

## Phosphorus Status of Selected Indiana Lake and Reservoir Sediments

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### Introduction

Eutrophication is the natural aging process of lakes that is characterized by increasing organic productivity and accelerated by excessive nutrient input. There is good evidence to show that phosphorus (P) is a limiting nutrient for algal growth in many lake systems and the key element in the eutrophication process (Vollenweider, 1971; Syers *et al.*, 1973). Soluble inorganic phosphorus (SIP) is the major form of P taken up by aquatic plants and, thus, the P form most responsible for eutrophication. This form of P is also involved in equilibrium sorption-desorption reactions with lake sediments. Sediments may serve as sinks for SIP present in lake water or sources of SIP for algal uptake depending upon the nature of the equilibrium. It is apparent from studies on Wisconsin lakes that the adsorptive site for SIP is an aluminum and iron rich amorphous gel complex. This appears to be true for both calcareous and noncalcareous sediments. (Williams *et al.*, 1971a; 1971b).

The sorption-desorption equilibrium of P, as affected by sediment and limnological conditions, determines the ultimate concentration of SIP maintained in the water phase by sediment. The concentration of SIP in the water phase at which P is neither sorbed or desorbed from the sediment phase is a unique property of a sediment known as equilibrium phosphate concentration (EPC). It has been shown that when sediment and phosphate solutions were equilibrated in the laboratory there was desorption of sediment P at low concentrations of added P, whereas at higher SIP concentrations P was sorbed by the sediment. The EPC value is the point of zero sorption and is determined from a plot of SIP concentration at equilibrium versus P sorbed.

Little is known about the P status of Indiana lake and reservoir sediments. Therefore, the objectives of this study were: to survey the forms of P in selected lake and reservoir sediments, to determine the nature of P exchange between sediment and water phases, and to relate sediment characteristics to existing water quality.

### Materials and Methods

Wet sediment samples were collected by an Ekman dredge from the deepest portion of lakes and reservoirs, passed through a 4-mesh sieve, and thoroughly mixed. Sediments were stored as slurries in sealed glass containers at 4°C until analyzed. Solids content of sediments was determined by drying at 105°C and pH was estimated by glass electrode. An amount of wet sediment equivalent to 0.5 g oven-dry weight was used in all sorption and extraction studies. Sorption and release of P by sediments was studied by shaking each sediment with 40 ml of 0.01M calcium chloride solution containing from 0 to 400 µg P/ml as monopotassium phosphate for 24 hours, centrifuging the mixture for 10 minutes at 12,000 x g, filtering the supernatant through Whatman 2V paper, and determining SIP in the filtrate by the method of Murphy and Riley (1962). The amount of SIP sorbed or

desorbed was calculated as the difference between the amount added and the amount remaining in solution at equilibrium. Amounts of SIP sorbed by the sediment were plotted against the equilibrium concentrations of SIP to permit graphical estimation of EPC for each sediment (Taylor and Kunishi, 1971). Data obtained from sorption studies were also plotted in the form of Langmuir adsorption isotherms from which adsorption maxima, buffering capacity, and binding energy values were calculated (Syers *et al.*, 1973).

Availability of P in sediments was estimated by extraction with reagents known to selectively remove P associated with specific components. Aluminum-bound P was determined by the 0.5M ammonium fluoride (pH 8.2) extraction method described by Jackson (1970). Phosphorus associated with amorphous iron oxides was estimated by the extraction with ammonium oxalate-oxalic acid reagent (Saunders, 1965) and P bound to amorphous plus crystalline iron oxides was determined by the 0.5M sodium hydroxide extraction method described by Jackson (1970). Calcium-bound P was determined by extraction of sodium hydroxide-treated samples with 0.5N sulfuric acid as described by Jackson (1970). The amounts of labile P present in selected sediments was estimated by the <sup>32</sup>P isotopic dilution technique (Olson and Dean, 1965).

Subsamples of wet sediment were air-dried, passed through a 2 mm sieve and subjected to particle size analysis (Kilmer and Alexander, 1946). Air-dry sediment was further ground to < 80-mesh and analyzed for total N (Nelson and Sommers, 1972), total P (Sommers and Nelson, 1972), organic carbon (Mebius, 1960), and inorganic carbon (Allison, 1960). Data reported are on an oven-dry basis and represent the average of samples collected from a particular lake or reservoir. Methods described by Steel and Torrie (1960) were used for correlation analyses.

### Results and Discussion

TABLE 1 provides data on the general characteristics of the lake and reservoir sediments studied. There were large differences in composition between lake and reservoir sediments likely because of variations in watershed conditions, sediment parent material, and age of the impoundments. Lake sediments contained much higher levels of organic carbon (ave. of 12.3% versus 2.1%), inorganic carbon (ave. of 5.9% versus 0.4%), and total nitrogen (ave. of 0.83% versus 0.18%) than did reservoir sediments. Reservoir sediments contained higher concentrations of clay-size material than did lake sediments (an ave. of 28 and 7%, respectively).

TABLE 1. *General characteristics of lake and reservoir sediments.*

Sediment	Code	Organic C	Inorg. C	Total N	Clay	pH
-----%-----						
Lakes:						
Big Turkey	BT	8.2	7.8	0.53	12	7.8
Cedar	Cd	13.7	1.1	0.90	5	7.6
Maxinkuckee	Mx	9.0	8.5	0.64	8	7.8
Palestine	Pa	10.1	6.7	0.86	7	7.7
Sylvan	Sy	13.0	5.1	0.92	7	7.5
Wawasee	Wa	19.6	6.2	1.13	5	7.6
Reservoirs:						
Cataract	Ca	1.9	0.6	0.16	16	7.8
Mansfield	Mn	1.9	0.5	0.14	40	7.5
Mississinewa	Mi	2.1	0.4	0.19	38	8.1
Monroe	Mo	2.3	0.0	0.21	17	7.6

TABLE 2. *Phosphorus components present in lake and reservoir sediments.*

Sediment	Total P μg/g	Organic P	Inorganic P extracted by			
			NH <sub>4</sub> F	Oxalate	NaOH	H <sub>2</sub> SO <sub>4</sub> <sup>+</sup>
			-----% of total P-----			
BT	690	36	7	23	5	58
Cd	770	51	16	15	12	35
Mx	470	52	11	14	4	43
Pa	1150	56	8	10	7	36
Sy	1290	42	8	16	9	49
Wa	570	53	10	14	4	41
Ca	1170	44	13	24	22	29
Mn	1080	48	20	22	18	29
Mi	740	47	27	23	21	29
Mo	630	48	10	19	30	19

+ Extraction with H<sub>2</sub>SO<sub>4</sub> after NaOH extraction was completed.

However, pH values of lake and reservoir sediments were similar. Reservoir sediments tended to have compositions similar to the soils in the watershed, whereas lake sediments were very different from the soils surrounding the lake. All lake sediments contained significant amounts of free carbonates, but only small amounts of carbonates were found in reservoir sediments.

TABLE 2 provides data on the P components present in sediments. Lake and reservoir sediments contained similar levels of total P (an ave. of 823 and 905 μg/g, respectively) and organic P (an ave. of 395 and 425 μg/g, respectively). A higher proportion of total P was present as aluminum-bound and amorphous iron-bound P in reservoir sediments as compared to lake sediments. This finding is important because these P components are thought to be the most available for release to the water phase. Furthermore, the amount of sodium hydroxide-extractable P has been used as an index of the algal available P content of a sediment. Oxalate and sodium hydroxide extracted similar amounts of P from reservoir sediments suggesting that limited amounts of P are associated with crystalline iron oxides in these sediments. Surprisingly, oxalate extracted significantly more P from most lake sediments than did sodium hydroxide. The proportions of total P present as calcium-bound P (sulfuric acid extractable) were much higher for lake sediments (average of 44%) as compared to reservoir sediments (average of 27%). Calcium-bound P is thought to be largely unavailable for release to the water column.

Eutrophication indices for each lake and reservoir studied are given in Table 3. These indices were supplied by the U.S. Environmental Protection Agency and are based on extensive examination of water quality and productivity in the impoundments. In general, the lakes tended to have higher indices than the reservoirs indicating more advanced eutrophication in the former. Cedar, Sylvan, and Palestine Lakes were judged to be eutrophic, whereas Lake Maxinkuckee was probably oligotrophic. All reservoirs studied had relatively low eutrophication indices in the mesotrophic range.

TABLE 3 also gives data on the EPC, P adsorption maxima, and labile P values for sediments. The EPC values for reservoir sediments were low (average of 0.003 μg P/ml), whereas the lake sediments had relatively high EPC levels (average of 0.032 μg P/ml). This suggests that lake sediments had the capacity to buffer the SIP concentration in the water phase more than ten times higher than reservoir sediments. Big Turkey, Cedar, and Sylvan lake sediments had particularly high EPC values. On the average, reservoir sediments had higher capacities for adsorp-

TABLE 3. *Eutrophication indices of impoundments and EPC, phosphorus adsorption maxima, and labile P values for sediments.*

Sediment	Eut. Index	P		Labile P
		EPC μg/ml	abs. max. μg/g	μg/g
BT	42	0.042	3320	154
Cd	65	0.067	2420	—
Mx	18	0.006	2630	—
Pa	60	0.020	6940	—
Sy	62	0.053	1870	—
Wa	23	0.004	3700	—
Ca	26	0.004	7500	—
Mn	21	0.001	8350	89
Mi	20	0.001	3530	—
Mo	32	0.004	5020	—

tion of P than did lake sediments likely because of the higher levels of amorphous iron and aluminum in the former (Orme and Nelson, 1979). About 8 and 22% of the total P in Mansfield and Big Turkey sediments, respectively, was isotopically exchangeable. However, 18 and 5% of the total P in Mansfield and Big Turkey sediments, respectively, was extractable with sodium hydroxide. These findings indicate that the two methods (i.e. sodium hydroxide extraction and  $^{32}\text{P}$  exchange) used for estimating available P measure two different P pools in sediments.

TABLE 4 presents data on the relationships between eutrophication indices of impoundments and sediment P component concentrations. There was a direct correlation between the eutrophication index of lakes and reservoirs and the EPC values of the sediments (Figure 1). This finding indicates that sediment EPC is an important water quality determinant and suggests a direct role of sediments in supplying SIP to the water column. Eutrophication indices of lakes were also directly related to the levels of total P, oxalate-extractable P, ammonium fluoride-soluble P, and NaOH-extractable P in sediments, but reservoir eutrophication indices were not correlated with levels of these P components in sediments. When all impoundments were considered, eutrophication indices were related to levels of sulfuric acid-soluble P in sediments, however, no such relationship was observed when only lakes or reservoirs were considered separately.

TABLE 4. *Relationships impoundment eutrophication indices and sediment P components and between sediment EPC values and other P components of sediments.*

Variable 1	Variable 2	Sediments considered:		
		Lake	Reservoir	All
-----Corr. coeff., r-----				
Eut. index	EPC	+ .81*	+ .89	+ .87*
Eut. index	Total P	+ .81	NS	NS
Eut. index	Oxalate P	+ .67	NS	NS
Eut. index	NH <sub>4</sub> F-P	+ .86	-.98	NS
Eut. index	NaOH-P	+ .94*	NS	NS
Eut. index	H <sub>2</sub> SO <sub>4</sub> -P	NS	NS	+ .62
EPC	Total P	NS	NS	NS
EPC	Oxalate P	+ .69	NS	NS
EPC	NH <sub>4</sub> F-P	+ .73	-.84	NS
EPC	NaOH-P	+ .75	NS	NS
EPC	H <sub>2</sub> SO <sub>4</sub> -P	NS	NS	+ .55

\*Significant at 99% confidence level, NS, not significant at 90% confidence level.

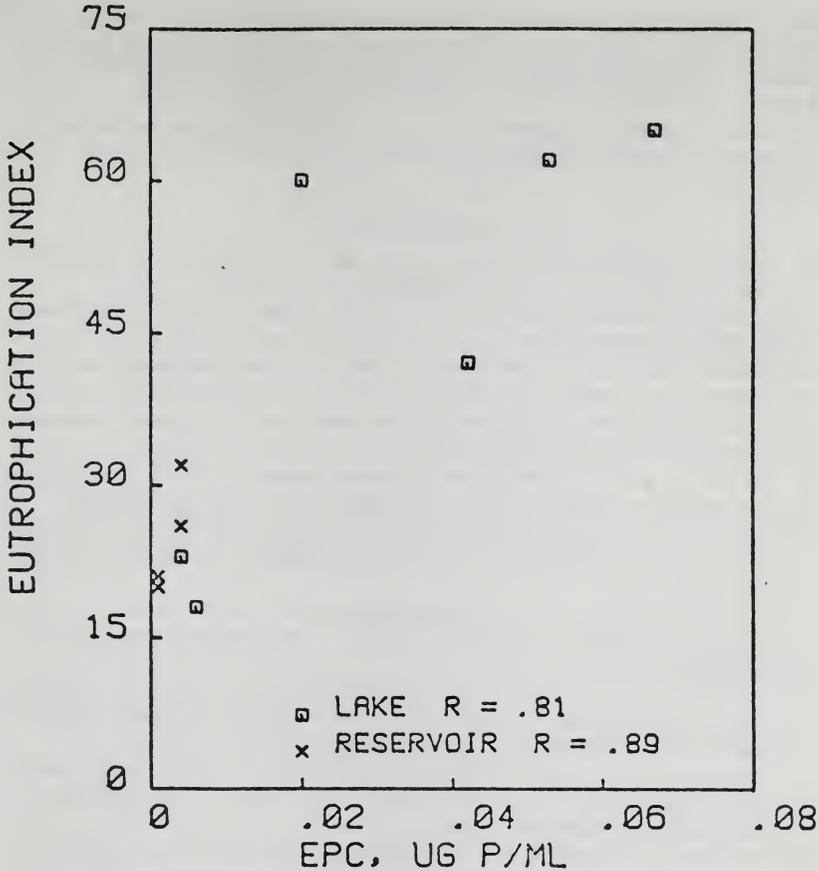


FIGURE 1. Relationship between impoundment eutrophication indices and sediment EPC values.

TABLE 4 also gives data on the relationships between EPC values and levels of sediment P components. Amounts of oxalate-, ammonium fluoride, and sodium hydroxide-extractable P in lake sediments were directly correlated with EPC values. No P component in reservoir sediments was directly related to EPC levels. When all sediments were considered the EPC values were positively correlated with the levels of sulfuric acid-soluble P. The significance of the latter finding is difficult to assess and it may result from the fact that lake sediments had higher EPC values and levels of sulfuric acid-extractable P without indicating a cause-effect relationship.

#### Conclusions

The following conclusions may be drawn from this work: (1) Lake and reservoir sediment have very different levels of clay, organic carbon, inorganic carbon, and total nitrogen, and consequently, differ in P retention capacity, (2) Reservoir sediments have P components similar to soil, whereas lake sediments have reduced

levels of iron and aluminum-bound P and increased levels of calcium-bound P, (3) From 7 to 23% of total sediment P is potentially available to algae, (4) Reservoir sediments appear to be sinks for P, but lake sediments may be P sources or sinks depending upon SIP concentration in the water column, (5) Eutrophication indices of lakes and reservoirs are directly related to sediment EPC values suggesting the involvement of sediment in biological productivity and overall water quality in impoundments.

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