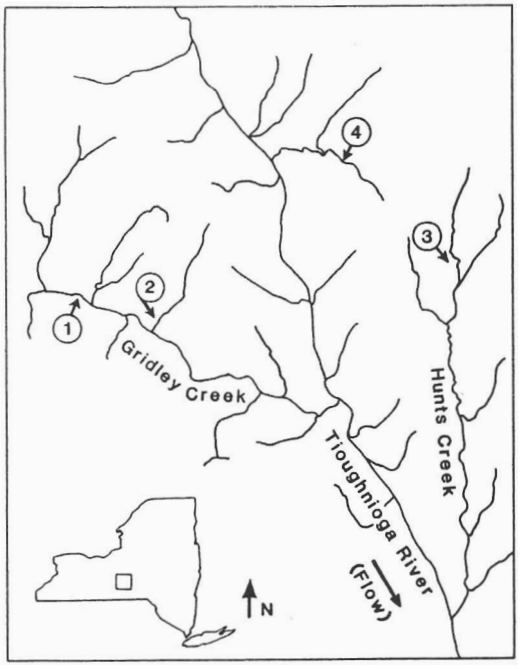

Fig. 1. Map of the study area.

dominantly agricultural watersheds and two drain forested watersheds, providing a range of physical, chemical, and biological regimes. Phosphorus limitation was measured by analyzing the alkaline phosphatase activity (APA) of sediment microorganisms. Alkaline phosphatases are induced under phosphorus-limiting conditions, the enzymes acting to cleave phosphate groups from organic and complexed phosphorus compounds, thus making phosphorus available to the organism. Bacteria (Torriani 1960) and algae (e.g. Fitzgerald and Nelson 1966) produce phosphatases under limiting inorganic phosphorus conditions; the level of phosphatase activity has been shown to be a good indicator of inorganic phosphorus deficiency (e.g. Rhee 1973; Healey and Hendzel 1979). Jansson (1981) showed that the level of phosphatase activity was correlated with aluminum concentration in acidic lakes; aluminum decreased phosphorus availability by complexing with the nutrient. The use of enzyme activity analyses in river sediments has generally been neglected (Duddridge and Wainwright 1982).

I thank J. L. Scholl for laboratory assistance, H. Doerr for computer assistance, and H. Keen, J. Meyer, and an anonymous reviewer for commenting on initial drafts of the manuscript.

Study area

Four streams in Cortland County in central New York State were chosen to determine differences between the two dominant watershed types in the region, agricultural and forested. A map of the stream sites is given in Fig. 1, watershed characteristics in Table 1, and stream chemistry parameters

Table 1. Characteristics of the four streams and watersheds.

	1	2	3	4
Land use (%)				
Agricultural	94.9	2.0	96.5	1.9
Wooded	5.1	98.0	3.5	94.2
Abandoned field	0	0	0	3.9
Watershed area (km^2)	49.2	18.8	16.5	17.6
Elevation at site (m)	413	407	389	298
Stream characteristics				
Total length (km)	13.1	2.86	3.89	4.24
Order	2nd	1st	1st	1st
Discharge ($m^3\ s^{-1}$) mean (SD)	1.79(5.70)	0.38(1.18)	0.34(1.09)	0.10(0.23)
Soil types (%)*	16 VHL 42 LVM 42 VML	100 LVM	50 LVM 50 VML	7 VML 93 LVM

* VHL: Valois–Howard–Langford; LVM: Lordstown–Volusia–Mardin; VML: Volusia–Mardin–Lordstown.

Table 2. Means (SD) of water quality parameters (measured in 1980–1981) at sites 1–4.

Parameters	*n*	1	2	3	4
Conductivity (μmhos)	14	198(203)	70(42)	103(59)	77(38)
NO_3^--N (mg liter^{-1})	11	0.907(0.530)	0.108(0.085)	1.494(0.653)	0.441(0.161)
Ca (mg liter^{-1})	14	32.2(14.2)	17.2(8.24)	26.2(5.52)	18.1(5.70)
K (mg liter^{-1})	14	1.47(0.53)	0.65(0.20)	1.29(0.43)	0.69(0.22)
Mg (mg liter^{-1})	14	5.82(2.49)	3.21(1.42)	3.83(1.14)	2.94(1.06)
Na (mg liter^{-1})	12	No data	1.58(1.44)	2.08(0.74)	1.32(0.62)

in Table 2. The streams were circumneutral (pH 7.2–7.7) with alkalinities ranging from 28 to 55 mg liter^{-1} $CaCO_3$ (November 1984 analysis, 1 sample per site).

Methods

A composite sample totaling 1 liter of the upper 7 cm of stream sediment was collected from 10 locations at each site and used to determine APA. Samples were collected approximately biweekly from March 1982 to July 1983 and taken to the laboratory in plastic bottles for analysis within 3 h. Sediments were first sieved (2-mm mesh) to eliminate large material and provide a uniform sample for subsequent analysis within 30 min. APA was determined by the method of Sayler et al. (1979), which is 100% efficient in recovery of APA from different sediments. Briefly, duplicate sieved sediment subsamples (1 ml) were placed in test tubes, 3 ml of 1 M THAM [Tris (hydroxymethyl) amino-methane] buffer (pH 8.6) was added, and the samples were sonicated (Bronwell Biosonik III) for 45 s to release cell-bound phosphatase. After sonication, 1 ml of *p*-nitrophenylphosphate (*p*-NPP; Sigma; 1 mg per ml buffer) was added to samples at timed intervals and incubation immediately started. After 60 min incubation in a 37°C waterbath, the reaction was stopped with 1 ml of 1 N NaOH, the samples were centrifuged, and the supernatant liquid analyzed on a Bausch and Lomb Spectronic 70 at 418 nm for *p*-nitrophenol (*p*-NP, product formed following cleavage of P from *p*-NPP). Absorbance readings were converted to concentration by comparison with a *p*-NP (Sigma) standard curve. Spectrophotometric blanks were prepared by adding buffer without *p*-NPP to the reaction mixture.

Respiration was used as a biological unit to express results as specific APA and was determined as oxygen uptake by 50-ml sediment subsamples. A biological unit is necessary since sediment grain size differed between sites, the smaller size fractions having greater surface area per volume for microbial colonization. The oxygen consumption chamber consisted of a 500-ml filtering flask fitted with a two-hole rubber stopper with an inlet and an outlet tube and a bubble vent tube attached to the side tubularity. The chamber with 50 ml of sediments was filled with aerated water (purified by reverse osmosis) through the inlet tube, air bubbles were released through the bubble vent tube, and the chamber was sealed by closing all tubes with clamps and incubated in darkness at 37°C for 4 h. Respiration measurements were done in duplicate and expressed as oxygen uptake per hour. Specific APA was determined by dividing the mean of the APA determinations by the mean of the respiration measurements and was expressed as μmol NP produced mg^{-1} oxygen consumed h^{-1}.

Total reactive phosphorus was determined in unfiltered stream water samples the day of collection by the ascorbic acid method (Am. Public Health Assoc. 1975). Before the present study, various nutrients were determined at the sites in 1980–1981. Nitrate was analyzed by cadmium reduction (Am. Public Health Assoc. 1975) on the day of collection; colorimetric analyses were made with a Carey recording spectrophotometer. Calcium, potassium, magnesium, and sodium concentrations were determined with a Perkin-Elmer model 303 atomic absorption spectrophotometer.

The ability of the sediments to sorb phosphorus was determined twice from phosphate sorption isotherms by the techniques of Meyer (1978) and Hill (1982) during Sep-

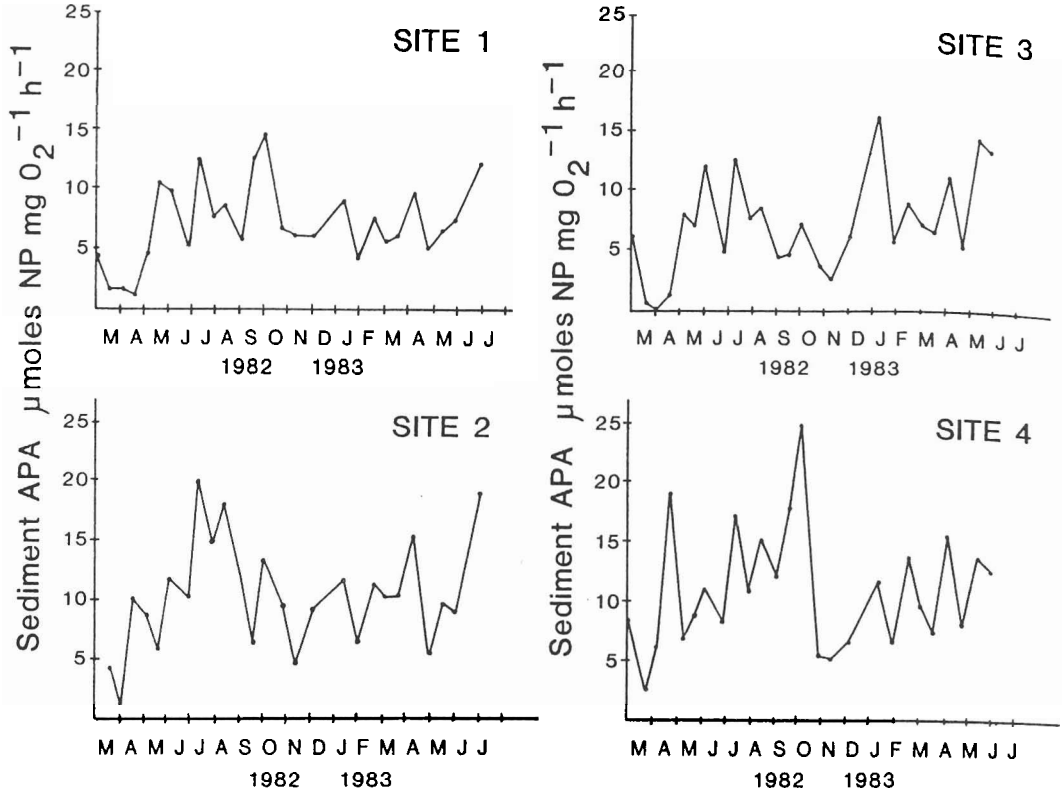

Fig. 2. Specific alkaline phosphatase activity (APA) of sediments at the four sites measured over an annual cycle.

tember and October 1983. The data allowed calculation of the phosphate sorption index, a useful measure of the phosphate buffering capacity of sediments (Bache and Williams 1971). A high value for the index indicates that a large amount of phosphorus can be sorbed by the sediment without increasing the phosphorus concentration in the water at equilibrium. The phosphorus sorption index was measured by incubating 6 ml of sieved sediments (2-mm mesh, collected in normal fashion) for 1 h at 20°C with 50 ml of 0.01 M $CaCl_2$ spiked with 2,000 μg liter^{-1} P ($KH_2PO_4^{3-}$) in duplicate. The flasks were vigorously shaken for 5 s every 10 min. The index was calculated from the relationship: $X/\log_{10}C$, where X is the phosphorus (in μg g^{-1} dry wt sediment^{-1}) sorbed from an initial concentration of 2,000 μg P liter^{-1} and C is the final phosphorus concentration (μg P liter^{-1}) in the solution after 1 h. The equilibrium phosphorus concentration (EPC) was also determined and is the dissolved phosphorus concentration in the water at which there is neither adsorption nor desorption of phosphorus by the sediments. Duplicate 6-ml sieved sediment subsamples (2-mm mesh) were incubated 1 h at 20°C in 50 ml of 0.01 M $CaCl_2$ spiked with $KH_2PO_4^{3-}$. Flasks were shaken vigorously for 5 s every 10 min. EPC was measured by plotting the μg P sorbed g^{-1} dry wt sediment vs. initial phosphorus concentrations of 0, 10, 20, and 50 μg P liter^{-1}. The EPC is the intersection of the plot with the X-axis. For the sorption experiments, soluble reactive phosphorus was determined by the ascorbic acid method (Am. Public Health Assoc. 1975) after filtration through acid-washed 0.45-μm membrane filters. Sediments were dried at 80°C to express sorption per unit dry weight; mean dry weights for 6 ml of sediments for sites 1–4 were 5.23, 8.21, 7.04, and 7.70 g.

The influence of biological activity on the

phosphate sorption index was determined by inhibiting biological activity in sediment subsamples with carbonylcyanide *m*-chlorophenylhydrazone (CP), an inhibitor of phosphorylation. Tarapchak et al. (1981) found that CP effectively inhibited biological phosphate uptake while preventing cellular release of phosphorus, making it superior to other biological inactivation techniques. The phosphate sorption indices of untreated and CP-treated (7.5×10^{-2} and 1.0×10^{-3} M) sediments were calculated to determine the biological contribution to phosphate sorption. Phosphate sorption by living vs. autoclaved (1.03 bars, 121°C, 20 min) sediments was also determined for comparison with the CP technique; percent sorption was calculated as the ratio of the phosphate sorption indices of autoclaved vs. living sediments. Sediments were not rinsed after autoclaving.

The sediment extractable phosphate was determined by the technique of Williams et al. (1980). Fifty milligrams of dry sediment was extracted overnight with 50 ml of 1 M NaCl in 0.1 N NaOH solution and the filtrate (0.45 μm) analyzed for inorganic phosphorus. Organic matter content of sediments was determined by weight loss of dried samples at 500°C in a muffle furnace. Size fractionation of sediments was performed by sieving fresh samples collected on 19 September 1983 through 2-mm mesh, drying at 80°C, and then sieving through 1.10-, 0.55-, and 0.25-mm mesh. Size fractions were expressed as percent of total dry weight.

Results

Results of the biweekly analyses of sediment APA are plotted in Fig. 2 and summarized in Table 3; biweekly respiration measurements used to calculate specific APA of the sediment are given in Fig. 3. Mean annual sediment APA was 6.97 and 7.21 μmol *p*-NP produced (mg O_2 consumed)$^{-1}$ h^{-1} for agricultural sites 1 and 3 and 10.02 and 11.00 for forested sites 2 and 4. Duplicate samples for both NP and O_2 consumed differed by about 6%. Analysis of variance showed the agricultural sites to be significantly different from the forested sites (Table 3). With all sites grouped together, absolute sediment APA (unadjusted for microbial activity) showed little correlation with sediment respiration ($r = 0.028$, $n = 103$).

Table 3. APA of stream sediments. Units are μmol *p*-nitrophenol produced (mg O_2 consumed)$^{-1}$ h^{-1}. One-way ANOVA (0.001 level) with the Student-Newman-Keuls procedure (0.05 level) showed sites 1 and 3 differed significantly from sites 2 and 4.

Site	Annual mean	SD	*n*
1—Agricultural	6.97	3.39	26
2—Wooded	10.02	4.30	25
3—Agricultural	7.21	4.17	26
4—Wooded	11.00	5.17	26

Concentrations of stream total reactive phosphorus during this period are presented in Table 4 and show no relationship with watershed type. Agricultural site 1 had the highest mean phosphate concentration (10.5 μg P liter^{-1}) followed by wooded site 4 (9.6), agricultural site 3 (6.0), and wooded site 2 (4.1). With all sites grouped together, sediment APA had a low correlation with stream water phosphate ($r = 0.184$, $n = 73$). Only at site 3 was there a significant correlation between APA and phosphate concentration ($r = 0.718$, $P = 0.001$, $n = 19$).

To elucidate mechanisms controlling sediment APA, I prepared phosphate sorption isotherms for fresh sediments (Fig. 4). Agricultural sites 1 and 3 showed rapid phosphorus sorption and an ability to sorb large amounts of the nutrient. The greater phosphate buffering capacity of the agricultural streams' sediments is shown by the high phosphate sorption indices (Table 5; determined on a different date from Fig. 4) for sites 1 and 3 (8.34 and 12.32) vs. forested sites 2 and 4 (2.45 and 1.89). Comparison of sites 1 and 3 in Fig. 4 and Table 5 shows that site 1 had a higher phosphorus sorption index on 5 September 1983 (Fig. 4), but site 3 was greater on 11 October 1983 (Table 5). However, on both dates the agricultural sites had much higher indices than the forested sites.

Sediments were treated with CP and autoclaved to inhibit biological phosphorus uptake and determine the relative importance of biotic vs. abiotic factors to the phosphorus sorption index. Phosphate

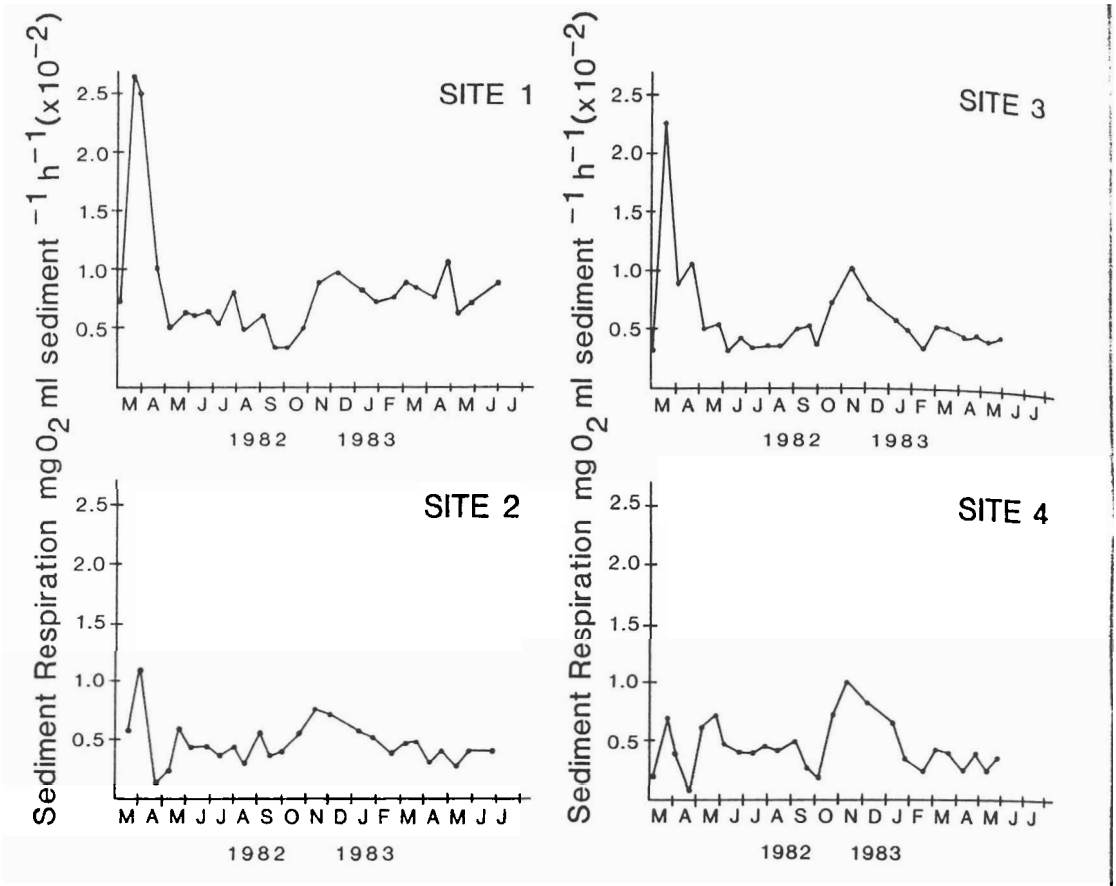

Fig. 3. Microbial respiration (oxygen consumption by sediments) at the four sites measured over an annual cycle.

sorption did not decrease with CP-inhibited (10^{-3} M) sediments, but did decrease for autoclaved sediments (Table 5). An analysis for site 1 sediments with 7.5×10^{-2} M CP (the highest concentration that solubility characteristics permitted) showed phosphate sorption by CP-treated sediments to be 96% of sorption by the fresh sediments.

Table 4. Concentrations of total reactive phosphorus at the four sites. Units are μg P liter^{-1}. One-way ANOVA (0.004 level) with the Student-Newman-Keuls procedure (0.05 level) revealed significance for sites 2 3 4 1.

Site	Annual mean	SD	*n*
1—Agricultural	10.5	8.1	16
2—Wooded	4.1	3.9	19
3—Agricultural	6.0	5.3	19
4—Wooded	9.6	5.6	19

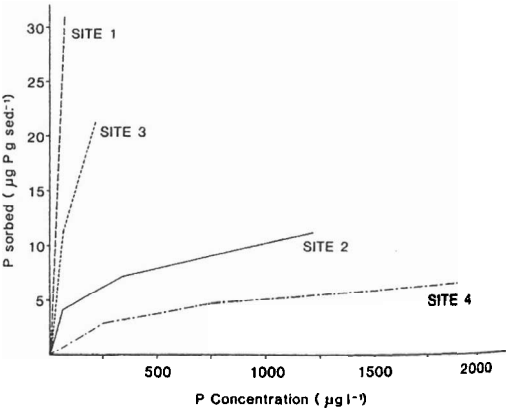

Fig. 4. Phosphorus sorption isotherms for sediments collected and analyzed on 5 September 1983. Initial phosphorus concentrations were 0.1, 0.75, 1.5, and 3.0 mg P liter^{-1} in 25 ml of 0.01 M $CaCl_2$ and 3.0 ml of sediments.

Table 5. Phosphorus sorption indices of living and CP-inhibited sediments, and the ratio of the indices for autoclaved vs. living sediments. The index was calculated as: $X/\log_{10}C$, where X is P sorbed (in μg g^{-1} dry wt sediment) from an initial concentration of 2,000 μg P liter^{-1} and C is the final P concentration (μg P liter^{-1}) in solution after 1 h. Sediments were collected and analyzed on 11 October 1983 for CP study and on 6 July 1984 for autoclaving study.

Site	P sorption index		Autoclaved: Living (%)
	Living	CP inhibited*	
1—Agricultural	8.34	8.91	72
2—Wooded	2.45	2.55	77
3—Agricultural	12.32	12.48	77
4—Wooded	1.89	1.94	75

Carbonylcyanide *m*-chlorophenylhydrazone (10^{-3} M).

Abiotic sediment characteristics which may be responsible for differences in P sorption between sites are presented in Table 6 and Fig. 5. Sediments from the two agricultural stream sites had a greater percentage of organic matter and more extractable available phosphate than sediments from forested stream sites. The EPC of the sites showed no relationship with watershed type; site 1 was lowest at 0.35 μg P liter^{-1}, followed by site 2 at 0.55, site 3 at 1.26, and site 4 at 2.25. Particle sizes within the range used for APA determination varied with stream type, with the agricultural sites having a higher percentage of the smaller size fractions (Fig. 5).

Discussion

The sediments from two streams draining forested watersheds were significantly more P limited, as measured by APA, than the two streams draining agricultural watersheds (Table 3). When all sites were grouped together, sediment APA had a low correlation with stream total reactive phosphorus ($r = 0.184$, $n = 73$), indicating that the phosphate concentration of the water was not a major factor controlling sediment phosphorus limitation. The sediments from the streams of different types differed dramatically in their ability to sorb phosphorus, and this factor probably was responsible for the differences in sediment APA. The phosphate sorption indices and isotherms (Table 5 and Fig. 4) showed the agricultural streams (1 and 3) to have a greater potential to sorb large amounts of phosphorus rapidly from the water. This potential was evidenced by the higher phosphorus content of the agricultural stream sediments (Table 6). Mayer and Gloss (1980) found through repeated desorption studies that sediments can supply significantly more phosphorus than is indicated by EPC values. This phosphorus would be released from the sediments in the presence of agents like bacteria and algae. The larger capacity for phosphorus sorption of sites 1 and 3 provided more available phosphorus for benthic organisms and lower sediment APA.

The greater ability of the agricultural stream sediments to sorb phosphorus is probably due to their chemical and physical properties; biological activity was less important in these sediments (Table 5). The CP concentration used (10^{-3} M) for inhibition of biotic sorption adequate (Tarapchak et al. 1981) for phytoplankton samples does not appear sufficient when larger quantities of sediment are present. Site 1 sediment analyzed with CP at 75 times this concentration (the highest concentration solubility characteristics permitted) was found to have 96% of the sorption of untreated sediments. CP inhibits biological phosphate uptake while preventing cellular release of phosphorus—the latter a problem associated with autoclaving. The autoclaved samples represent the minimum values for abiotic contribution to phosphate sorption by the sediments and probably substantially underestimate the true abiotic sorption index because autoclaving releases

Table 6. Characteristics of the sediments at the four sites (mean ± SD).

Site	EPC (μg liter^{-1})	Extractable P (mg P mg^{-1} sed.)	Organic content (%)
1	0.35±0.01	1.46×10^{-4} ± 0.00	3.54±0.04
2	0.55±0.00	0.39×10^{-4} ± 0.20×10^{-4}	1.80±0.52
3	1.26±0.00	0.99×10^{-4} ± 0.04×10^{-4}	2.97±0.17
4	2.25±0.14	0.30×10^{-4} ± 0.20×10^{-4}	2.15±0.17

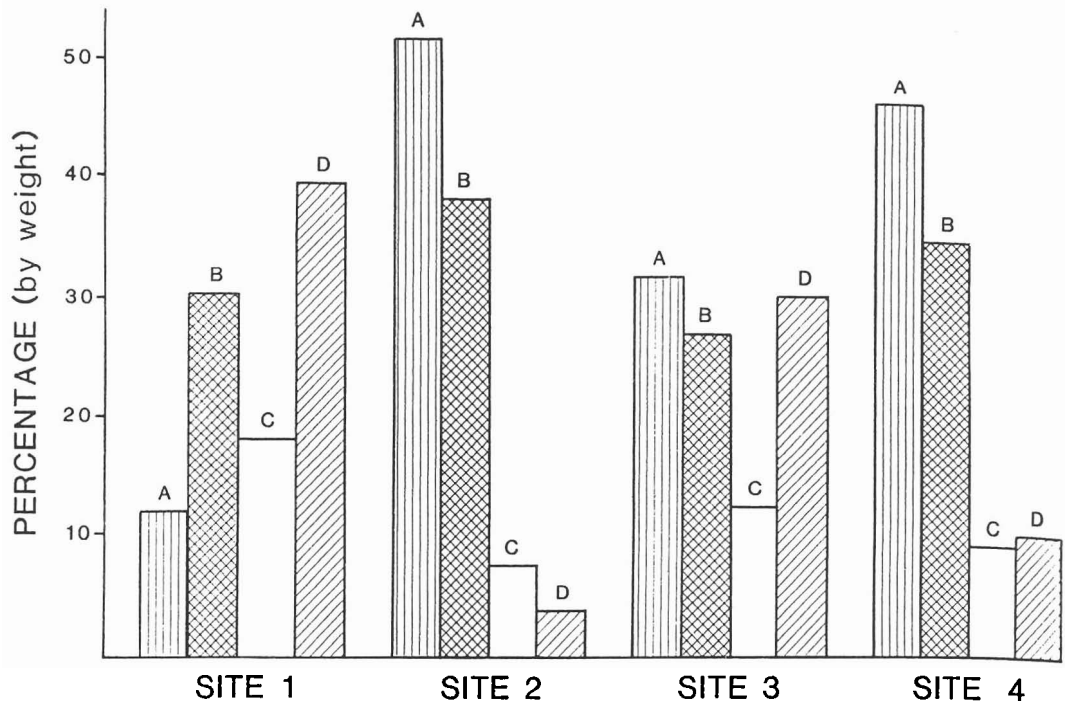

Fig. 5. Size fractions of sediments passing through a 2-mm mesh at the four sites as percentage of total dry weight. Collected 19 September 1983. A—1.10–2.0 mm; B—0.55–1.10 mm; C—0.25–0.55 mm; D—<0.25 mm.

bound phosphorus to the water (Meyer 1978). The differences between measured sorption indices for autoclaved vs. living sediment could be accounted for if the net release of phosphorus due to autoclaving the 6-ml sediment samples used in the sorption analyses was about 5% of the extractable phosphorus content of the sediments (Table 5). Meyer (1979) also found similar differences in phosphate sorption after 1 h between autoclaved and untreated sediments and concluded that microbial uptake played a relatively minor role in phosphorus sorption by stream sediments from Bear Brook, a heterotrophic headwater stream draining an undisturbed watershed in the Hubbard Brook Experimental Forest, New Hampshire.

One abiotic feature of sediments associated with phosphorus sorption is particle size. Fine-grained silty sediments were found to have a higher phosphorus sorption capacity than coarse sandy sediments in Bear Brook (Meyer 1979). Hill (1982) concluded that phosphorus sorption in two southern Ontario streams with substantial agricultural activity was probably related to particle size. The fine-grained sediments of the agricultural streams of my study (Fig. 5) may therefore have been responsible for the higher phosphorus sorption indices of those streams. Chemical factors were also found to influence sediment phosphorus sorption, the most important being aluminum, iron, and organic content (Meyer 1979). The organic content of the agricultural sediments of my study was greater than that of the forested sediments (Table 5); perhaps this acted in conjunction with particle size to increase phosphorus sorption.

My findings indicate that watershed land-use practices and geology affect phosphorus limitation of stream sediment organisms. Processes in the watershed which lead to greater input of fine-grained sediments will tend to decrease phosphorus limitation. Also, stream reaches with low gradients and reduced velocities would be predicted to have lower sediment APA due to the greater sorptive capacity of the fine-grained sedi-

ments that would settle out. Geology and land-use practices would also determine iron and aluminum content of stream sediments, and therefore phosphorus limitation.

Phosphorus limitation of any ecosystem component is intimately linked to the cycling of the nutrient. In streams, nutrient cycling is tied to downstream transport of the nutrient, causing a nutrient to follow a spiral pathway as it is successively taken up, regenerated, and transported downstream. This concept, known as spiralling (Webster 1975; Webster and Patten 1979), has been measured in Walker Branch, a first-order phosphorus limited stream in Tennessee by Elwood et al. (1981) and Newbold et al. (1981), who found that factors affecting phosphorus uptake from the water column are the primary determinants controlling the overall rate of phosphorus utilization. This conclusion agrees with the results of my study if the sorption capacity of the sediments is closely associated with phosphorus uptake rate, which it probably is. Phosphorus limitation of sediments was controlled mainly by the abiotic sorption characteristics of the sediments, not the phosphorus concentration in the water. Hill (1982) showed that sediment sorption was a major mechanism for phosphorus retention during summer low flows in two Ontario streams. Streams possessing sediments with high phosphorus sorption indices will have shorter spiralling lengths, and will make more efficient use of phosphorus, than streams with lower indices, other factors being equal. Phosphorus sorption by other stream compartments (e.g. leaf packs: Meyer 1978) may have a greater biotic contribution. Similar results have been obtained for organic matter processing in streams. Stream retention was shown to be a primary factor determining organic matter turnover time and distance in streams from four distinct geographic areas in the northern United States (Minshall et al. 1983).

The phosphorus sorption indices and EPC values of my study (Tables 5 and 6) were comparable to those obtained by Meyer (1978) for Bear Brook. She found mean phosphorus sorption index values of 10.3 for silty sediments (similar to my 8.3 and 12.3 values for agricultural sites 1 and 3) and 2.1 for sandy sediments (similar to my 2.5 and 1.9 values for forested sites 2 and 4). The EPC for Bear Brook sandy sediments averaged 1.5 μg P liter^{-1} and for silty sediments 2.2—not a significant difference and also similar to the sediments in my study (0.35–2.25). Meyer conducted the studies cited above at 11°–13°C, while my studies were done at 20°C. Meyer (1978) showed that an increase in temperature resulted in an increase in the rate of the sorption reaction, resulting in a higher phosphorus sorption index; for silty sediments the index was 7.6 at 0°C, 8.3 at 10°, and 10.4 at 24°. My techniques would be expected to produce slightly higher P sorption values due to the higher temperature.

Two phosphorus-rich streams in southern Ontario were found to have high phosphorus sorption indices and EPC values (Hill 1982), resulting in significant phosphorus retention during low summer flows. Hill's phosphorus sorption index values of 142 for Duffin Creek and 85.6 for Nottawasaga River sediments represent relatively large buffering capacities. EPC values of the two streams were also relatively high, ranging between 10 and 25 μg P liter^{-1}, and may in part account for higher phosphorus concentrations in the river waters. Again technique may be responsible for some, but not all, of the difference between Hill's and my values. Hill shook the sediment samples for a longer time (30 s vs. 5 s) every 10 min during the 1-h incubation period. Since sorption differences by sediments determine phosphorus limitation, as I have shown here, then one would expect APA values for Bear Brook sediments to be similar to those of the stream sediments of my study and values for Duffin Creek and Nottawasaga River to be lower, representing less phosphorus limitation. Clearly the large range for phosphorus sorption index values indicates that rivers in different areas may show greater differences in phosphorus limitation for benthic microorganisms than the two stream types of my study.

Meyer (1979) showed EPC values of stream sediments to correspond with the stream water phosphate concentration. The lack of correspondence in my study between the EPC values (Table 6) and the phosphate

measurements (Table 4) is explained by the fact that the phosphorus analyses were done on unfiltered water, while EPC really should be compared to the dissolved phosphate concentration. Analyses of filtered (0.45 μm) stream water samples on two dates in June 1984 showed a good correspondence with EPC, with soluble reactive phosphorus values for sites 1–4 of 0.85, 0.75, 1.14, and 5.47 μg liter^{-1}.

Other studies have demonstrated phosphorus limitation in streams; however these enrichment experiments required high levels of phosphorus. Elwood et al. (1981) enriched sections of a second-order woodland stream in Tennessee with averages of 60 and 450 μg PO^{3-}_4-P liter^{-1} and found that both levels significantly increased the nitrogen content and mass loss of leaf packs; however only the higher level significantly increased the respiration rates of the leaf packs. Stockner and Shortreed (1978) found that tripling the phosphate concentration in a Vancouver Island stream led to higher algal biomass with or without a similar nitrate increase. I found that phosphorus limitation of the stream benthos was correlated with phosphorus sorption by the sediment and not with the phosphorus concentration of the water; indeed a river with a higher phosphorus concentration can show greater phosphorus limitation of benthic microorganisms than another river with lower phosphorus concentration (sites 4 and 3: Tables 3 and 4). The phosphorus sorption isotherms (Fig. 4) show why this is so. For sites 1 and 3, the concentration of phosphorus in the water necessary for a certain level of sorption was less than that required for the same sorption for sites 2 and 4 sediments. Differences in sediment sorption characteristics probably influenced the sediment phosphorus content (Table 6); phosphorus content for the high sorption index sites 1 and 3 (1.46 and 0.99 $\times$ 10^{-4} mg P mg^{-1} sed.) was higher than for the low index sites 2 and 4 (0.39 and 0.30 $\times$ 10^{-4}). This higher sediment phosphorus content resulted in less phosphorus limitation for the benthic microorganisms at site 3 than at site 4 despite lower phosphate concentrations in the water at site 3.

This is the first study to show significant differences in sediment phosphorus limitation between streams over an annual cycle and to elucidate the factors responsible for them. Sayler et al. (1979), with just one sampling date per site, measured differences in the absolute phosphatase activity between sediments of various stream sites, but concluded that the differences were due to variation in the microbial biomass and not the specific activity of the enzyme. There was no correlation between absolute phosphatase activity and unit respiration in my study. The factor most responsible for the phosphorus limitation of benthic microorganisms in this study was sorption of phosphorus by the sediments, primarily by abiotic processes.

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Submitted: 20 January 1984
Accepted: 26 December 1984