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Phosphorus Uptake and Release by Lake Ontario Sediments



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PHOSPHORUS UPTAKE AND RELEASE BY
LAKE ONTARIO SEDIMENTS

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ABSTRACT

Sediment cores were obtained from 15 lake stations representing the three major basins and the Inshore Zone of Lake Ontario. Cores were sectioned for characterization of the surface sediments according to inorganic P chemical mobility. Physical mobility was characterized by measurement of P release from intact cores incubated under controlled laboratory conditions. The proportions of potentially chemically mobile inorganic P were usually high (30 to 60%) in the central basin sediments and low (2 to 8%) for the inshore zone sediments. Although the amounts of inorganic P desorbed after three successive equilibrations (in .1M NaCl) of Lake Ontario sediments represented only 3 to 17% of the potentially mobile inorganic P, sufficient inorganic P was desorbed to restore a large part of the original interstitial inorganic P concentrations. Interstitial inorganic P (mobile P) concentrations ranged from 14 to 1280 $\mu\text{g/l}$ and were higher than dissolved inorganic P concentrations in the overlying water. Diffusion rates estimated from the range of observed interstitial inorganic P values ranged from about 0.05 to 0.6 $\text{mg m}^{-2} \text{ day}^{-1}$ and were in agreement with the range of 0.03 to 0.8 $\text{mg m}^{-2} \text{ day}^{-1}$ estimated from P release from intact cores incubated under controlled laboratory conditions. Based on an inorganic P flux of 0.2 $\text{mg m}^{-2} \text{ day}^{-1}$, the estimated annual contribution of inorganic P to Lake Ontario water is equal to about 10% of the external P loading.

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SECTION I

CONCLUSIONS

The proportion of potentially chemically mobile inorganic P (NaOH-P) was high (30 to 60%) in the basin postglacial muds and in some regions of the southern Inshore Zone of Lake Ontario, and was low (2 to 8%) for the glaciolacustrine clay and most of the Southern Inshore Zone. While similar results were observed for NaOH-P and exchangeable inorganic P, the proportion of exchangeable P was lower (13 to 18%) for basin sediments.

Amounts of inorganic P desorbed after three successive equilibrations of Lake Ontario sediments represented only 3 to 17% of the potentially chemically mobile inorganic P (NaOH-P). However, the appreciable amounts of inorganic P in solution after each equilibration indicated that the potentially mobile sediment inorganic P could largely restore in situ interstitial inorganic P concentrations.

Levels of interstitial inorganic P (mobile P) ranged from 14 to 1280 $\mu\text{g/l}$. Concentrations were usually higher in the basin than in the inshore sediments. This trend was in agreement with the high proportion of potentially mobile inorganic P in the basin sediments.

The IIP values were always higher than the DIP levels in the overlying lake water. This suggests a potential exists, due to the concentration gradient, for release of mobile P to the overlying water.

The physical mobility of sediment inorganic P was sufficient to release DIP to the overlying lake water from intact cores under controlled laboratory conditions. The highest levels of P obtained in the overlying lake water for individual cores ranged from 5 to 250 $\mu\text{g/l}$. The levels of P released reached 10 $\mu\text{g/l}$ or higher between 12 and 25 days of incubation for most cores and surpassed the mean concentration of about 11 $\mu\text{g/l}$ for "soluble phosphate" in Lake Ontario bottom waters. For deep lakes like Lake Ontario, the physical mobility of sediment P is likely controlled mainly by diffusion of IIP from the sediments to overlying water. Diffusion rates estimated from the range of observed IIP values (100 to 1000 $\mu\text{g/l}$) ranged from about

0.05 to 0.6 $\text{mg m}^{-2} \text{ day}^{-1}$ and were in agreement with the range of 0.03 to 0.8 $\text{mg m}^{-2} \text{ day}^{-1}$ estimated from the cores incubated in the laboratory. Based on the inorganic P flux of 0.2 $\text{mg m}^{-2} \text{ day}^{-1}$ (mean for incubated cores), the estimated annual contribution of inorganic P to the lake water from the sediments is 1.4×10^6 kg of P per year. The estimated sediment contribution is about 10% of the external P loading (1.3×10^7 kg/yr).

SECTION II

RECOMMENDATIONS

Results of this investigation indicated that the sediment contributes about 10% of the external P loading for Lake Ontario. The significance of the sediments as a source of P would increase, however, if other external sources of P were reduced. It is recommended, therefore, the mechanism and magnitude of P release from the sediment be further investigated.

Since interstitial inorganic P is the most mobile fraction of the sediment P, more complete investigation of IIP concentrations should be pursued with emphasis on seasonal variations and the technique of interstitial water separation.

Although diffusion is probably a principle means of P transport, evaluation of other transport mechanisms, such as turbulent mixing could further clarify the physical mobility of sediment P. The accuracy of the determination of the amounts of inorganic P released from the sediment by diffusion would be increased by an experimentally determined diffusion coefficients for Lake Ontario sediments.

The extent to which inorganic P released from the sediments is transported to the photic zone should be evaluated.

SECTION III

INTRODUCTION

The degree to which sediments are able to replenish dissolved inorganic phosphorus (DIP) in the overlying lake water is of major concern in relation to attempts to retard or reverse lake eutrophication. In terms of total P, the sediments probably serve as a "sink" for P as a result of sorption and sedimentation processes. However, release of inorganic P from sediments may play a role in controlling the levels of DIP in the overlying water.

Release of inorganic P from sediments is expected to be controlled by both the chemical and the physical mobility of sediment inorganic P (Syers et al. 1973). Chemical mobility refers to the rate and extent of sediment inorganic P interaction with the surrounding (interstitial) water and is controlled by the forms of inorganic P contained in the sediment. According to this concept, inorganic P in solution or interstitial water inorganic P (IIP) is completely mobile, while sediment inorganic P in equilibrium with the IIP is potentially mobile, and inorganic P which does not interact with the interstitial water is immobile. Available evidence indicates that the important sediment inorganic P compounds are P sorbed on hydrous Fe and Al oxides (nonoccluded P), P sorbed on CaCO_3 , and apatite (Williams and Mayer 1972; Syers et al. 1973). Occluded P or P contained within Fe oxides may also be present in some sediments. Except for apatite and possibly vivianite, discrete P compounds have not been identified in sediments. Nonoccluded P is in equilibrium with IIP and is potentially mobile, while occluded P and apatite are immobile.

The chemical mobility of sediment P can be determined by measurements of IIP and by using extraction procedures (Chang and Jackson 1957; Williams et al. 1967) developed for sediments (Williams et al. 1971 a; 1971 b) which allow measurement of nonoccluded and apatite P by sequential extraction with NaOH, citrate-dithionite-bicarbonate (CDB), and HCl reagents, respectively. Furthermore chemical mobility of sediment P has been related to the availability of sediment P to algae. Recent evidence (Sagher 1974) has shown that algae in close

contact with sediments are able to utilize the dissolved inorganic P and the potentially mobile sediment inorganic P fraction (NaOH-P).

Physical mobility of phosphorus refers to the transport of P within sediments and across the sediment-water interface. In shallow waters, transport may involve resuspension of bottom sediments by wave action. However, in deeper waters, transport likely involves the chemically mobile sediment P and the processes of diffusion or partial mixing of surface sediments (Lee 1970; Williams and Mayer 1972; Syers et al. 1973).

In many lakes, sediment IIP levels exceed dissolved inorganic P concentrations in the overlying water (Stumm and Leckie 1971; Bannerman 1973) and a tendency exists for dissolved inorganic P to move from the sediments to the lake water. Furthermore, the amounts of potentially mobile P in equilibrium with IIP are frequently high. The relationships between phosphorus chemical and physical mobility are not understood sufficiently to allow precise predictions of inorganic P release rates from sediments. However, measurements of chemical mobility will facilitate evaluation of the potential for inorganic P release.

While considerable information is available on the sediments of Lake Ontario and the other Great Lakes (Kemp and Lewis 1968; Kemp 1971; Thomas et al. 1972), the nature and mobility of sediment P in the Great Lakes has received limited attention.

Important information on the phosphorus characteristics of deep sediment cores from Lake Ontario was provided by Kemp et al. (1972) and Williams and Mayer (1972). The interstitial water composition (not including phosphorus) was determined for Lake Ontario by Weiler (1973) and for Lake Michigan by Callender (1969). Electrodialysis was investigated as a technique for extracting mobile P from Lake Ontario sediments (Kemp and Murochova 1971).

The purpose of this investigation was to evaluate the chemical and physical mobility of inorganic P in Lake Ontario sediments to

facilitate evaluation of the impact of the bottom sediments on the P status of the lake water.

SECTION IV

METHODS AND MATERIALS

SAMPLING PROCEDURES

Cores of Lake Ontario sediment were obtained with a Benthos Gravity corer. Cores were divided into 3 or 5 cm sediment sections to a depth of 15 or 25 cm below the sediment surface. Sediment sections were extruded into small plastic bags for transport to the laboratory or in situ manipulation of the sediment. Intact cores were also transported to the laboratory for measurement of P release under controlled conditions. All sediment samples were stored cold (ice chest or 4°C). The samples were collected from 10 or more sampling sites during three sampling trips on Lake Ontario.

For the initial sampling trip (June 21, 1972), ten sampling stations were selected to allow comparison of the three major lake basins and the postglacial mud and glaciolacustrine clays (Figure 1). Four cores were taken at each station to allow comparison of station and interstation variability. Based on the general sediment classification of Thomas et al. (1972), IFYGL station identifiers 83, 75, 92, 45, 32 and 10 were postglacial muds, stations 34 and 52 were glaciolacustrine clays, and station 62 was near a between basin sill of glaciolacustrine clay (Figure 1). The Kingston Basin was also sampled at station 96. All cores were divided into 5 cm sediment sections and transferred to plastic bags in the field. Samples were transferred to glass jars purged with N₂ upon return to the laboratory. The P measurements included total P, total inorganic P, total organic P, forms of inorganic P, and sorption characteristics.

For the second sampling trip (November 6, 1972), IFYGL station identifier 30 (located in the inshore silts according to the classification of Thomas et al. 1972) and 60 of the inshore zone were selected in addition to those sampled in June 1972, except that stations 96 and 32 were not sampled (Figure 1). Cores were obtained at stations 10, 34, 45 and 75 to provide intact cores for transport to the laboratory. Additional cores at some stations were obtained for comparison of station or

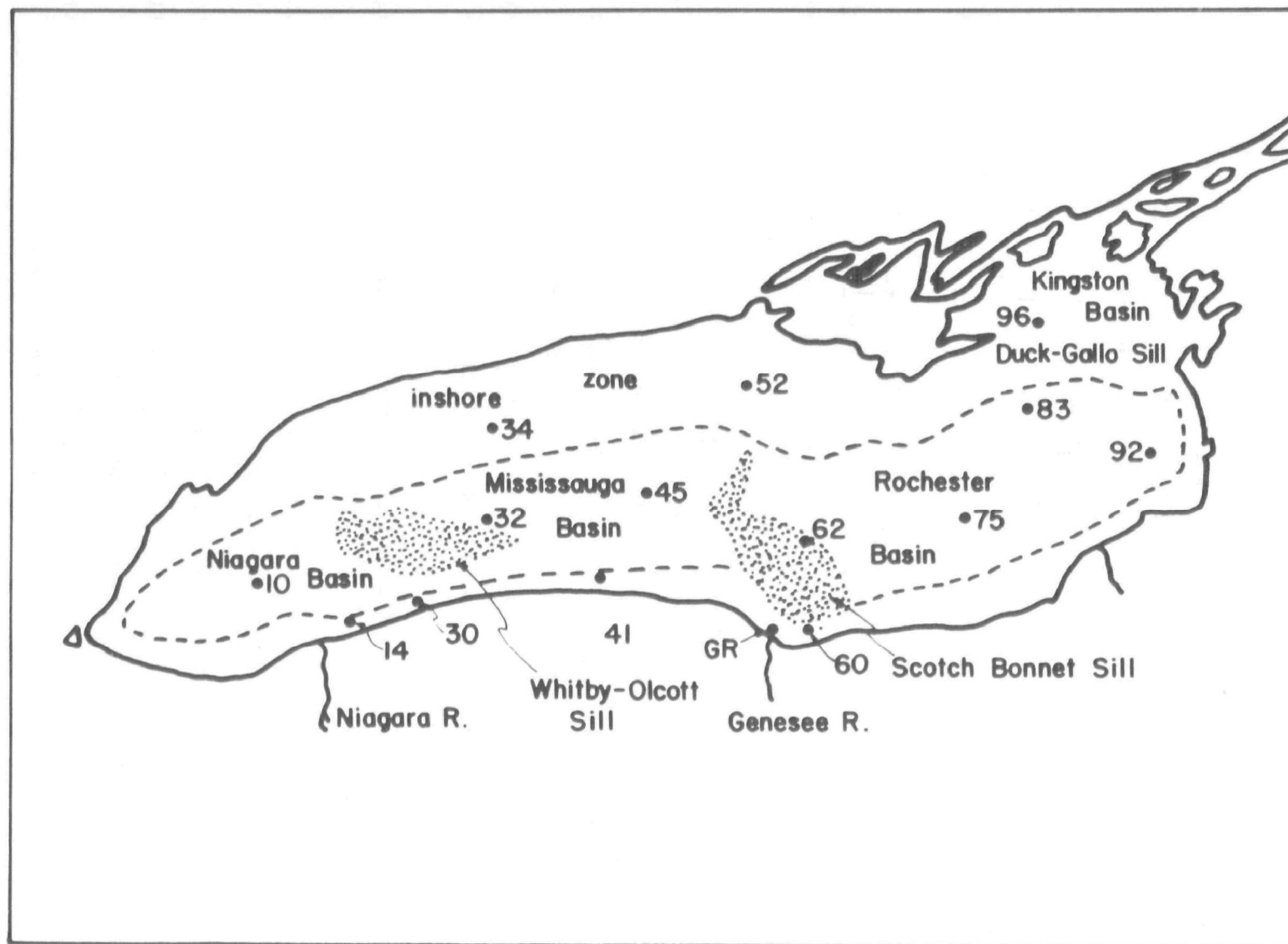


Figure 1. Sampling Sites (IFYGL Station Identifiers) for Lake Ontario Sediments.

interstation variability. Measurements made on the 5 cm sediment sections obtained included total P, total organic and inorganic P, forms of inorganic P, sediment exchangeable P and sorption and desorption characteristics.

The third sampling trip (October 9, 1973) included IFYGL station identifiers 14 and 41, located in the inshore silts according to Thomas et al. (1972), and the mouth of the Genesee River (GR) in addition to those sites sampled in June, 1972, except that stations 83, 52 and 32 were not sampled. The first 15 cm of one core at each station was divided into 3 cm sediment sections and immediately squeezed in a pressure membrane device (Reeburgh 1969) to obtain the interstitial water. The interstitial water in the 6 to 9 ml aliquot was retained for analysis. The first 6 ml of interstitial water squeezed was disregarded because of observations of lower inorganic P values present in the initial aliquots squeezed from a membrane squeezer, also reported by others (Bray et al. 1973; Weiler 1973). An effort was made to maintain the original sediment temperature and oxidation status during the squeezing process. Effects of oxidation were minimized by rapid transfer of the sediment sample from the core barrel to the squeezer, purging the squeezer with N₂ before closing, and storage of unsqueezed samples in a N₂ atmosphere. Temperature was controlled by squeezing and storing sediment inside a refrigerator. The interstitial water was subsequently analyzed for DIP and total Fe. A lake water sample from directly above the sediment-water interface was filtered immediately (0.45 μ m filter), and the DIP levels were determined upon return to the laboratory. The 5 cm core sections obtained for analyses other than IIP were immediately transferred from the small plastic bags to glass jars purged with N₂. The sediment P analyses included measurement of total P, total inorganic P, total organic P, forms of inorganic P and desorption characteristics. Intact cores from stations 10, 30 and 60 were transported to the laboratory for measurement of P release under controlled conditions.

ANALYTICAL METHODS

Subsamples were used in the wet state for all experiments. Moisture contents of the bulk samples were determined by drying a subsample at 110°C overnight. Total organic P was determined by sequential acid and alkali extractions of the sediment and analysis of inorganic P and total P in the pooled extracts (Mehta et al. 1954; Sommers et al. 1972). Total inorganic P was taken as the inorganic P in the combined extracts prior to digestion. Total P was obtained from perchloric acid digestion of the combined extracts. Perchloric acid digestion was found to yield total P values slightly higher or equal to the values from persulfate digestion (Amer. Public Health Assoc. 1971). Sediment exchangeable inorganic P was determined by the procedure described by Li et al. (1973), except that the ^{32}P was added before the sediment suspension was equilibrated.

The forms of inorganic P (NaOH-P, CDB-P and HCl-P) in the sediments were determined by inorganic P fractionation based on the procedures described by Williams et al. (1971 a). The reagent sequence was 0.1N NaOH, 1M NaCl, 17 hours (NaOH-P), citrate-dithionate-bicarbonate, 85°C 15 min (CDB-P), and 1N HCl for 4 hours (HCl-P). The NaOH extraction was conducted on duplicate samples receiving 0 or 300 ug/g of inorganic P added with the NaOH reagent. Recovery of added P in the NaOH extract was usually greater than 90% except for station 34 which gave recoveries of 0 to 8% for the different sediment layers. The NaOH-P values for this sediment were corrected by dividing the amount of P extracted in the unamended sediment by the fraction of added P recovered in the amended sediment (Williams et al. 1971 b). The added P not recovered in the NaOH extract was recovered in the subsequent CDB extract. Consequently, the CDB-P values for station 34 were decreased by the amount that NaOH-P was increased by the correction procedure. Inorganic P was measured in neutralized NaOH and HCl extracts by the method of Murphy and Riley (1962) and in CDB extracts by the method of Watanabe and Olsen (1962).

Total Fe was measured on interstitial water samples by atomic absorption using the Murphy and Riley P analysis sample due to the limited volume of interstitial water available.

EQUILIBRATION PROCEDURES

Sediments used for determination of desorption, sorption and exchangeable inorganic P characteristics were equilibrated as a 4% suspension containing 1.6 g sediment (dry weight basis) in 40 ml of distilled water (sorption, exchange and desorption) or 0.1M NaCl (desorption). The sediment suspensions were equilibrated for 40 hours in polycarbonate centrifuge tubes (50 ml; screw cap) on a wrist action shaker at 25°C. The equilibrated samples were centrifuged at 10,000 rpm (12,062 relative centrifugal force) on a Sorvall refrigerated centrifuge for 15 minutes, decanted into clean centrifuge tubes, and centrifuge again, except for the desorption equilibrations performed in a 0.1M NaCl which were filtered (0.45 μ m) after the initial centrifugation step. A N₂-filled plastic glove bag was used during manipulations of the samples to limit contact with oxygen. For example, the steps involving decanting, filtration, addition of inorganic P, addition of ³²P, addition of the distilled water, and addition of 0.1M NaCl solution were all conducted in the glove bag. The distilled water and 0.1M NaCl solutions used for sediment equilibration were stripped with N₂ for about 2 hours prior to mixing with the sediment. For successive equilibrations, the tubes were re-weighed and the sediment resuspended in the appropriate amount of distilled water or 0.1M NaCl solution for a final volume of 40 ml. The tubes were placed in glass jars purged with N₂ during equilibration on the wrist action shaker. The effects of filter size (0.45, 0.22 and 0.10 μ m Millipore filters), and 0.1M NaCl and distilled water on equilibration P values were evaluated by using the above equilibration procedure. Measurement of inorganic P desorption under oxic and anoxic conditions involved handling in air and equilibration in air-containing solutions (oxic) or equilibration at room temperature for 11 days under O₂-free conditions (anoxic).

The release of inorganic P from intact sediment cores was evaluated using the sampling core barrel as the incubation column by placing the cores in a refrigerator at the in situ sediment temperature, and incubating the cores under quiescent conditions after placing 2 liters of filtered Lake Ontario water in the column above the core. A glass liner (5.8 cm i.d.) was placed inside the plastic core barrel holding the sediment and water to prevent sorption of inorganic P by the plastic liner. The glass liner was pre-soaked in phosphate solution (2 mg/l) to prevent sorption of DIP released from sediments.

A short piece of plastic core barrel capped by a cork was placed over the column. Holes drilled in the plastic and/or cork provided ports for sample withdrawal and introduction of air or N₂ while helping to maintain the desired atmosphere in the water above the core by limiting exchange with the atmosphere. For some columns, air or N₂ was introduced beneath the surface of the overlying water column through 6 mm pyrex tubing. The N₂ was prepurified and was passed through pyrogallol 15% (w/w) in KOH (20% w/w) prior to passage into the water column to remove traces of O₂. Both the N₂ and air were also passed through distilled water to maintain saturation and reduce evaporation in the core. Other cores were incubated with the overlying column exposed to the atmosphere without introduction of air or N₂. The concentration of DIP in the overlying lake water was measured over a period of 60 to 70 days. The three intact cores obtained at station 10 on the November 6, 1972 sampling trip received intermittent N₂ treatment, air, and no treatment, respectively. Cores from stations 34, 45 and 75 of the same sampling trip were not treated with air or N₂. Cores from stations 10, 30 and 60 of the October 9, 1973 sampling trip were treated initially with air, and after 35 days, one of the two cores for each station was treated with N₂ for the remainder of the incubation.

SECTION V

RESULTS AND DISCUSSION

FORMS AND AMOUNTS OF SEDIMENT P

Total P and total inorganic P concentrations in the upper 20 cm of Lake Ontario sediments ranged from 500 to 1500 and 500 to 1230 $\mu\text{g/g}$, respectively, and were usually closely related (Table 1). Amounts of total P were similar to those reported by Kemp *et al.* (1972) and somewhat lower than found by Williams and Mayer (1972). Values for cores taken at different times from the same station agreed closely, indicating that sediment sampling and station locating techniques were adequate. In most cases, levels were higher in the deep basin sediments than in sediments from the Inshore Zone. An increase in total P content with increasing depth of the water column is a common observation in small lakes (Rohlich 1963; Delfino *et al.* 1969; Williams *et al.* 1970) and apparently reflects transport and deposition of fine-textured materials in deep water areas. Total inorganic P tended to decrease with depth over the upper 20 cm for station 30 (inshore silts), station 34 (glaciolacustrine clays), station 10 (postglacial muds), and station 60 (Inshore Zone). This trend was previously observed for a longer sediment core (1.5 m) from the Mississauga Basin (Williams and Mayer 1972).

Amounts of organic P were usually low (0 to 290 $\mu\text{g/g}$) and were lower in the glaciolacustrine clays than in the postglacial muds (Table 1). Concentrations tended to be lower over the 5 to 15 cm interval than at the 0 to 5 and 15 to 20 cm depths. Amounts of organic P in cores from the Mississauga Basin were comparable to the levels reported by Williams and Mayer (1972).

Differences among stations were more apparent in the forms of inorganic P present than in the total P or total inorganic or organic P contents of the sediment. For the upper 5 cm layer, the Inshore Zone sediments tended to contain small amounts of NaOH-P and CDB-P and a high proportion of HCl-P (Table 2). In contrast, basin sediments contained comparable proportions of NaOH-P and HCl-P and smaller amounts of CDB-P. Similar trends were found for basin sediment samples

Table 1. TOTAL P, TOTAL INORGANIC P, AND TOTAL ORGANIC P AT VARIOUS SEDIMENT DEPTHS IN LAKE ONTARIO CORES^a
(µg/g)

Station Identifier	Sampling Date	Total P				Total Inorganic P				Total Organic P			
		0-5	5-10	10-15	15-20	0-5	5-10	10-15	15-20	0-5	5-10	10-15	15-20
Inshore Zone													
52	21 JUN 72	911+111				891+108				20+3			
34	6 NOV 72	955	890	900	1010	940	890	900	885	15	0	0	125
30		888	685	610	612	790	675	600	550	98	10	10	62
60		548	500	500	567	548	500	500	522	22	0	0	45
14	9 OCT 73	737				675				62			
41		755				713				42			
GR ^b		825				712				113			
Rochester Basin													
83	21 JUN 72	1078				867				211			
92		1195				1000				195			
75		1001+22				871+30				130+53			
92	6 NOV 72	1270	966			1140	860			130	100		
62		950	980			810	945			140	35		
75		1163	1103			1050	1020			113	83		
Mississauga Basin													
32	21 JUN 72	1272				995				278			
45		1461				1176				286			
45	6 NOV 72	1356	1028			1095	883			261	195		

						<u>Niagara Basin</u>								
10	21 JUN 72	1444+65				1229+85					214+20			
10	6 NOV 72	1448	1108	1335	1182	1218	935	1132	895	230	173	202	287	
						<u>Kingston Basin</u>								
96	21 JUN 72	857+24				810+2					47+27			

^aSediment depth intervals in cm. P concentrations are in ug/g sediment on a dry-weight basis. Deviations shown are for two cores at the same station. Average deviations for five cores at station 45 were 59, 50 and 20 ug/g for total P, total inorganic P, and total organic P, respectively.

^bThe Genesee River.

Table 2. FORMS OF INORGANIC P IN LAKE ONTARIO SEDIMENTS

Station Identifier	Sampling Date	Phosphorus forms at various depths below sediment surface ^a											
		0-5 cm			5-10 cm			10-15 cm			15-20 cm		
		NaOH	CDB	HCl	NaOH	CDB	HCl	NaOH	CDB	HCl	NaOH	CDB	HCl
<u>Inshore Zone</u>													
34	21 JUN 72	2	6	91									
52		4 ₊₁	5 ₊₁	90 ₊₂									
30	6 NOV 72	28	16	53	10	5	72	8	6	82	6	7	88
60		8	6	81	4	1	95	2	4	91	2	4	95
34		3	6	85	2	6	86	2	5	97	2	8	88
14	9 OCT 73	4	4	74									
41		5	5	74									
GR ^b		14	14	46									
<u>Rochester Basin</u>													
83	21 JUN 72	30	17	48									
92		33	14	41									
75		46 ₊₅	6 ₊₁	42 ₊₁									
62	6 NOV 72	22	18	57	15	18	65						
92		37	15	36	30	15	50						
75		40	17	29	50	11	32						

<u>Mississauga Basin</u>											
45	21 JUN 72	60	15	31							
32		53	14	42							
45	6 NOV 72	46	16	29	45	8	35				
<u>Niagara Basin</u>											
10	21 JUN 72	48 ₊₅	10 ₊₁	32 ₊₁							
10	6 NOV 72	50	19	22	51	7	35	50	6	32	58 8 39
<u>Kingston Basin</u>											
96	21 JUN 72	18 ₊₁	10 ₊₀	72 ₊₂							

^aConcentrations expressed as per cent of sediment total inorganic P. Deviations shown are for two cores at the same station. The average deviations between 5 separate cores at station 45 were 3, 1, and 3% for NaOH-P, CDB-P and HCl-P, respectively.

^bGenesee River.

by Williams and Mayer (1972). Stations 30, GR, 62 and 96 were exceptions (Table 2). Station 30 and GR (Inshore Zone) contained appreciable amounts of NaOH-P and were more similar to basin sediments than other Inshore Zone sediments. Below 5 cm, the P distribution at station 30 was similar to that for other inshore stations. Both stations showed a relatively large decrease in sediment water content from the upper 5 cm core section to the 5 to 10 cm section (Table 3). The trends for NaOH-P and sediment water content values may reflect the deposition of some recent sediments of high P content over the coarse-textured materials generally found along the southern shore. These trends are apparently variable along the southern shore, as stations 14, 41 and 60, also in the southern Inshore Zone, did not show a high proportion of NaOH-P in the upper 5 cm or large decreases in sediment water content with depth below the sediment surface. Station 62, located near the Scotch Bonnet Sill, exhibited a P distribution and sediment water content intermediate between the postglacial muds and glaciolacustrine clays. The sediment water contents of the basin sediments were higher than those observed for the Inshore Zone (Table 3). Evidently, as a result of the higher elevation of the sill, this region is not subject to deposition of more recent sediments to the extent occurring in the surrounding basins. The proportion of NaOH-P was lower in the Kingston Basin (station 96) than in the other basins, suggesting less deposition of recent high P content sediment in the Kingston basin. Based on P distribution changes with depth, sediments were generally uniform over the upper 20 cm for the basin sediments (station 10) and the Inshore Zone glaciolacustrine clays (station 34).

The results obtained from inorganic P fractionation (Table 2) indicate that the proportion of potentially chemically mobile inorganic P (NaOH-P) is high in the basin postglacial muds and in some regions of the southern Inshore Zone, and is low in most southern Inshore Zone sediments and in the glaciolacustrine clays. The NaOH-P fraction is thought to include

Table 3. SEDIMENT WATER CONTENT OF LAKE ONTARIO CORES

(%)

Station Identifier	Sampling Date	Water Content at Following Depths Below the Sediment Surface ^a		
		0-5 cm	5-10 cm	10-15 cm
<u>Inshore Zone</u>				
52	21 JUN 72	37+8		
34	6 NOV 72	57+1	56+2	58
30		52+2	30+1	28
60		26	21	19
GR ^b	9 OCT 73	35	23	
30		42	26	
41		26	24	
14		27	31	
<u>Rochester Basin</u>				
92	6 NOV 72	60+3	54+0	
62		51+6	42+1	
83		68	63	
75		76+2	70+1	67
92	9 OCT 72	69	65	
<u>Mississauga Basin</u>				
32	21 JUN 72	73+1	72	73
45	6 NOV 72	75+1	71+1	
45	9 OCT 73	80	78	
<u>Rochester Basin</u>				
10	6 NOV 72	75+2	70+1	65
<u>Kingston Basin</u>				
96	9 OCT 73	75	63	

^a% water = weight of water divided by weight of water + sediment.
 Deviations shown are for two or more cores at the same station.

^bGenesee River.

inorganic P in equilibrium with inorganic P in solution based on investigations of the nature of the inorganic P in this fraction (Williams et al. 1971 a; 1971 b; Syers et al. 1973) and relationships between the amounts of NaOH-P and isotopically exchangeable inorganic P (Li et al. 1972). Levels of sediment exchangeable inorganic P in Lake Ontario sediments (Table 4) were in agreement with the chemical mobility trends for inorganic P observed based on measurement of inorganic P forms (Table 2). The basin sediments contained a high proportion of exchangeable P relative to the Inshore Zone sediments. An exception was station 30 surface sediment which contained a higher proportion of NaOH-P than other Inshore Zone sediments (Table 2), but did not contain appreciable exchangeable inorganic P (Table 4). The level of NaOH-P for station 62 (22%) was intermediate between major basin sediments (30 to 60%) and the glaciolacustrine clays (2 to 4%), while the proportion of exchangeable P at this station was comparable to that for the glaciolacustrine clays. According to a map prepared by Thomas et al. (1972), station 62 is located in the Scotch Bonnet Sill which is composed of glaciolacustrine clay, while the basin sediments are predominantly postglacial muds. The results of inorganic P fractionation and exchange investigations indicate that station 62 is more closely related to Inshore Zone sediments than to basin sediments.

While similar trends were observed for NaOH-P and exchangeable P the proportion of exchangeable P was lower. For example, the major basin sediments contained 30 to 60% NaOH-P, but only 13 to 18% exchangeable inorganic P. Similar relationships were observed for sediments from small lakes (Li 1973; Li et al. 1972). These results indicate that NaOH-P may overestimate the potentially mobile P fraction, or that this fraction is underestimated by exchangeable P measurements in some sediments (Li 1973). Recent results (Sagher 1974) have shown that algae are able to remove a high proportion of the NaOH-P fraction from Wisconsin lake sediments, although removal was incomplete in some cases. This evidence supports the concept that NaOH-P corresponds to the potentially mobile sediment inorganic P fraction.

Table 4. SEDIMENT EXCHANGEABLE INORGANIC P IN THE 0 to 5 CM SEDIMENT
LAYER OF LAKE ONTARIO CORES OBTAINED NOVEMBER 6, 1972

Station Identifier	^{31}P Soln ug/g	Sed Exch ug/g	$^{31}\text{P}_\text{I}$ ^a %	Total Exch ug/g	P_I %
<u>Inshore Zone</u>					
34	2.4	13	1	16	2
30	0.5	9	1	10	1
60	1.0	20	4	21	4
<u>Rochester Basin</u>					
62	4.1	29	4	33	4
92	1.5	167	15	169	15
75	1.2	193	18	195	18
<u>Mississauga Basin</u>					
45	0.9	140	13	140	13
32 ^b	2.5	153	15	156	15
<u>Niagara Basin</u>					
10	1.2	194	16	195	16

^aSed exch P_I is expressed as percent of inorganic P in sediment phase;
total exch P_I is expressed as a percent of inorganic P in the sediment
and water phases.

^bSampled June 21, 1972.

Lake Ontario sediments contained varying amounts of inorganic P in the CDB-P fraction. The chemical forms of inorganic P in this fraction are somewhat uncertain. In soil inorganic P fractionation, this fraction (also termed "reductant soluble P") is attributed to P occluded in Fe oxides. However, in lake sediments, the NaOH-P and CDB-P may be of similar nature and associated with hydrous Fe and Al oxides (Williams et al. 1971 c; Williams and Mayer 1972; Syers et al. 1973). In terms of chemical mobility, it is likely that the NaOH-P represents a more mobile inorganic P fraction than CDB-P in the sequential extraction scheme.

Large amounts of inorganic P were present as HCl-P. This fraction accounted for about 90% of the inorganic P in the glaciolacustrine clays (stations 34 and 52). The HCl-P fraction contains mainly apatite (Williams and Mayer 1972; Syers et al. 1973). The concept that this fraction is immobile is supported by investigations of uptake of sediment inorganic P by algae (Sagher 1974). Algae were unable to utilize sediment inorganic P contained in this fraction.

The combined amounts of sediment inorganic P contained in the three inorganic P fractions (NaOH-P, CDB-P, HCl-P) were frequently less than the total inorganic P content of the sediment (Tables 1 and 2). This occurred because the fractionation scheme used was not intended to provide complete recovery of total inorganic P. More comprehensive fractionation schemes (Williams et al. 1971 a; 1971 b) involve determination of residual inorganic P following HCl-P extraction, but residual inorganic P was not of interest in this investigation of inorganic P mobility.

INTERSTITIAL INORGANIC P

Levels of interstitial inorganic P (mobile P) ranged from 14 to 1280 ug/l. Concentrations were usually higher in the basin than in the inshore sediments (Table 5). This trend was in agreement with the high proportion of potentially mobile inorganic P in the basin sediments (Table 2). The glaciolacustrine clay sediments (station 34) exhibited

Table 5. INTERSTITIAL INORGANIC P IN LAKE ONTARIO SEDIMENTS
($\mu\text{g/l}$)

Station Identifier	Interstitial Inorganic P at Following Depths below the sediment surface (cm) ^a					
	Lakewater	0-3	3-6	6-9	9-12	12-15
<u>Inshore Zone</u>						
34	15	19	14	14	14	28
14	3	249	592	252	67	22*
30	15	498	569	392	37*	116*
41	18	92	115	50*	33*	111*
GR ^b	4	158	47*	311	663	182
60	8	83	58	69	133*	39*
<u>Rochester Basin</u>						
62	20	1050	1010	954	382	444
75	19	1070	1040	899	997	1190
92	16	145	55	87	107	46
<u>Mississauga Basin</u>						
45	25	1260	537	693	422	749
<u>Niagara Basin</u>						
10	20	140	446	684	90	99
<u>Kingston Basin</u>						
96	19	1280	1040	1160	637	537

^aFor values indicated by *, the time required to separate the interstitial waters was greater than one-half hour.

^bGenesee River.

the lowest IIP values, and these sediments also contained a high proportion of HCl-P (immobile P). Southern Inshore Zone sediments contained higher IIP levels than station 34, but the values were generally lower than for basin sediments.

For basin sediments, IIP values for the surface 3 cm were generally in the range of 1000 $\mu\text{g/l}$. However, stations 92 and 10 were exceptions, even though the proportion of potentially mobile inorganic P for these stations were comparable to other basin stations. The lower IIP values at stations 92 and 10 may reflect differences in sediment characteristics, most likely Eh, or changes in IIP during analysis. However, the trend of lower values at these stations for all depths suggests that IIP concentrations were lower at stations 92 and 10 than at other basin stations.

The IIP levels in the 0 to 3 cm section were usually higher than in the 3 to 6 cm section. However, below the 3 to 6 cm a clear trend in IIP levels was not apparent. The decrease in IIP between the 6 to 9 and 9 to 12 cm sections at stations 14, 30, 62 and 10 was possibly a result of storing these sections during squeezing IIP from the first 3 sections (Table 5). Alternatively, the unusually long squeezing time required to obtain sufficient interstitial water for analysis of these sections may have contributed to the low values.

Intentional excessive handling, storage and exposure of sediments to air prior to obtaining interstitial water was shown to have a major effect on IIP values. Sediments from stations 92 and 10 (a mixture of the upper 9 cm) were analyzed after storage in plastic bags exposed to air for various periods of time (Table 6). IIP values decreased with increased storage time. Handling of these sediments prior to the initial analysis caused the IIP value to be lower than values obtained for the individual sections taken directly from the cores (Table 5). The likely explanation for the effects of storage and excessive handling of sediments on IIP levels is the oxidation of dissolved and solid phase Fe and subsequent sorption of inorganic P.

Table 6. EFFECT OF SEDIMENT STORAGE ON INTERSTITIAL INORGANIC
P VALUES

Storage Time, min	Interstitial Inorganic P, μg/l
	<u>Station 92</u>
0	85
90	55
600	33
	<u>Station 10</u>
0-10	20
15-30	12
34-44	21
67-80	14
100-110	12

IIP values in successive aliquots from the Reeburgh squeezer indicated that the peak IIP value was obtained in the 9 to 12 ml aliquot for most stations (Table 7). A gradual initial increase followed by a decrease in IIP values in successive aliquots from the Reeburgh squeezer was also reported by Bray *et al.* (1973) and Weiler (1973). Since the 6 to 9 ml aliquot was used in this investigation, the IIP values were probably underestimates of in situ values.

Measurements of interstitial Fe were made to evaluate whether sediments were sufficiently reduced for reduction of Fe^{3+} to Fe^{2+} to occur and thereby affect IIP concentrations. The values observed were higher than for the overlying lake water, but were highly variable between sediments (Table 8). Interstitial Fe levels were similar to those reported by Weiler (1973) for comparable locations. Apparently, some Fe^{2+} was present in most of the sediments, but the concentrations varied due to differences in Eh, Fe content, and/or distribution of Fe between the solid and solution phases.

DESORPTION AND SORPTION OF SEDIMENT INORGANIC P

The desorption and sorption of inorganic P by Lake Ontario sediments were investigated to provide information on the ability of sediments to control or "buffer" the dissolved inorganic P (DIP) concentration in the surrounding water upon addition or removal of inorganic P in the water phase of sediment-water systems. It was necessary to conduct desorption-sorption in sediment-water suspensions containing a lower sediment:water ratio than that found for undisturbed lake sediments. A 1:25 sediment:water ratio (dry weight sediment basis) equilibration system was used, while for Lake Ontario sediments, the sediment:water ratio ranged from about 3:10 to 3:1. Furthermore, in spite of efforts to transport and store sediment samples without exposure to air and to conduct desorption-sorption experiments under oxygen-free conditions, it was observed that DIP concentrations tended to decrease with storage of sediments, apparently due to partial oxidation of Fe^{2+} and sorption of dissolved inorganic P. Consequently, desorption-sorption

Table 7. INTERSTITIAL INORGANIC P IN SUCCESSIVE ALIQUOTS
SQUEEZED FROM LAKE ONTARIO SEDIMENTS
($\mu\text{g/l}$)

Aliquots ml	Interstitial Inorganic P at Following Depths Below the Sediment Surface (cm)				
	0-3	3-6	6-9	9-12	12-15
<u>Station 75</u>					
0-3	810	130	112	201	368
3-6	1180	706	619	781	978
6-9	1070	1040	899	997	1190
9-12		1080	1022	1010	1080
12-15	1120	981	1048	885	847
<u>Station 45</u>					
6-9	537	1260			
9-12	557	1300			
12-15	542	1180			
<u>Station 60</u>					
0-3	33				
3-6	94				
6-9	83				

Table 8. TOTAL FILTERABLE Fe IN THE INTERSTITIAL WATER
OF SEDIMENTS FROM LAKE ONTARIO
(mg/l)

Station Identifier	Interstitial Fe ^a at the Following Depths Below the Sediment Surface (cm)				
	0-3	3-6	6-9	9-12	12-15
<u>Inshore Zone</u>					
34	0.5	0.4	0.4	0.4	0.3
14	3	4	16	12	9
30	3	7	8	3	7
41	1	1	1	1	3
GR ^b	5	6	25	46	37
60	8	1	1	7	1
<u>Rochester Basin</u>					
62	0.3	0.2	0.3	0.4	4
75	4	4	5	4	7
92	6	13	21	27	31
<u>Mississauga Basin</u>					
45	3	6	9	9	14
<u>Niagara Basin</u>					
10	1	1	2	2	2
<u>Kingston Basin</u>					
96	1	1	12	13	15

^aConcentrations in the lake bottom water were less than 0.3 mg/l.

^bGenesee River.

experiments provided information on comparative trends for sediments from different sites, but the equilibrium inorganic P concentrations are not directly comparable to IIP levels.

Initial desorptions were conducted in distilled water (Tables 9 and 10). Amounts of inorganic P desorbed appeared to decrease with increasing depth below the sediment surface with the largest change occurring between the 0 to 5 and 5 - 10 cm section (Table 9). However, the sediment samples from the 5 to 10 cm section were stored 3 weeks longer than the 0 to 5 cm section before equilibrating, and storage effects may have contributed to the observed changes. Sediment from the 0 to 5 cm sections of stations 45, 75 and 10 equilibrated in separate experiments several weeks apart demonstrated a large decrease in desorption values for the second equilibration of the same sediment samples (Tables 9 and 10). Values for DIP increased during successive desorption steps in some cases (Tables 9 and 10), in contrast to the gradual decrease expected based on sorption-desorption isotherms. This suggested that some fine particles were not removed from suspension by the centrifugation procedure and that these particles reacted in the measurement of inorganic P. To evaluate this possibility, an experiment was conducted to compare inorganic P concentrations in distilled water and 0.1M NaCl systems after centrifuging and filtering the supernatant solution. The 0.1M NaCl was added to flocculate the sediment. Comparisons were made for samples centrifuged twice (double centrifuge) or filtered through 0.45, 0.22, or 0.10 μ m Millipore filters following the double centrifugation steps (Table 11).

In sediment from station 75 equilibrated in distilled water the level of inorganic P in solution increased with each desorption step. The values were decreased somewhat by filtration, but even for the 0.10 μ m filter, the concentration after the third equilibration was four times that of the first equilibration. In the 0.1M NaCl system, small increases in values occurred with successive equilibrations and small decreases were observed with decreasing pore size of the filter. These results suggest that the sediments tended to disperse in the distilled

Table 9. DESORPTION OF INORGANIC P FROM LAKE ONTARIO SEDIMENT
AFTER SUCCESSIVE EQUILIBRATIONS IN DISTILLED WATER
($\mu\text{g/g}$)^a

Station Identifier	Sediment Section, cm	Inorganic P Desorbed in Successive Equilibration steps					
		1st	2nd	3rd	4th	5th	6th
<u>Inshore Zone</u>							
34	0-5	2.5					
	5-10	2.0	2.5	3.4	2.4	2.0	2.0
	10-15	1.0	1.3	1.5	1.2	1.2	1.0
52	0-5	2.7	2.4				
	5-10	1.8	1.9	1.8	1.8	1.6	1.6
30	0-5	6.1	14.1				
	5-10	1.0	1.2				
60	0-5	1.4	2.6				
	5-10	0.8	1.0				
<u>Rochester Basin</u>							
75	0-5	9.8					
	5-10	6.4	16.6				
	10-15	5.0	10.8	10.2	2.3	2.4	2.3
83	0-5	1.6	6.0				
	5-10	0.6	1.0	2.6	1.8	1.9	2.1
62	0-5	4.3	5.1				
	5-10	4.5	4.6				
92	0-5	3.4	8.0				
	5-10	1.5	2.6				
<u>Mississauga Basin</u>							
45	0-5	23.0					
	5-10	2.0	3.6	5.8	6.2	6.5	6.1
<u>Niagara Basin</u>							
10	0-5	7.6					
	5-10	1.8	6.0				

^a $\mu\text{g/l} = 40 \times \mu\text{g/g}$.

Table 10. DESORPTION OF INORGANIC P FROM THE 0 TO 5 CM SEDIMENT SECTION OF LAKE ONTARIO CORES AFTER SUCCESSIVE EQUILIBRATIONS IN DISTILLED WATER ($\mu\text{g/g}$)^a

Station Identifier	Inorganic P Desorbed in Successive Equilibration Steps					
	1st	2nd	3rd	4th	5th	6th
<u>Inshore Zone</u>						
34	2.6	3.9	4.8	3.8	4.4	
34 ^b	1.3	1.2	1.4	3.1	2.6	1.8
30	0.8	2.2	4.7	4.6		
60	1.2	2.2	2.1	2.0	1.5	
<u>Rochester Basin</u>						
75	2.0	4.9	8.8	10.0	11.6	9.1
75 ^b	1.5	2.5	2.7	3.8	3.8	4.4
92	1.3	3.2	3.8	5.2	4.2	
62	4.5	5.1	4.4	4.4		
<u>Mississauga Basin</u>						
45	1.8	4.5	7.1		9.6	
<u>Niagara Basin</u>						
10	1.6	4.9	7.3	9.6		

^a $\mu\text{g/l} = 40 \times \mu\text{g/g}$.

^b Oxidic conditions (contact with oxygen was not limited during procedure).

Table 11. DETERMINATION OF THE EFFECT OF 0.1 M NaCl SOLUTION ON
DESORPTION OF INORGANIC P IN SEDIMENT SUSPENSION OF SEDIMENT FROM
THE 5 TO 10 CM CORE SECTION OF STATION 75
($\mu\text{g/l}$)^a

Filter Pore Size ^b μm	Inorganic P Desorbed In Following Successive Equilibrations ^b		
	First	Second	Third
<u>Distilled Water</u>			
Double Centrifuge	47 \pm 3	162 \pm 3	222 \pm 20
0.45	55 \pm 3	161 \pm 5	216 \pm 5
0.22	45 \pm 1	98 \pm 2	154 \pm 8
0.10	40 \pm 0	82 \pm 5	152 \pm 3
<u>.1 M NaCl Solution</u>			
Double Centrifuge	43 \pm 1	50 \pm 1	53 \pm 1
0.45	34 \pm 2	42 \pm 7	46 \pm 10
0.22	33 \pm 3	40 \pm 2	40 \pm 3
0.10	28 \pm 0	27 \pm 1	28 \pm 2

^a $\mu\text{g/g} = \mu\text{g/l} \div 40$; error values are average deviation for triplicate samples.

^bFiltered samples centrifuged twice prior to filtration.

water system and that an appreciable amount of the dispersed sediment was less than 0.10 μm diameter material. The 0.1M NaCl system was effective in flocculating the sediment, although some particulate material apparently remained after double centrifugation. Other data obtained after equilibration in distilled water and filtration through various pore size filters following double centrifugation indicated that dispersion also occurred for other sediments (Table 12).

Values for the first equilibration suggest that the 0.1M NaCl did not cause appreciable desorption or sorption of inorganic P (Table 11). Concentrations in the double centrifuged samples were similar for NaCl and distilled water systems. The tendency for dispersion in the distilled water system apparently increased as dissolved ions were washed out in successive equilibrations, and dispersion was unimportant in the first equilibration. Based on these results, it was concluded that relationships between DIP and sediment inorganic P during successive equilibrations could be evaluated more accurately in the 0.1M NaCl than in distilled water.

The amounts of inorganic P in solution after the first equilibration ranged from 0.6 to 35.8 $\mu\text{g/g}$ for the various Lake Ontario sediments investigated (Table 13). This corresponds to a concentration range of 24 to 1432 $\mu\text{g/l}$. Except for stations GR, 41 and 92, these values were somewhat less than the IIP values observed for these sediments (Table 5).

Desorption of inorganic P was usually greater for the sediment from 0 to 5 cm section (Table 13). Amounts of inorganic P desorbed were higher for basin sediments than inshore sediments. Inorganic P levels in the second equilibration of sediment from the 0 to 5 cm section were usually lower than the levels in the first equilibration. This was most evident for station 30 and the Genesee River station of the Inshore Zone and all of the basin stations. Small decreases usually occurred between the second and third equilibrations. Desorption usually increased slightly between the first and second

Table 12. EFFECT OF FILTER PORE SIZE ON INORGANIC P DESORPTION VALUES FOR
SEDIMENT FROM THE 0 TO 5 CM SECTION OF LAKE ONTARIO CORES SUSPENDED IN
DISTILLED WATER

($\mu\text{g/l}$)^a

Filter Pore Size ^b	Inorganic P Desorbed in Successive Equilibration Steps	
	First	Second
	<u>Station 30</u>	
Double Centrifuge	17	50 \pm 2
0.45	18	53 \pm 3
0.22	17	44 \pm 4
0.10	19	42 \pm 4
	<u>Station 34</u>	
Double Centrifuge	117 \pm 2	
0.45	116 \pm 4	
0.22	108 \pm 0	
0.10	90 \pm 1	
	<u>Station 75</u>	
Double Centrifuge	33 \pm 1	110 \pm 4
0.45	28 \pm 1	109 \pm 6
0.22	31 \pm 2	86 \pm 5
0.10	30 \pm 1	71 \pm 6

^a $\mu\text{g/g} = \mu\text{g/l} \div 40$; deviations are average deviations for triplicate samples.

^bFiltered samples centrifuged twice prior to filtration.

Table 13. DESORPTION OF INORGANIC P FROM LAKE ONTARIO SEDIMENT AFTER
SUCCESSIVE EQUILIBRATIONS IN A 0.1 M NaCl SOLUTION^a

($\mu\text{g/g}$)

<u>Inorganic P Desorbed In Successive Equilibration Steps</u>						
Station	0-5 cm layer			5-10 cm layer		
Identifier	1st	2nd	3rd	1st	2nd	3rd
<u>Inshore Zone</u>						
60	1.5	1.8	0.9	1.2	1.4	1.1
30	4.0	1.8	1.2	2.2	2.8	2.7
GR ^b	7.7	2.8	5.0	1.4	3.1	3.5
14	2.3	1.9	2.4	1.8	3.1	4.1
41	4.0	4.5	3.6	1.4	1.8	1.4
34	0.6	0.8	0.8	0.2	0.2	0.2
<u>Rochester Basin</u>						
92	35.8	15.8	13.6	6.1	7.3	5.8
<u>Mississauga Basin</u>						
45	20.1	10.4	11.0	13.3	11.3	1.3
<u>Kingston Basin</u>						
96	12.3	6.8	5.1	2.0	3.2	3.4

^a $\mu\text{g/l} = 40 \times \mu\text{g/g}$.

^bGenesee River.

equilibrations for the sediment from the 5 to 10 cm sections. Similar amounts of P were desorbed during the second and third equilibrations of the 5 to 10 cm section, except for station 45.

Although the concentrations of inorganic P in solution after each equilibration were appreciable, the amounts of P desorbed were small compared to the amounts of potentially mobile P in the sediments. The combined amounts of P desorbed during the three successive equilibration steps correspond to about 3 to 17% of the NaOH-P. This reflects the low ability of water to act as a "sink" for sediment P and that multiple desorptions would be required to completely desorb the potentially mobile P fraction.

Most desorption experiments were conducted under conditions chosen to minimize changes in sediment Eh. These sediments are designated as "unchanged." For comparison, desorption was also evaluated under oxic (exposed to air) and anoxic (equilibration at room temperature for 11 days) conditions for several sediments equilibrated in 0.1M NaCl (Table 14). For Inshore Zone sediments, the amounts of P desorbed under oxic conditions were similar for the different sediments and were somewhat lower than amounts desorbed from "unchanged" sediments (Table 13). Desorption increased slightly under anoxic conditions. For the basin sediments, desorption was considerably less for oxic than for "unchanged" sediments. Sediments equilibrated in distilled water also gave higher P desorption values for the "unchanged" conditions as compared to oxic conditions (Table 10). Apparently, the conditions for "unchanged" sediments were intermediate between oxic and anoxic conditions. The anoxic values likely reflect the effect of reduction of Fe^{3+} to Fe^{2+} and resulting desorption of inorganic P. Whether these sediments became sufficiently reduced to promote complete reduction of Fe^{2+} was not determined. Possibly, with addition of a carbon energy source for sediment microorganisms, a further decrease in sediment Eh and release of inorganic P would have occurred. This may explain the low desorption value for station 75 sediment under anoxic conditions.

Table 14. DESORPTION OF INORGANIC P FROM SEDIMENT IN THE FIRST 5 CM
SECTION OF LAKE ONTARIO CORES AFTER SUCCESSIVE EQUILIBRATIONS IN A
.1 M NaCl SOLUTION UNDER OXIC OR ANOXIC CONDITIONS
($\mu\text{g/g}$)^a

Station	<u>Oxic Equilibrations</u>		Anoxic Equilibration
Identifier	First	Second	
<u>Inshore Zone</u>			
60	0.3	0.5	0.9
GR ^b	1.2	1.8	1.4
14	1.2	0.8	1.3
41	1.7	2.2	3.6
<u>Rochester Basin</u>			
92	2.4	3.6	56.2
75	0.7	1.7	3.5
<u>Mississauga Basin</u>			
45	0.9	0.6	32.1

^a $\mu\text{g/l} = 40 \times \mu\text{g/g}$.

^bGenesee River.

Sorption of added inorganic P was investigated to evaluate the ability of sediments to "buffer" the interstitial water inorganic P concentration upon addition of inorganic P. Sorption of added inorganic P was evaluated by adding inorganic P to sediments suspended in distilled water (1:25 sediment:water ratio). In most cases, the Inshore Zone sediments sorbed less than the basin sediments (Tables 15 and 16; Figure 2) Stations 30 and 62 were exceptions. Station 62 was similar to Inshore Zone sediments, while station 30 (surface 5 cm) resembled basin sediments. These trends correspond to chemical mobility characteristics. Little change in sorption ability was observed with depth below the sediment surface as discussed previously for these sediments (Table 15). At levels of added inorganic P comparable to the interstitial water and bottom lake water concentrations (2.5 to 25 ug/g), the basin sediments sorbed most of the inorganic P. However, the amounts of P remaining in solution at equilibrium sometimes exceeded the values of DIP found in the water column of Lake Ontario (Shiomi and Chawla 1970).

For inshore sediments (34, 60), equilibrium DIP values increased sharply upon sorption of low amounts of inorganic P and exceeded observed IIP values (Table 5) for these sediments (Figure 2). For basin sediments, there was little change in equilibrium DIP values upon sorption of up to 100 ug/g of added inorganic P. These results indicate that addition of inorganic P (e.g., through mineralization of organic P) to inshore sediments could increase IIP values considerably, but would have little effect on IIP levels in basin sediments.

Sediments which sorbed the most inorganic P during the sorption step (basin sediment) usually released the least P during a subsequent desorption step (Table 17). Consequently, the net sorption of added inorganic P, expressed as a percentage of the total added P, was usually higher for basin sediments, than the inshore zone sediments. Station 62 was an exception in that the net sorption was comparable to inshore zone rather than other basin sediments. This is in

Table 15. SORPTION OF ADDED INORGANIC P BY LAKE ONTARIO SEDIMENTS
OBTAINED JUNE 21, 1972

Station	Core	Added P Sorbed (%) For Added P				
Identifier	Section, cm	Level (μg of P per g) ^a of	2.5	25	250	2500
<u>Inshore Zone</u>						
34	0-5	80	80	48	20	
	5-10	83	72	41	25	
52	0-5	73	60	24	17	
	5-10	93	78	50	37	
	10-15	95	85	57	31	
<u>Rochester Basin</u>						
92	0-5	100	98	82	52	
75 ^b	0-5	100	88	82	52	
75	5-10	100	93	79	48	
<u>Mississauga Basin</u>						
32	0-5	100	100	87	57	
	5-10	100	100	48	46	
	10-15	100	95	89	52	

^a $\mu\text{g}/\text{liter} = \mu\text{g}/\text{g} \times 40.$

^bSediment in 3% sediment suspension

Table 16. SORPTION OF ADDED INORGANIC P BY LAKE ONTARIO SEDIMENTS
FROM THE 0 TO 5 CM CORE SECTIONS OBTAINED NOVEMBER 6, 1972

Station	Added P Sorption (%) For Added P Level ($\mu\text{g/g}$) ^a Of				
Identifier	6.25	12.5	25	50	100
<u>Inshore Zone</u>					
34	71	70	65	59	
30	100		98	99	99
60	91		89	75	62
<u>Rochester Basin</u>					
92	100		98	98	98
62	66		66	53	46
75	93	98	98	98	
<u>Niagara Basin</u>					
45	98		99	99	99

^a $\mu\text{g/l} = 40 \times \mu\text{g/g}$.

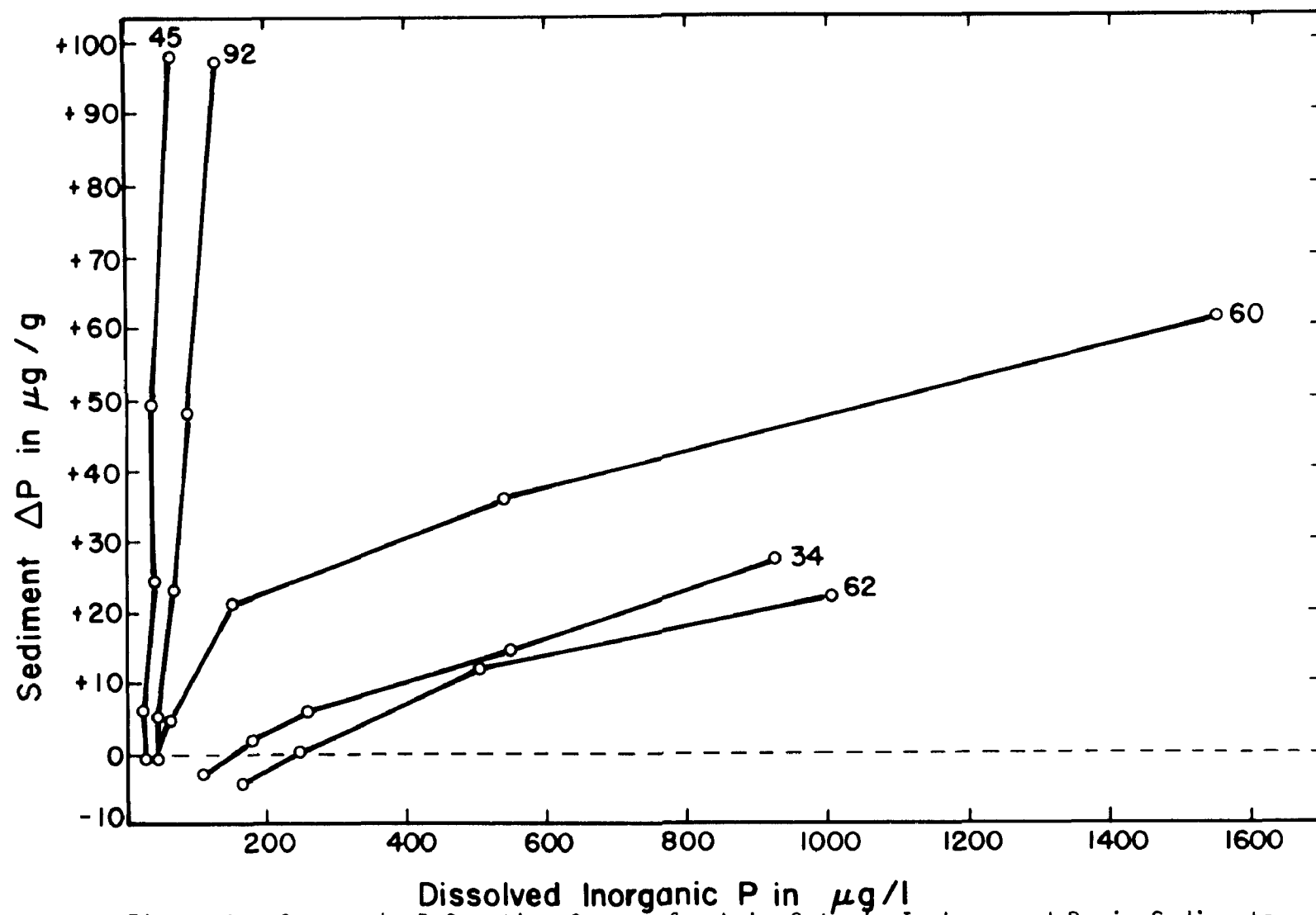


Figure 2. Inorganic P Sorption Curves for Lake Ontario Inshore and Basin Sediments.

Table 17. DESORPTION OF ADDED INORGANIC P BY SEDIMENTS IN THE
0 TO 5 CM SECTION OF LAKE ONTARIO CORES OBTAINED NOVEMBER 6, 1972

Station Identifier	Add P Desorbed as % Added P Sorbed For The Added Levels of ($\mu\text{g/g}$) ^a				Net Added P Sorbed as % Total Added P			
	6.25	25	50	100	6.25	25	50	100
<u>Inshore Zone</u>								
60			32				51	
<u>Rochester Basin</u>								
62			8				49	
92			4				94	
<u>Mississauga Basin</u>								
45	6	2	1	2	92	98	98	97

^a $\mu\text{g/l} = \mu\text{g/g} \times 40$.

agreement with the chemical mobility characteristics discussed previously. Because these experiments were conducted in distilled water, values were corrected for sediment dispersion based on control samples.

P RELEASE FROM INTACT CORES

Dissolved inorganic P (DIP) was released to the overlying lake water from intact sediment cores under controlled laboratory conditions (Figures 3 and 4). The initial levels of DIP in the lake water were low (0 to 2 $\mu\text{g/l}$), but began to increase after several days of incubation. The effects of lowering the levels of dissolved oxygen (to about 3 mg/l) in the overlying lake water by stripping with N_2 were inconsistent. P release from the station 10 core aerated with air was greater than for the duplicate core treated with N_2 after 35 days (Figure 4). Release from the air-treated core from station 60 was lower prior to the introduction of N_2 into the duplicate core at 35 days. However, P release appeared to be related to N_2 treatment for stations 10 (Figure 3) and 30 (Figure 4). The rate and extent of P release might have increased if the overlying water had been anaerobic. Apparently the Eh of the sediment decreased sufficiently with time to allow increased rates of P release, although the water column for some cores was saturated with air. These conditions exist in the bottom waters of Lake Ontario, where mean dissolved oxygen levels of about 12 mg/l have been measured during the summer (Dobson 1967).

The highest levels of P obtained in the overlying lake water ranged from 5 to 250 $\mu\text{g/l}$ (Figures 3 and 4). However, only cores from stations 34 and 10 (Figure 3) had maximum values below 10 $\mu\text{g/l}$, and most cores gave maximum values between 30 and 90 $\mu\text{g/l}$. The levels of P released reached 10 $\mu\text{g/l}$ or higher between 12 and 25 days of incubation for most cores, and surpassed the mean concentration of about 11 $\mu\text{g/l}$ for "soluble phosphate" in Lake Ontario bottom waters (Shiomi and Chawla 1970).

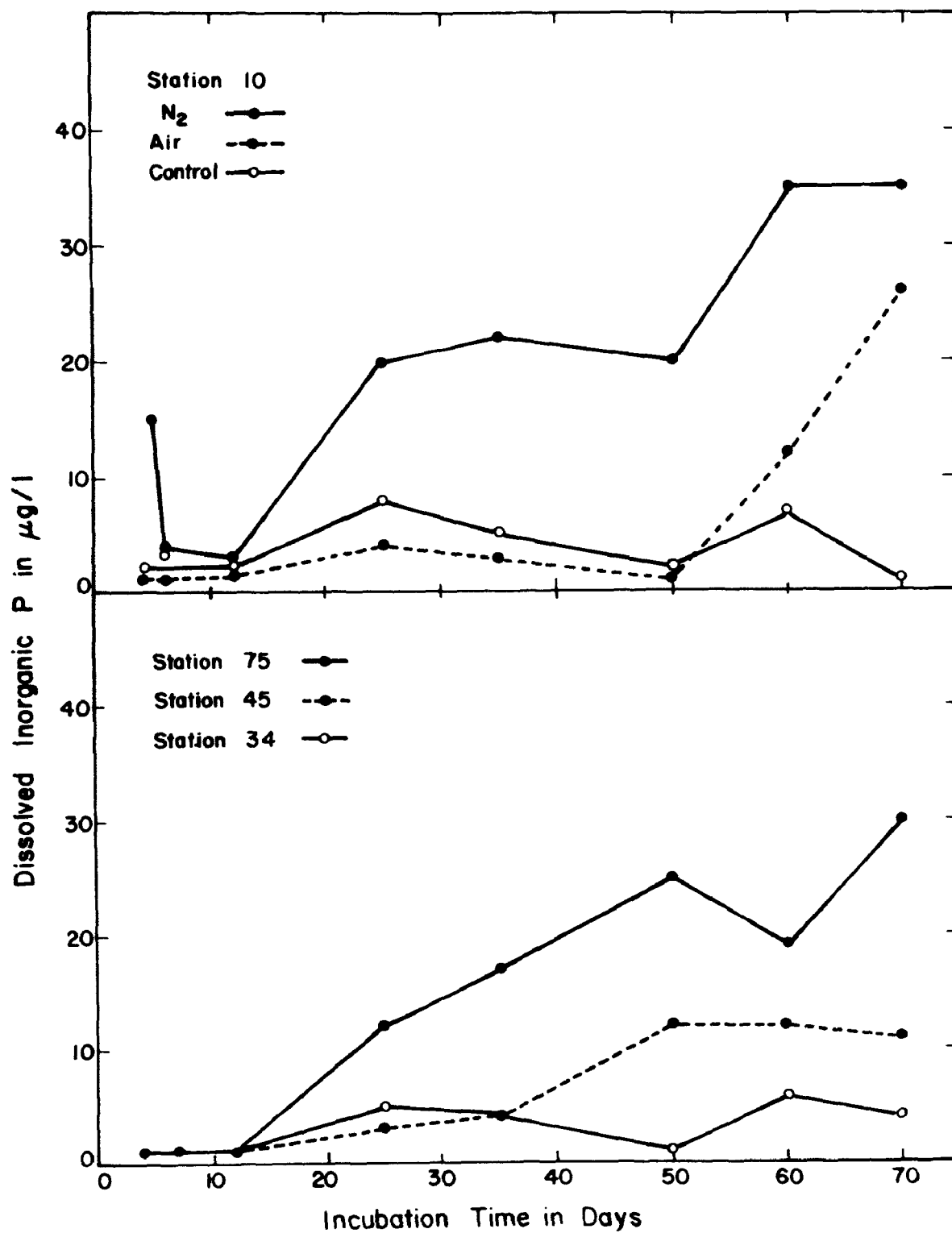


Figure 3. Levels of Dissolved Inorganic P Released from Intact Cores Obtained November 6, 1972

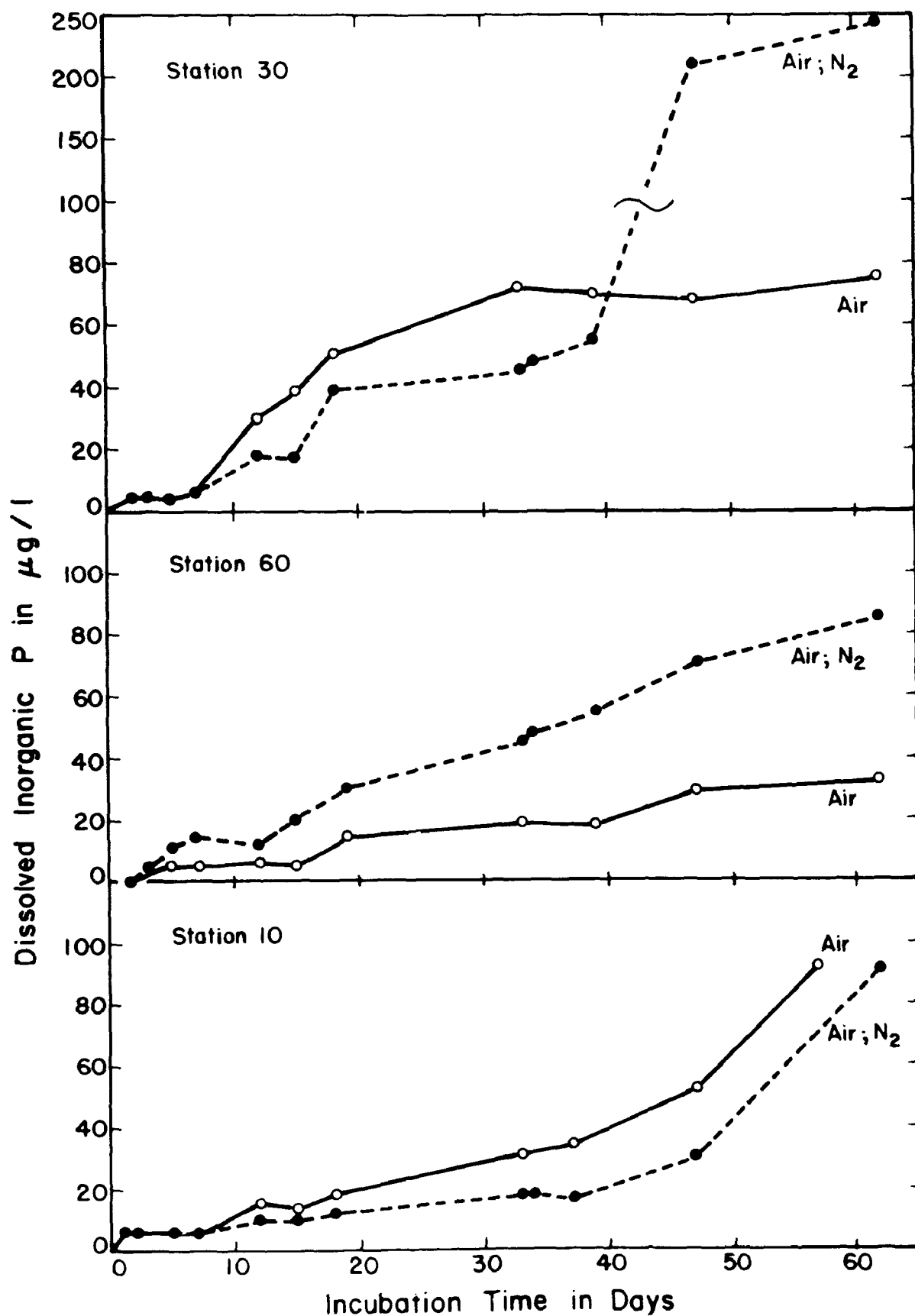


Figure 4. Levels of Dissolved Inorganic P Released from Intact Cores Obtained October 9, 1973; for Cores Designated Air, N₂ the N₂ was Introduced after 25 Days.

Rates of P release were calculated for cores treated with air, since the bottom waters of Lake Ontario contain high concentrations of dissolved oxygen (Dobsin 1967). Rates were calculated based on the increase in DIP in the overlying water between days 12 and 33 of the incubation period; a constant release rate was assumed. This interval represented a period following the initial lag and prior to the marked changes in rates occurring with continued incubation for several cores. The calculated release rates ranged from about $0.03 \text{ mg m}^{-2} \text{ day}^{-1}$ for stations 34 and 45 to $0.8 \text{ mg m}^{-2} \text{ day}^{-1}$ for station 30. The average rate for the 7 cores investigated was about $0.2 \text{ mg m}^{-2} \text{ day}^{-1}$.

It was observed that the calculated release rates were not related to IIP values measured for the upper 3 cm of these cores after incubation. A direct relationship might be expected if release were controlled by diffusion of IIP to the overlying water. However, IIP values may have changed between day 33 and day 62, the end of the incubation period. Furthermore, an IIP concentration gradient may exist within the upper 3 cm. Finally, the volume of water over the sediment cores was relatively small, and DIP concentrations may have been controlled by sorption-desorption reactions at the exposed sediment surface as well as by diffusion of IIP from the sediment.

For deep lakes like Lake Ontario, the physical mobility of sediment P is likely controlled mainly by the diffusion of IIP from the sediments to the overlying water. Little disturbance due to bottom currents is expected in the deep basins although wave action and currents are likely important in shallow near-shore areas (Williams and Mayer 1972). Some disturbance of the sediment-water interface by benthic organisms may occur, but less benthic activity occurs in the deep sediments than in shallow water regions (Kemp et al. 1972).

Rates of diffusion of IIP from Lake Ontario sediments were estimated from IIP values measured in sediment cores, based on a DIP concentration of $10 \text{ } \mu\text{g/l}$ in the overlying water (Shiomi and Chawla 1970), Fick's first

law of diffusion, and a diffusion coefficient of $10^{-6} \text{ cm}^2 \text{ sec}^{-1}$ (Stumm and Leckie 1971). The value of the diffusion coefficient is somewhat uncertain (Weiler 1973). For an IIP range of about 100 to 1000 $\mu\text{g/l}$ for the upper 3 cm of sediment (Table 10), the estimated diffusion rates range from about 0.05 to 0.6 $\text{mg m}^{-2} \text{ day}^{-1}$. This is in agreement with the range of 0.03 to 0.8 $\text{mg m}^{-2} \text{ day}^{-1}$ estimated from cores incubated in the laboratory. While the two different approaches of estimating the physical mobility of sediment P are in agreement, the calculated rates may be inaccurate for several reasons: the diffusion coefficient may be inaccurate; the upper value may overestimate rates for basin sediments, as IIP concentration gradients may exist in the upper 3 cm; the lower range may underestimate release from near shore sediments due to mixing by wave and current action, and benthic organisms. However, the rates obtained provide a basis for evaluating the impact of sediment inorganic P release on the overlying lake water.

The annual contribution of sediment inorganic P to the P content of the overlying water can be estimated based on the inorganic P flux of 0.2 $\text{mg m}^{-2} \text{ day}^{-1}$ (mean for incubated cores) and a sediment area of 19,000 km^2 (Williams and Mayer 1972). The estimated annual contribution is 1.4×10^6 kg of P per year. This compares to an estimated annual loading from external sources of 1.3×10^7 kg per yr; about one-half of this arises from municipal waste waters (Great Lakes Water Quality Board, 1973). Thus, the estimated sediment contribution is about 10% of the external P loading. The estimated annual P release from sediments would correspond to about 5% of the potentially mobile inorganic P (NaOH-P) in the upper 3 cm of sediment.

SECTION VI

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TECHNICAL REPORT DATA

(Please read instructions on the reverse before completing)

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16. ABSTRACT Sediment cores were obtained from 15 lake stations representing the three major basins and the Inshore Zone of Lake Ontario. Cores were sectioned for characterization of the surface sediments according to inorganic P chemical mobility. Physical mobility was characterized by measurement of P release from intact cores incubated under controlled laboratory conditions. The proportions of potentially chemically mobile inorganic P were usually high (30 to 60%) in the central basin sediments and low (2 to 8%) for the inshore zone sediments. Although the amounts of inorganic P desorbed after three successive equilibrations (in .1M NaCl) of Lake Ontario sediments represented only 3 to 17% of the potentially mobile inorganic P, sufficient inorganic P was desorbed to restore a large part of the original interstitial inorganic P concentrations. Interstitial inorganic P (mobile P) concentrations ranged from 14 to 1280 µg/l and were higher than dissolved inorganic P concentrations in the overlying water. Diffusion rates estimated from the range of observed interstitial inorganic P values ranged from about 0.05 to 0.6 mg m ⁻² day ⁻¹ and were in agreement with the range of 0.03 to 0.8 mg m ⁻² day ⁻¹ estimated from P release from intact cores incubated under controlled laboratory conditions. Based on an inorganic P flux of 0.2 mg m ⁻² day ⁻¹ , the estimated annual contribution of inorganic P to Lake Ontario water is equal to about 10% of the external P loading.				
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