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PHOSPHATE EXCHANGE BETWEEN
LITTORAL SEDIMENT AND LAKE WATER

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Major professor

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PHOSPHATE EXCHANGE BETWEEN LITTORAL SEDIMENT AND LAKE WATER

By

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ABSTRACT

PHOSPHATE EXCHANGE BETWEEN LITTORAL SEDIMENT AND LAKE WATER

By

Robert Paul Glandon

Soluble phosphate is an important form of phosphorus in the environment. Current models, which consider a largely hydrostatic sediment-water interface, hold that aerobic sediments act as a barrier to sediment phosphate flux to overlying water. However, differences between littoral sediment interstitial and lake water phosphate levels indicate potential for diffusive flux. Further, water movement that results in perfusion of epilimnetic water or resuspension of littoral sediment particulates, can modify the particle-solution phosphate system. Information concerning mechanisms of particle response to changes in ambient phosphate or volume of ambient water can enhance models of phosphate exchange under hydrodynamic conditions.

Interstitial phosphate of sediments underlying 0.75-1.00 m water in a shallow lake was variable in space. Levels were generally greater than those of overlying water and gradients could be used to estimate static-water phosphate efflux through surficial sediment layers. Assuming solution calcium activity and pH similar to that of overlying water, mean soluble phosphate of surficial sediments approached predicted levels in equilibrium with hydroxyapatite. Particulate response to ambient perturbation could be directed by phosphate mineral equilibria and limited by kinetics of associated phosphate exchange.

Sediment material was taken from the site of interstitial sampling and a portion was treated to modify characteristics of particulate surfaces. Experimental observations of response of particulates to alterations in lake water phosphate levels implicated controlling mechanisms other than calcium phosphate solubility. Langmuir-type analysis suggested that ambient phosphate level is governed by the reservoir of phosphate sorbed on sediment particles. Relative to experimental conditions, particle-solution phosphate relationships were described using quantified parameters related to phosphate sorption maximum and binding energy. A model, incorporating concepts drawn from experimental data, indicates that particulate response to perturbation of a sediment-phosphate system depends on phosphate activity of interstitial and infusing water, and particle weight to solution volume ratio resulting from disturbance.

DEDICATION

To my son, Kevin

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INTRODUCTION

The general relationship, developed from a large number of lakes, between annual loading of total phosphorus from external sources and mean annual chlorophyll-a content of the open water, highlights the singular importance of phosphorus to primary production in lacustrine systems (Vollenweider, 1980). However, the empirical nature of the relationship limits identification of mechanisms underlying variability between lakes with similar hydrologic characteristics. In some of these, fluctuations in autotrophic production are observed in the absence of temporally corresponding changes in allochthonous phosphorus input. Detailed lake studies, based on comparisons of total phosphorus import and export over time, generally indicate that exchange between sediments and overlying water is an important component of phosphorus dynamics. While phosphorus budget analyses suggest that annual import and export differences result from net sedimentation, examination of water column phosphorus over time frequently shows periods of net sediment phosphorus release (Hutchinson, 1957). The extent and ecological impact of phosphorus regeneration from sediments is highly influenced by morphometric and associated hydrodynamic features of the lake.

The influential early work of Mortimer (1941, 1942), subsequently verified by many investigators, signaled the importance of oxidation state of surficial sediments in influencing the direction of net flux of sediment phosphorus. Chemical reduction of inorganic phosphate binding metal oxides and hydroxides, particularly those of iron, leading to liberation of soluble phosphate to overlying anoxic water represents a potentially significant mechanism of phosphate release, particularly from deep-water sediments. However, any realized impact of that on biological species dependent on water column phosphate levels is contingent upon the relative volume of anoxic water, area of underlying sediment surface, and frequency and extent of circulation to zones of maximum phosphate utilization. By contrast, a majority of lakes in the north temperate region are shallow, and characterized by a relatively large volume of oxygenated water overlying extensive littoral sediments (Wetzel, 1975). In these systems, the significance of sediment phosphate release depends to a larger degree on extent of diffusion-driven transport across an aerobic sediment-water interface, and on direct phosphate release from the surface of particles brought into the water column by turbulent mixing.

The potential of sediment particulates to influence soluble phosphate following transport to media of low ambient levels has been evidenced in phosphorus uptake by phytoplankton cultured axenically in media initially containing only sediment phosphate (Golterman, et al. 1969; Williams, et al. 1980). Further, sediments introduced to water containing relatively high levels of soluble phosphate may cause ambient phosphate reduction (Carritt and Goodgal, 1954; Taylor and Kunishi, 1970). Particle-solution phosphate exchange in sediments is largely controlled by chemical equilibria (Hayes, 1964; Pomeroy, 1965; Li, et al. 1972).

Distribution of soluble phosphate in sediment-solution systems has been considered with respect to solubility equilibria of certain aluminum, iron, and calcium phosphate minerals (Stumm and Leckie, 1971; Stumm and Morgan, 1981). Solubility product calculations suggest that excess accumulation or depletion of soluble phosphate is buffered by precipitation or dissolution of phosphate minerals, principally variscite ($AlPO_4$), strengite ($FePO_4$), dicalcium phosphate ($CaHPO_4 \cdot 2H_2O$), octacalcium phosphate ($CaH(PO_4)_3$), or hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$). However, solubility-pH relationships suggest that variscite and strengite are unstable at pH levels greater than 6, and Bache (1963) suggests that these minerals are unlikely to persist in solid form at pH levels greater than 3. Syers, et al. (1973) conclude that while it is highly unlikely that discrete phase iron and aluminum phosphates exist in sediments, hydroxyapatite is commonly found. In lakes that experience decalcification of the water column the calcium phosphate system is believed to be one of the principle control mechanisms for the distribution of phosphate to overlying water (Stumm and Leckie, 1971).

Williams, et al. (1970); Ryden, et al. (1973) and others suggest that the balance between soluble and particulate phosphate in sediments is predominantly influenced by the extent of association of the phosphate anion with preexisting solids, rather than through formation and dissolution of insoluble precipitates. Support for the dominance of sorption/desorption reaction with sediment solids stems in part from differences between observed rate and extent of phosphate exchange (Hayes, et al. 1952; Li, et al. 1972) and that expected from relevent precipitation reactions (Lindsay and Moreno, 1960; Stumm and Leckie, 1971).

Proposed mechanisms of phosphate sorption involve the nature of the solid surface. Chen, et al. (1973), working with well characterized clay minerals, proposed that a pH dependent electrostatic attraction between surface aluminate groups and solution phosphate anions could account for their sorptive ability. Edzwald (1977) presents evidence that metals associated with clays, probably as hydrous metal oxide coatings, have an overriding influence on phosphate sorption. This is supported by observed correlations between content of amorphous iron, aluminum, and silica compounds and phosphate sorption capacity of bottom sediments of the Maumee River (McCallister and Logan, 1978). Strong correlations between surficial sediment phosphorus levels and extractable amorphous iron oxides indicate that iron plays a particularly important role in this relationship (Shukla, et al. 1971; Williams, et al. 1971).

Soluble phosphorus of interstitial water is the sediment phosphorus fraction with the highest chemical mobility (Syers, et al. 1973). In shallow, surficial sediments, it appears that phosphate precipitation reactions with calcium or sorption reactions, principally involving amorphous metal oxides, can have a significant influence on interstitial phosphorus levels. These chemical reactions can also determine particulate response to changes in those levels. These considerations may be contrasted with those that characterize aerobic sediments as a barrier preventing phosphorus release to overlying water (Ruttner, 1963; Wetzel, 1975). The latter imply uni-directional association of phosphate with sediment particulates and ignore the operational significance of the reciprocal nature of the particle-solution phosphate relationship. Phosphate exchange reactions may result in interstitial phosphorus levels that are greater than those of overlying water; indicating gradients along which diffusive flux may occur. Further, resuspension of littoral sediment particulates by wind-induced currents has been commonly observed (Davis and Brubaker, 1973). This has the potential to alter the particle-solution relationship and result in particle-induced changes in water column phosphate levels.

The aim of this work is to evaluate the influence of shallow sediment particulates on soluble phosphorus levels. More specifically, particle influenced levels of soluble phosphorus were examined through measurements of interstitial phosphorus in a hydrodynamically active littoral zone. Phosphate exchange characteristics and capacity of particulates to modify changes in ambient phosphate levels were examined in experimental sediment particle-lake water systems. Results were evaluted with respect to the role of precipitation reactions, through considerations of calcium phosphate equilibria; and sorption reactions, through Langmuir analysis.

MATERIALS AND METHODS

Lake Lansing, the site of this study, exemplifies a system in which the functional role of shallow sediments in phosphorus dynamics can be of major significance. Approximately 80% of the lake volume is contained above the three meter contour and is well mixed by wind-driven circulation throughout the summer months. The oxygen content of the circulating stratum remains near equilibrium saturation with the atmosphere. During the mid to late summer period, littoral and epilimnetic water attains saturation with respect to calcium carbonate. Seasonal dynamics of this compound in Lake Lansing are marked by evidence of a mid-summer decline in soluble calcium levels.

Interstitial phosphorus profiles of shallow sediments of the south basin of Lake Lansing were measured *in situ* periodically during the summer and early fall of 1978. The sampling device consisted of a compartmented dialysis sampler fitted with a biologically inert polycarbonate membrane (Nucleopore, 0.2 μm pore size). Each sampler was machined from plexiglass into a tapered block encasing twenty rows of ports, with four ports per row. Each port was 2.5 cm in diameter and 13 ml in volume. To prepare samplers for placement in the lake, acid washed ports were filled with ion-free water and covered with a sheet of membrane that was held in place by a plexiglass cover fastened to the sampler with nylon screws. Holes in the cover matched open surfaces of the ports.

Time required for equilibration of soluble phosphorus across the membrane was determined in the laboratory by placing a prepared sampler in a bath of phosphate solution containing 9.7 μM PO_4 l^{-1}. Daily measurements of port-water phosphate were compared to those of bath water. After nine days, port phosphate levels equaled those of the bath and that period was taken as the minimum duration of sampler exposure in the lake.

Samplers were placed in the aqueous sediments of the east and west littoral zones of the south basin at a water depth of 0.75 - 1.00 m. Sampler position relative to the sediment-water interface was maintained by securing samplers to a cross bar connected to aluminum conduit that was driven deep into the sediment. Clamps connecting the cross bar to the conduit were tightened at the desired sampler position. Samplers were left in place for ten to fourteen days.

At the end of the period, samplers were returned to the laboratory. Particulate material clinging to or near the membrane surface was removed to prevent sample contamination. Measured volumes of port water were pipetted from sampler ports and colorimetrically analyzed for total phosphorus following persulfate digestion (A.P.H.A., 1976).

Complemetary information concerning the response of sediment particulates to changes in ambient phosphate was gathered through laboratory experiments. Interstitial phosphorus levels may be viewed as an approximate integration of particulate response to physico-chemical changes experienced throughout the period of measurement. These provided a means of estimating diffusive phosphorus flux along interstitial gradients. Estimation of sediment response to a given alteration in ambient phosphate level required direct examination.

Sediment material used in the laboratory was extracted from south basin with an Eckman dredge at a water depth of 0.5 - 0.75 m. Sediments were taken from the west littoral zone near the point of interstitial water sampling. Small amounts of litter of terrestrial origin, and fragments of viable aquatic macrophytes in samples were discarded. Excess water was removed from representative subsamples of material by concentrating sediment particulates on 0.5 μm glass-fiber filters with the assistance of a mechanically generated vacuum of 12 psi. Filter-retained sediment, designated as whole sediment in this study, was refrigerated in a wet state at $4^{O}C$. Experiments were conducted within thirty-six hours of collection.

Laboratory work consisted of following particle induced changes in total and reactive filterable phosphate in lake water as a function of initial level of dissolved reactive phosphorus in that water. Five grams of wet sediment material was placed into each of eighteen, 300 ml Erlenmeyer flasks containing 100 ml of filtered (0.5 μm) lake water. Dry weight of added sediment was 15.2% of total sediment weight. Reaction flasks differed with respect to initial levels of soluble reactive phosphate. Particulate response to six initial phosphate levels, ranging from 0.1 to 303 μM PO_4 l^{-1}, was examined. Each reactive phosphate level above that of lake water was obtained by adding the appropriate quantity of phosphate salt (KH_2PO_4) to a measured volume of lake water. Aliquots were withdrawn from each batch solution for direct analysis of total dissolved and reactive phosphorus prior to sediment addition. Each sediment/solution phosphorus combination was prepared in triplicate so that the extent of solution phosphorus change could be measured following each of three pre-selected exposure intervals. The intention was to identify the steady state or "quasi-equilibrium" condition through observed decrease in the rate of change in experimental systems.

Initital pH of each sediment/solution suspension was recorded immediately following sediment introduction. A calibrated Corning Model 6 pH meter and Orion Model 91-25 epoxy combination probe was used for these measurements. Flasks were then covered with porous foam plugs to retard evaporation and placed on an oscillating shaker table to maximize sediment-solution contact. Reaction vessels, representing each initial solution phosphate level, were removed from the table after 0.5, 2.0, and 48 hour exposures. Final pH was recorded and sediment particulates removed by filtration. The 0.5 μm filter (glass-fiber) was assumed to have separated soluble from insoluble particulate components of sediment-solution systems. Filtrate was analyzed for content of total and reactive phosphate.

Dissolved reactive phosphate was determined colorimetrically using the single reagent ascorbic acid method without prior persulfate digestion of filtrate (A.P.H.A., 1976). Results of these measurements have been taken to indicate levels of ionic phosphate in solution. The difference between total phosphorus content of filtrate, determined following persulfate digestion, and reactive phosphorus content was taken as a measure of the soluble nonreactive fraction. Soluble nonreactive phosphorus may include dissolved condensed and organic phosphates (A.P.H.A., 1976); in natural systems not heavily influenced by wastewater, the soluble nonreactive fraction is typically dominated by a dissolved organic phosphate component (Clesceri and Lee, 1965; Sonzoni, et al. 1981).

Lake Lansing sediments were previously determined to contain high levels of total arsenic (Batterson, 1980). Since any solubilized arsenate represents a potential positive interference in phosphate measurements (Shapiro, 1973), all samples and standards were subjected to an arsenate reductant (Johnson, 1971). The reductant was shown to be effective in analytical results presented here (Appendix 1).

Experimental conditions were intended to reflect particle-solution phosphorus exchange in an aerobic environment. It was assumed that chemical reduction of iron could influence sediment response and that a functional change in redox potential would be indicated by an increase in soluble iron content. In order to monitor transformation of ferric to soluble ferrous form, solution iron content was measured prior to and following sediment exposure. In an effort to distinguish relative importance of pertinent precipitation and sorption mechanisms, solution calcium levels were also measured. The intention was to incorporate calcium phosphate solubility expressions in the analysis of observed response of experimental systems. Aliquots of filtrate from each sediment-solution suspension were acidified (4ml double distilled nitric acid per liter; pH = 2) and stored for later analysis of iron and calcium content and comparisons with lake water content prior to sediment addition. Soluble calcium and iron was determined by atomic absorption spectrophotemtry. Lanthanum chloride was added to calcium samples and standards to eliminate phosphate interference. (U.S.E.P.A., 1979).

To estimate soluble phosphorus, iron, and calcium contributions of the aqueous component of wet sediment, weighed subsamples were dried in a forced-air oven at 100°C to constant weight. Weight loss upon drying was coupled to measured levels of total and reactive phosphorus, iron, and calcium in the filtrate obtained during sediment preparation to estimate mass of these materials introduced with the aqueous sediment component. Water volume of whole sediments was considered in determining total aqueous volume in experiments.

Reactions between particulate and solution components are influenced by the chemical nature of the particulate surface (Stumm and Morgan, 1981). For example, carbonates may be a much less energetic phosphate retention agent than hydrated metal oxides (Shukla, et al. 1971; McCallister and Logan, 1978). Sediments used in the second phase of the laboratory work here were processed to alter particle surface characteristics. Specifically, processing was intended to enhance the relative influence of carbonate precipitates on particle-induced changes in solution phosphate. Observations of particle-solution phosphate exchange were contrasted with those of whole sediments.

For this work, small sized particulate fractions were obtained by passing a total of five liters of sediment through a series of three standard U.S.G.S. sieves. Sieves were stacked in order of decreasing pore size; the smallest (227 μm) was placed over an enamel collecting tray. A total of fifteen liters of filtered lake water, of known phosphorus, calcium, and iron content was introduced with sediment to the top-most sieve. Added lake water sorted and carried fine particles through the series. Water in the enamel collecting tray was evaporated in a forced-air oven at 80°C. Remaining particulates were removed from the tray and stored until use. Estimated quantities of formerly soluble phosphorus, calcium, and iron deposited during evaporation are presented here (Appendix 2).

Certain effects of fine sediment processing were expected from considering potential changes in aqueous chemical composition during evaporative concentration. The reaction path of natural waters during isothermal evaporation depends on the Ca^{2+} : HCO_3-, which is reflected in the alkalinity and calcium content of water prior to evaporation (Stumm and Morgan, 1981). The alkalinity of lake water used in processing fine sediment was 2.4×10^{-3} eq l^{-1}. Calcium content was 7.98×10^{-4} moles l^{-1}. Predicted calcium carbonate precipitation and increase in solution pH during evaporation of water, characterized by 2 (moles Ca^{2+} l^{-1}) < alkalinity (in equivalents l^{-1}), were expected to have important effects on sorptive characteristics of exposed particles. The effect of increasing pH is, in many cases, to decrease phosphate sorption mediated by metal oxides and hydroxides associated with surfaces of particulate materials (Edzwald, 1977). Further, dessication may have a denaturing effect on metastable metal oxides, such as highly hydrated ferric hydroxide (Ponnamperuma, 1967). This may underly reduced phosphate sorption capability, observed elsewhere, of sediment particulates following drying (cf. Harter, 1968; also Fitzgerald, 1970). The treatment likely changed particle surface characteristics through alternation of particle-associated ferric hydroxide and through deposition of carbonate precipitates.

Exchange of filterable total and reactive phosphate between fine sediments and lake water was examined in a manner similar to that employed with whole sediment. One gram dry material was added to 100 ml lake water phosphate solutions.

In a separate experiment, extent of net phosphate release from fine sediment particulates following timed exposure to low initial levels of lake water phosphate was examined.

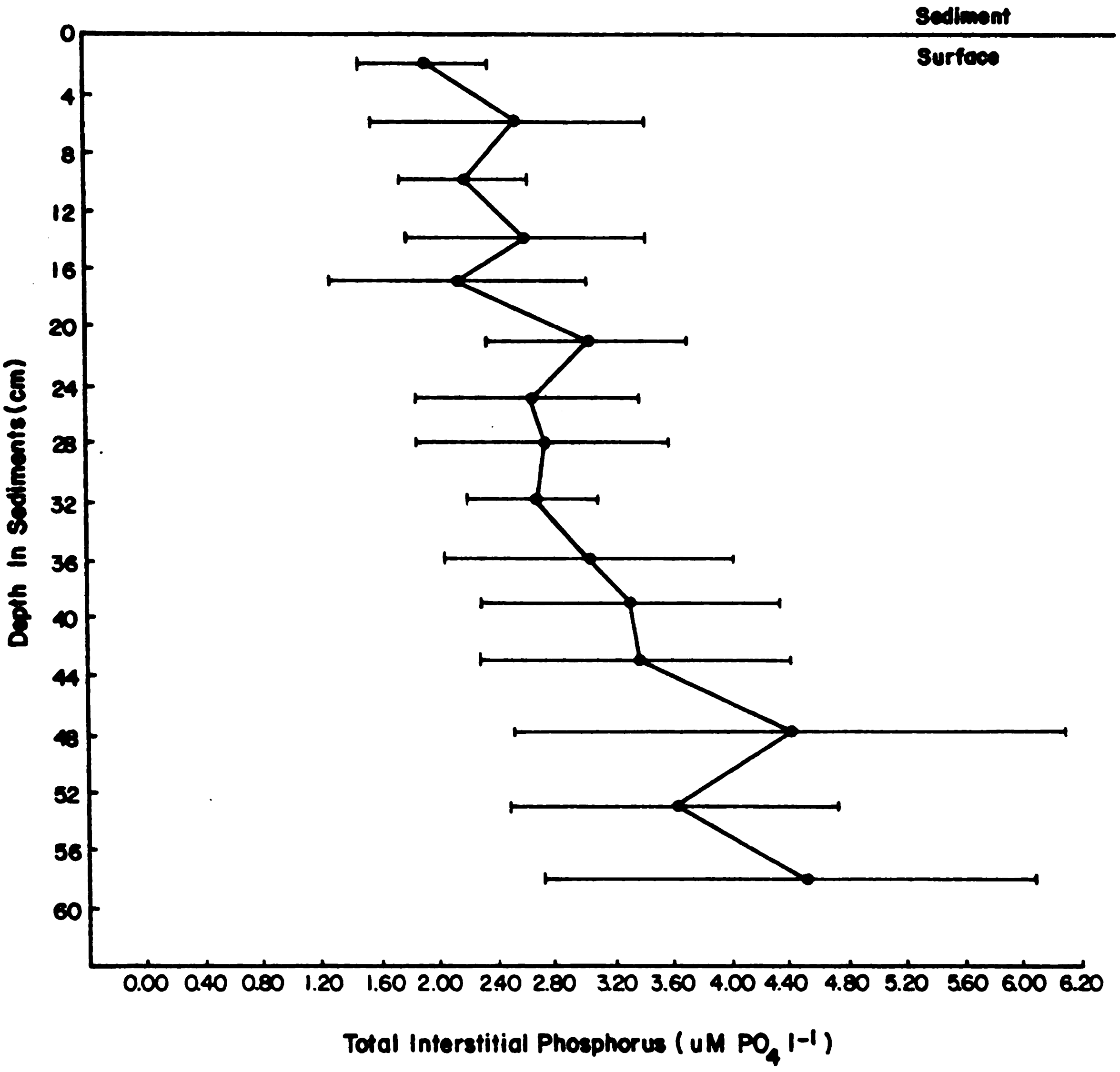
Here, 0.5 g fine sediment was added to each flask containing 100 ml filtered lake water. The sediment-water suspension was filtered after fifteen minutes exposure. Filter-retained sediment was reintroduced to a second 100 ml aliquot of filtered water by rinsing the filter in that volume. In total, each initial 0.5 g of material was transferred six times. Soluble reactive phosphate was measured following each exposure. For comparison, 0.5 g sediment was added to each of several flasks containing 100 ml lake water. A sample was filtered following 15, 30, 45, 90, and 120 minute exposures in order to follow the course and extent of phosphate release in the absence of medium renewal, ie. under conditions of ambient phosphate accumulation. Each experiment was replicated six times.

RESULTS

Levels of total soluble phosphorus in water equilibrated with interstitial water in Lake Lansing sediments can be characterized as highly variable (Figure 1). Variability in the data prevented discriminating between profiles of the east and west sampling locations in the south basin. Similarly, temporal differences between phosphorus profiles at a given location could not be discerned. As a result, data were combined with respect to depth to obtain mean interstitial phosphorus characterizing south basin sediments over the midsummer to early fall period (n = 8 to 10 per depth).

Combined soluble reactive plus nonreactive phosphorus ranged from 1.9 $\mu M\ PO_4\ l^{-1}$ near the sediment-water interface to 4.5 $\mu M\ PO_4\ l^{-1}$ at a depth of 58 cm below the sediment surface. These data contrast with those reported elsewhere (Holdren, et al. 1977; Carignan, et al. 1981) in that phosphorus levels here were relatively low and profiles lacked an apparent steep interstitial phosphorus gradient. Rapidly increasing levels of soluble phosphorus with depth in the sediment have been attributed to the presence of a redox boundary, below which phosphate-binding iron compounds are reduced (Mortimer, 1971). However, literature observations reflected conditions of experimental sediment cores or sediment underlying comparatively quiescent deeper water. Relatively high

Figure 1. Content of total interstitial phosphorus (mean ± 1 standard error) with depth in shallow sediments of the south basin of Lake Lansing in the interval from July - October, 1978.


Sediment
Surface
0
4
8
12
16
20
24
28
32
36
40
44
48
52
56
60
Depth In Sediments (cm)
0.00 0.40 0.80 1.20 1.60 2.00 2.40 2.80 3.20 3.60 4.00 4.40 4.80 5.20 5.60 6.00 6.20
Total Interstitial Phosphorus (uM PO4 l-1)

variability in interstitial phosphorus examined here may reflect effects of particulate resuspension or ambient medium displacement by seepage or turbulent movement of overlying water. This implies that interstitial phosphate gradients and associated diffusive flux were variable within the sediment.

The expected flux of phosphorus from sediment to overlying water due to molecular diffusion can be calculated from:

$$F = \Phi(-D\frac{dC}{dz})$$

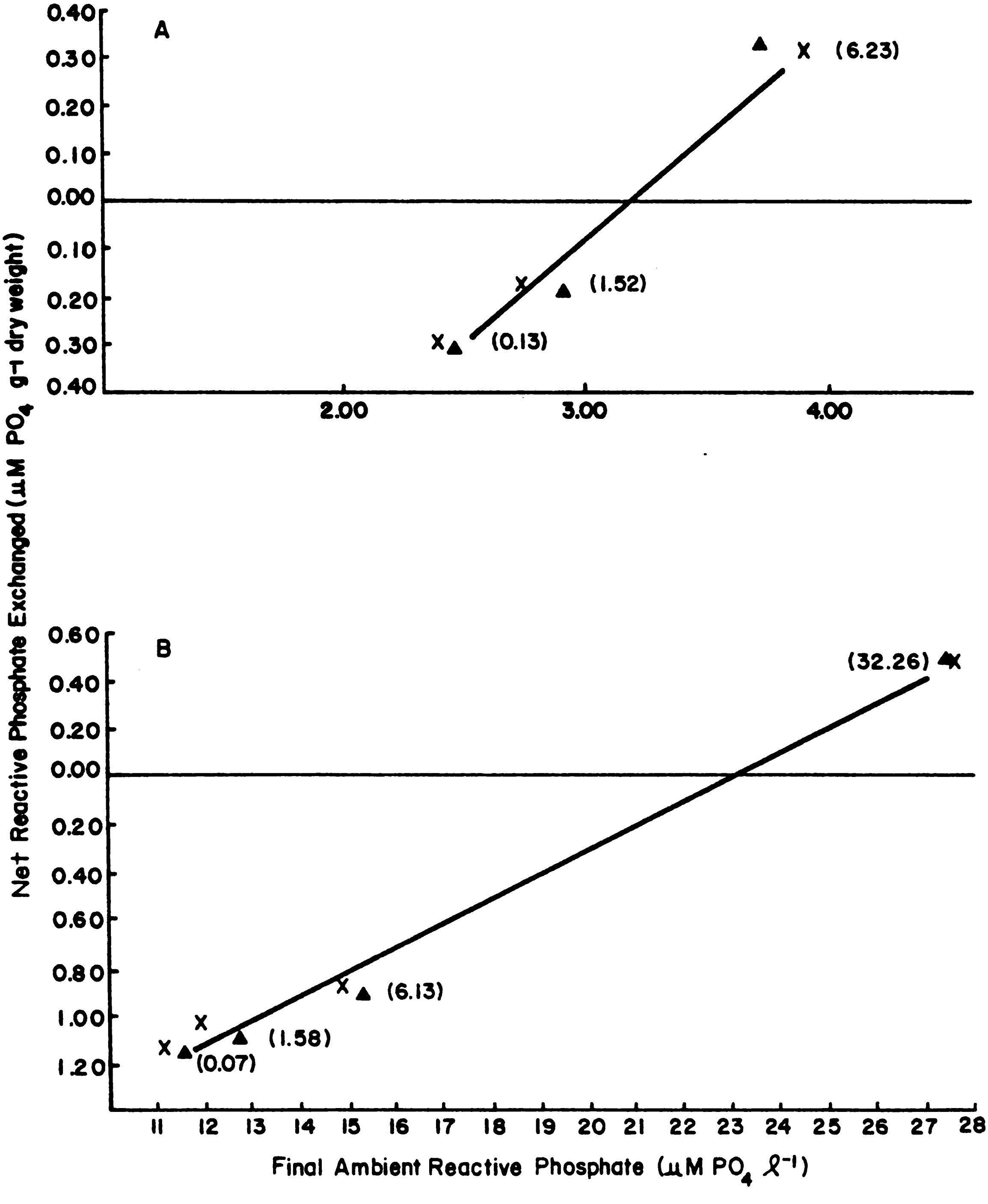
where D is the phosphate diffusion coefficient, 10^{-6} cm^2 sec^{-1} (Stumm and Leckie, 1971) and dC is the ambient reactive phosphate concentration difference across a distance, dz. The value of Φ for south basin sediments was near 0.96 (cf. Siami, 1981), and reflects the volume fraction of sediment occupied by water (Stumm and Morgan, 1981).

Driving force of molecular diffusion is the concentration gradient of soluble reactive phosphate within the region of interest. Since data obtained were the sum of soluble reactive and organic phosphorus, the reactive fraction could not be separately determined. If it is assumed that the level of soluble organic phosphorus was relatively constant along the diffusion path (cf. Holdren, et al. 1977), the data may be used to approximate the soluble reactive phosphorus gradient. Total interstitial phosphorus at 2 cm ranged from 0.581 to 3.871 μM PO_4 l^{-1}. For the region extending from the interface to a depth of 2 cm, the diffusion path, dz, was 1.0 cm; measured to the center of the 0-2 cm layer. Using constants given above, the rate of phosphate diffusion from this depth to overlying water (mean 0.10 μM PO_4 l^{-1}) could have ranged from 0.40 to 3.13 μM PO_4 m^{-2} day^{-1}.

Estimated maximum phosphate flux of 3.13 μM PO_4 m^{-2} day^{-1} could increase phosphate content of 1 m^3 lake water by 0.003 μM PO_4 l^{-1} day^{-1}, or approximately 3% of mean epilimnetic levels. By comparison, if turbulent movement of overlying water resulted in displacement of interstitial solution (at 3.9 μM PO_4 l^{-1}) to a depth of one centimeter, epilimnetic phosphate could be increased by 30% (when $\Phi = 0.96$). Further, phosphate release from surfaces of particulates swept from the sediment surface can contribute to phosphate levels of overlying water. Capacity of sediment solids to buffer interstitial phosphate or respond to changes in ambient levels is an important characteristic of particle-solution phosphate relationships that can give perspective to diffusive flux considerations presented here.

Results of experiments indicated a dynamic relationship between particulate and ambient reactive phosphate (Figure 2). The direction and extent of net movement of reactive phosphate between sediments and ambient lake water was depedent upon sediment type. On a dry weight basis, whole sediment particulates released 0.3 μM PO_4 g^{-1} during 48 hour exposure to initial ambient phosphate of 0.13 μM PO_4 l^{-1}. The result was an ambient level of 2.4 μM PO_4 l^{-1}. Extent of net release was restricted at higher initial levels of ambient phosphate, and direction of particulate-solution phosphate exchange reversed following

Figure 2. Net reactive phosphate exchange between sediment and lake water following 2 hours (▲-▲) and 48 hours (X-X) exposure to different initial reactive phosphate levels. Initial ambient levels (μM PO_4 l^{-1}) are indicated in parentheses. Horizontal axis shows final ambient reactive phosphate level. Panel A results from whole sediments. Panel B results from fine sediments.


A
0.40
0.30
0.20
0.10
0.00
0.10
0.20
0.30
0.40
2.00
3.00
4.00
(6.23)
(1.52)
(0.13)
B
0.60
0.40
0.20
0.00
0.20
0.40
0.60
0.80
1.00
1.20
11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28
(32.26)
(6.13)
(1.58)
(0.07)
Net Reactive Phosphate Exchanged (µM PO$_4$ g-1 dry weight)
Final Ambient Reactive Phosphate (µM PO$_4$ ℓ$^{-1}$)

sediment exposure to 6.23 μM PO_4 l^{-1}. Differences between 2 and 48 hour results have been taken to reflect experimental error imposed by uncontrolled variables.

In contrast to whole sediments, introduction of fine particulate material to lake water resulted in extensive net phosphate release. Nearly 1.2 μM PO_4 g^{-1} was liberated to phosphate-poor lake water, roughly four fold that of whole sediments. By comparison, this tendency was only moderately restricted at higher initial ambient phosphate levels. Net release was reduced by 9% in response to a ten fold increase in initial lake water phosphate to 1.58 μM PO_4 l^{-1}, one fourth the inhibition of whole sediment response to a similar ambient increase. This contrast between sediment types was reflected in the rate of development of the relationships of Figure 2. Under lake water conditions promoting sediment phosphate release, over 80% of the 48 hour fine sediment response occurred within 30 minutes; almost twice the short term progress of whole sediments. On the other hand, over 90% of the final whole sediment phosphate uptake from lake water occurred within 30 minutes, compared to 65% for fine sediments.

The whole sediment-lake water phosphate relationship implies that no net exchange would result from sediment exposure to lake water bearing 3.2 μM PO_4 l^{-1}. Limited by the experimental conditions employed, this "crossover" concentration can be taken as an estimate of the ambient reactive phosphate level in equilibrium with whole sediment particulates prior to use for experimentation (McCallister and Logan, 1978; Oloya and

Logan, 1980). The experimentally determined crossover phosphate level for whole sediments was in the range of summer-fall interstitial phosphorus measured in the south basin surficial sediments.

Crossover concentration can be considered a reference point in the phosphate exchange relationship permitting an estimate of the direction of net phosphate exchange, if the ambient level is altered. The relationship between the points can be used to estimate extent of exchange and expected new crossover value (Taylor and Kunishi, 1971). A greater slope in the relationship identifying a particular equilibrium crossover value would indicate a greater sediment-mediated resistance to change from that ambient level (ie. buffer capacity of the sediment-lake water system). Capacity of sediment particulates to buffer ambient phosphate would depend on extent of sediment surface exposure relative to ambient water volume. For a given sediment in suspension, this can be approximated by the sediment weight to solution volume ratio (sediment : solution). Under whole sediment : solution used (approximately 8 g dry weight per liter; considered similar to sediment density near the interface of the lake) buffering capacity was calculated from:

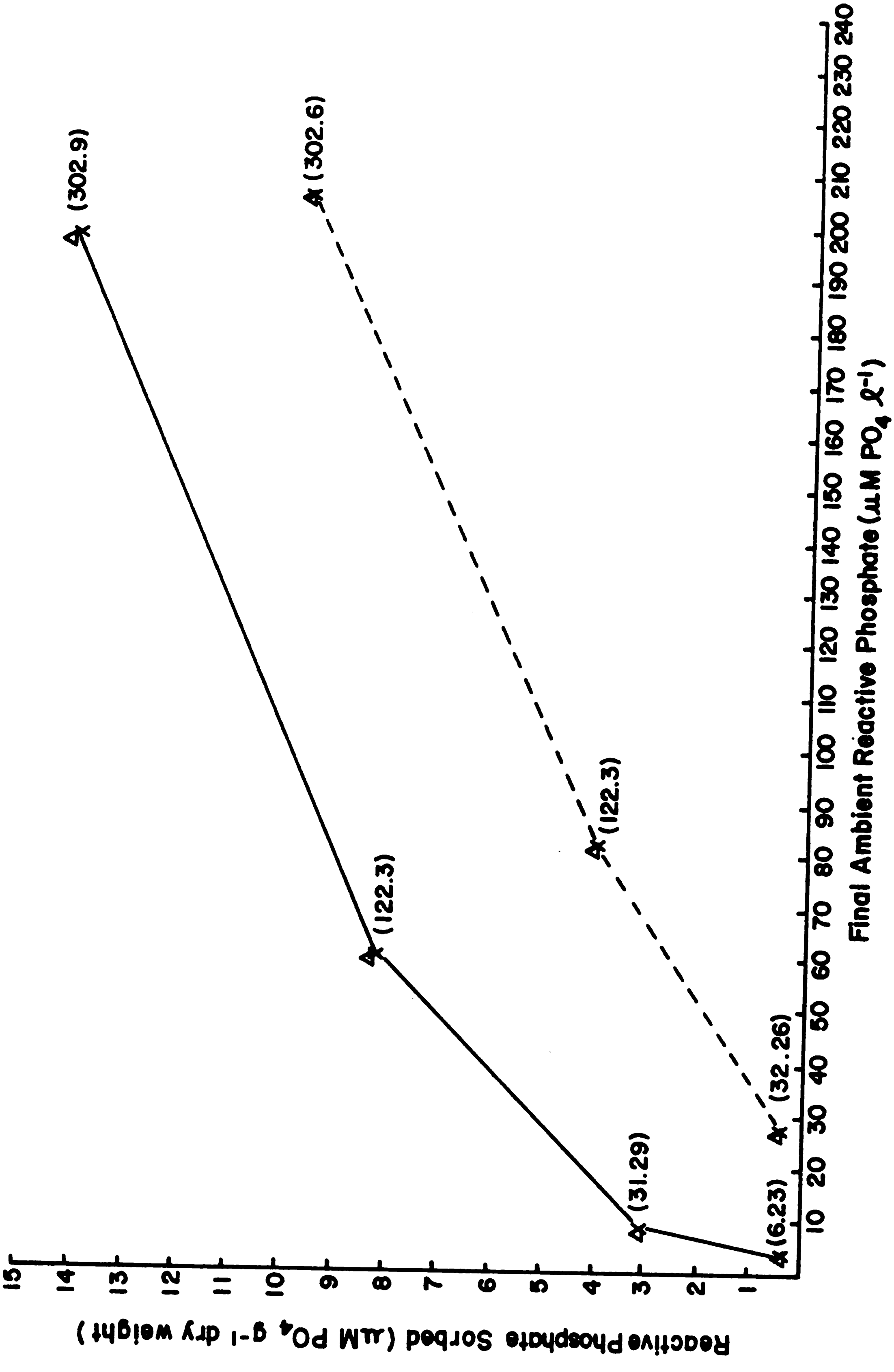
$$\frac{\mu\text{M } PO_4 \text{ g}^{-1} \text{ exchanged x g sediment l}^{-1}}{\begin{array}{l}\text{crossover phosphate} \\ \text{concentration}\end{array} - \begin{array}{l}\text{phosphate concentration} \\ \text{of new or infusing medium}\end{array}}$$

(modified from Mayer and Gloss, 1980). The equation yields the ratio of sediment phosphate exchanged, expressed as μM PO_4 l^{-1}, to the perturbation from crossover phosphate concentration, also expressed as $\mu M\ PO_4\ l^{-1}$. Data of Figure 2 indicate that under experimental conditions, the capacity of whole sediments to buffer ambient phosphate at 3.2 $\mu M\ PO_4\ l^{-1}$ was near 0.79.

In contrast to whole sediments, the strong tendency of fine sediments to release phosphate was reflected in the comparatively high crossover value of 23 $\mu M\ PO_4\ l^{-1}$, roughly seven fold that of whole sediments. The calculated capacity of fine sediments to buffer or resist changes in ambient phosphate near this relatively high level was 0.5.

Sediment response to relatively high initial levels of ambient phosphate can yield information on capacity of sediments to retain phosphate (Williams, et al. 1970) and potential of sediments to supply phosphate to overlying water (Woodruff and Kamprath, 1965). The amount of phosphate sorbed from relatively high initial lake water levels was dependent upon sediment type (Figure 3). Relatively high phosphate release from fine sediments (Figure 2) suggests that a portion of the difference between the curves of Figure 3 may be due to differences in initial phosphate content of sediment particulates. For either sediment, the changing slope of the relationship between net phosphate sorbed and corresponding ambient phosphate suggests that the degree of particulate response to ambient perturbation depends on the pre-existing equilibrium phosphate level. The relationships indicate reduced capacity of particulates to buffer high ambient levels, and suggest that the rate of change of diffusive flux of interstitial phosphate is a function of ambient phosphate level.

Figure 3. Net reactive phosphate sorbed by whole sediments (solid curve) and fine sediments (dashed curve) from lake water of different initial reactive phosphate levels, following 2 hours (Δ-Δ) and 48 hours (X-X) exposure. Horizontal axis indicates resultant ambient reactive phosphate level. Associated initial levels of ambient reactive phosphate ($\mu M\ PO_4\ l^{-1}$) are indicated in parentheses.


Reactive Phosphate Sorbed (μM PO$_4$ g-1 dry weight)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
Final Ambient Reactive Phosphate (μM PO$_4$ ℓ$^{-1}$)
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
220
230
240
(6.23)
(31.29)
(122.3)
(302.9)
(32.26)
(122.3)
(302.6)

The near linear relationship describing fine sediment response suggests a higher capacity of particulates to retain phosphate. This could reflect effects of greater weight-normalized surface area (Olsen and Watanabe, 1957). However, particle associated phosphate was considerably lower at observed ambient levels compared to whole sediments, possibly indicating a less energetic particle-phosphate bond. By comparison, only 50% of 48 hour fine sediment sorption occurred within the first 30 minutes of exposure, while over 90% of total phosphate sorbed by whole sediments occurred in that interval.

Net exchange of reactive phosphate dominated the movement of total soluble phosphorus between particulates and solution for both sediment types examined (Figures 4 and 5). The amount of net reactive phosphate release to lake water had no apparent effect on the extent of net soluble nonreactive phosphate release from sediment (Figure 4). While fine sediments released approximately 0.35 μM nonreactive $PO_4\ g^{-1}$, near seven fold that of whole sediments, the reactive : nonreactive phosphate release ratio ranged from 2 : 1 to 6 : 1 for both sediments. The variation in the release ratio was principally due to variation in the reactive phosphate fraction.

Under conditions of net reactive phosphate uptake from solution, nonreactive phosphate release apparently increased for both sediment types (Figure 5). Although the relationship between reactive phosphate uptake and nonreactive phosphate release was fairly insensitive for both sediments, it suggests

Figure 4. Relationship between release of soluble nonreactive phosphate and release of reactive phosphate by sediments following 0.5 hours (O-O), 2 hours (Δ-Δ), and 48 hours (X-X) exposure to lake water with low initial reactive phosphate levels. Solid line, results from whole sediments; dashed line from fine sediments.

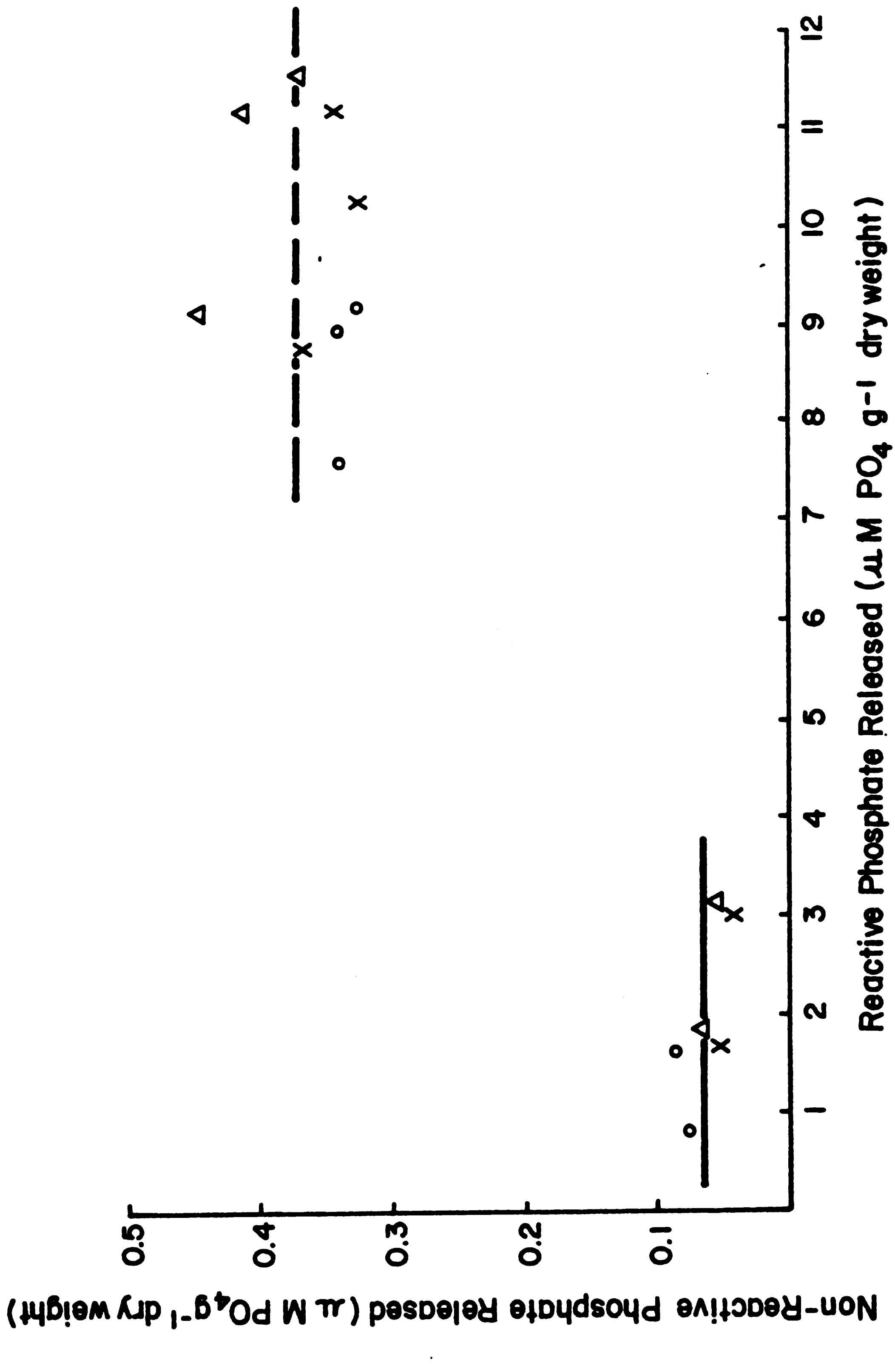

0.1
0.2
0.3
0.4
0.5
Non-Reactive Phosphate Released (µ M PO4 g-1 dry weight)
1
2
3
4
5
6
7
8
9
10
11
12
Reactive Phosphate Released (µ M PO4 g-1 dry weight)

Figure 4. Relationship between release of soluble nonreactive phosphate and release of reactive phosphate by sediments following 0.5 hours (O-O), 2 hours (Δ-Δ), and 48 hours (X-X) exposure to lake water with low initial reactive phosphate levels. Solid line, results from whole sediments; dashed line from fine sediments.

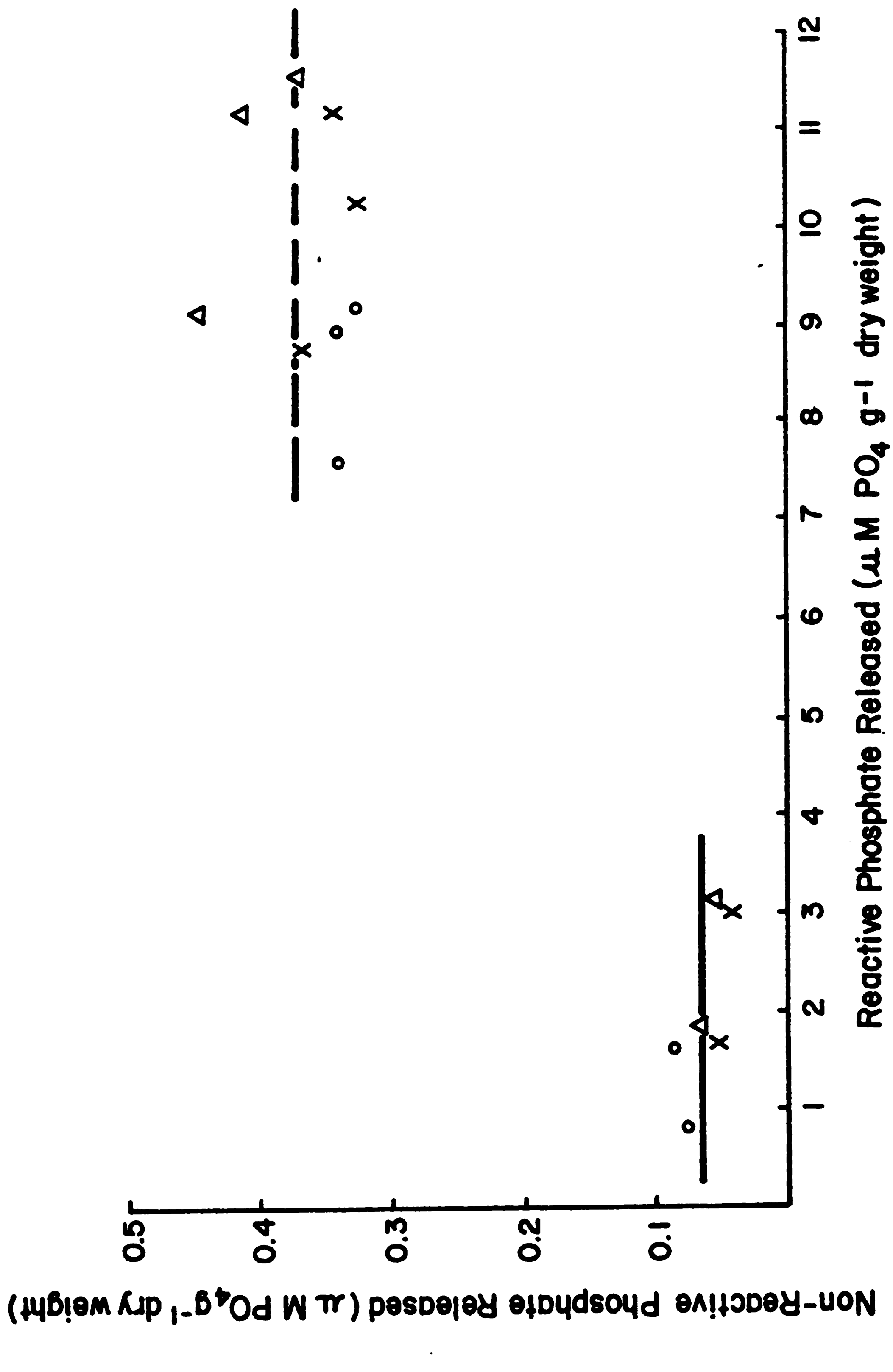
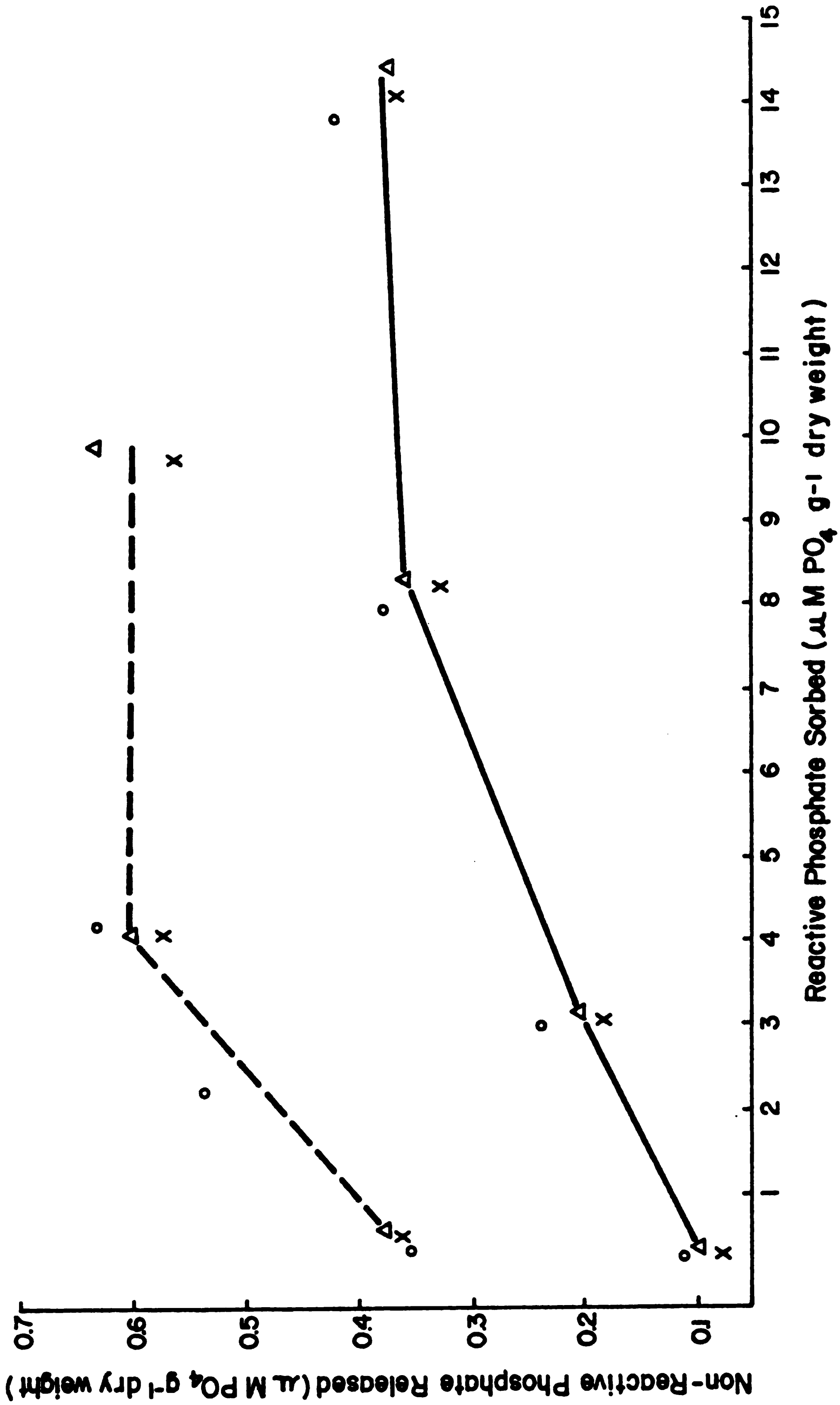

Non-Reactive Phosphate Released (μ M PO$_4$ g^{-1} dry weight)
0.5
0.4
0.3
0.2
0.1
Reactive Phosphate Released (μ M PO$_4$ g^{-1} dry weight)
1
2
3
4
5
6
7
8
9
10
11
12

Figure 5. Relationship between release of soluble nonreactive phosphate and sorption of reactive phosphate by sediments following 0.5 hours (O-O), 2 hours (Δ-Δ), 48 hours (X-X) exposure to lake water with high initial reactive phosphate levels. Solid line, result from whole sediments; dash line from fine sediments.

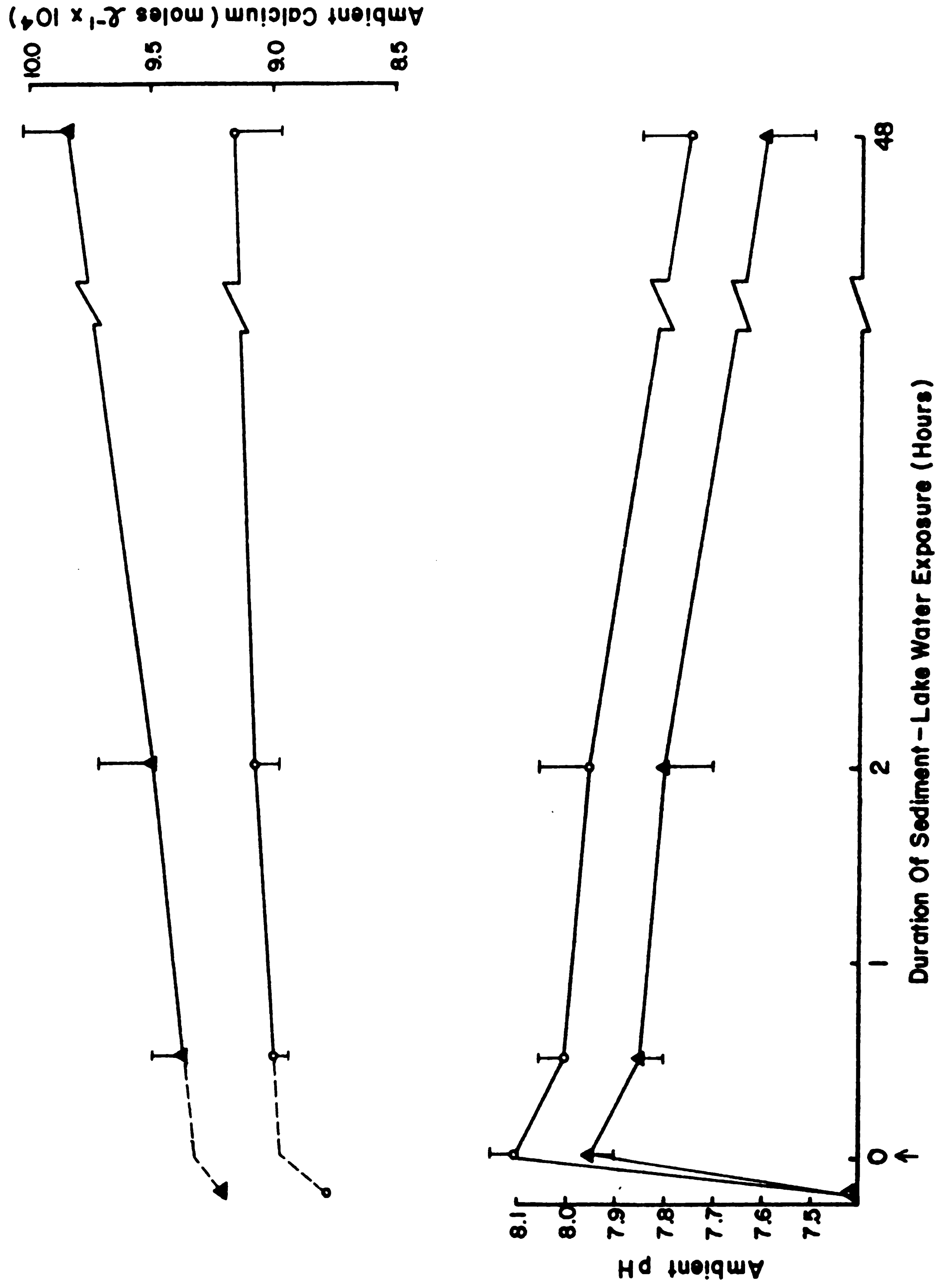

Non-Reactive Phosphate Released (µ M PO$_4$ g^{-1} dry weight)
0.1
0.2
0.3
0.4
0.5
0.6
0.7
Reactive Phosphate Sorbed (µ M PO$_4$ g-1 dry weight)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15

that mechanisms of sediment uptake of reactive phosphate may involve displacement of phosphate-containing organic molecules. The hypothesis that reactive phosphate added to soil systems displaced sorbed organic phosphate was not supported by the data of Wier and Black (1968). According to Latteral, et al. (1971), however, reactive phosphate added to and sorbed by sediments resulted in a substantial increase in the proportion of organic to reactive phosphate in equilibrium solution. This was interpreted as being caused by displacement of organic phosphorus from sediment sorption sites by the more strongly sorbed reactive phosphate.

Interpretation of changes in solution phosphate levels following sediment introduction partially rests on observations of other system variables that may influence results. Assessing potential impact of pH-dependent dissolution/precipitation reactions involving calcium phosphate compounds, or changes in oxidation-reduction potential leading to solubilization of phosphate binding sediment compounds is critical to a discussion of mechanisms of sediment-solution phosphate exchange. Toward this end, solution calcium, pH, and iron were monitored.

The general directions of change in ambient pH and calcium were similar in both whole and fine sediment-lake water systems (Figure 6). Further, for each sediment type, trends in ambient calcium and pH were similar at all phosphate levels examined, ie. there were no correlations between the extent of ambient calcium increase or pH decrease and initial ambient phosphate, or extent of inorganic phosphate exchange. Measurements of

Figure 6. Ambient calcium (mean and 1 standard deviation) and pH (mean and range) with duration of whole (▲-▲) and fine (o-o) sediment exposure to lake water phosphate solutions. The dashed lines indicate hypothesized course of change in ambient calcium within initial 30 minutes sediment-lake water exposure. Time 0 indicates point of sediment introduction to lake water.


Ambient Calcium (moles ℓ⁻¹ x 10⁴)
10.0
9.5
9.0
8.5
Ambient pH
8.1
8.0
7.9
7.8
7.7
7.6
7.5
0
1
2
48
Duration Of Sediment - Lake Water Exposure (Hours)

soluble calcium and ambient pH were grouped to obtain a mean for each exposure interval.

Lake water pH increased from 7.4 to 7.95 and 8.10 upon introduction of whole and fine sediment (time 0). Solution calcium increased over lake water levels by about 20 μM l^{-1} within 30 minutes sediment-lake water exposure. The dashed lines indicate hypothesized course of solution calcium change; suggesting that increases in soluble calcium corresponded to observed pH increases (cf. Turner and Clark, 1956). These trends may reflect response of calcium carbonate equilibria and as such were largely independent of observed phosphate reactions.

Calcium carbonate solubility is a function of pH and carbon dioxide content of water, the relationship can be described by:

$$\tfrac{1}{2}\,\mathrm{pCa} = \mathrm{pH} + \tfrac{1}{2}\log \mathrm{PCO_2} - 4.93$$

where pCa is the negative log of the molar concentration of calcium, and PCO_2 is the partial pressure of carbon dioxide. At equilibrium, partial pressure of aqueous CO_2 is equal to the partial pressure of atmospheric CO_2 (Turner and Clark, 1956).

Assuming lake water used for experimentation was in equilibrium with atmospheric CO_2 prior to sediment addition, PCO_2 = 0.0003 atm, and $\tfrac{1}{2}\log PCO_2 = -1.761$. At pH 7.4, predicted aqueous calcium level would be 3.8×10^{-2} molar. Measured levels were near 1×10^{-3} M. This indicates a tendency for calcium carbonate, in contact with lake water, to dissolve. Dissolution of $CaCO_3$, and subsequent increase in CO_3^{2-}, could incur a pH increase. A resultant disequilibrium between aqueous and atmospheric CO_2 would promote reinvasion of CO_2 from the atmosphere causing a gradual pH decrease in solution. The laboratory results suggest that the rate of potential calcium carbonate dissolution early in the exposure period was greater than the rate of invasion of atmospheric CO_2. The observation that pH-Ca equilibrium was not attained in the duration of the experiments (ie. final calcium levels were lower than predicted) may reflect insufficient calcium reserves or reduction in the rate of dissolution of $CaCO_3$ coated with adsorbed organic compounds (Wetzel, 1971, 1972). These considerations suggest that observed calcium increases may not involve dissolution of phosphate containing minerals.

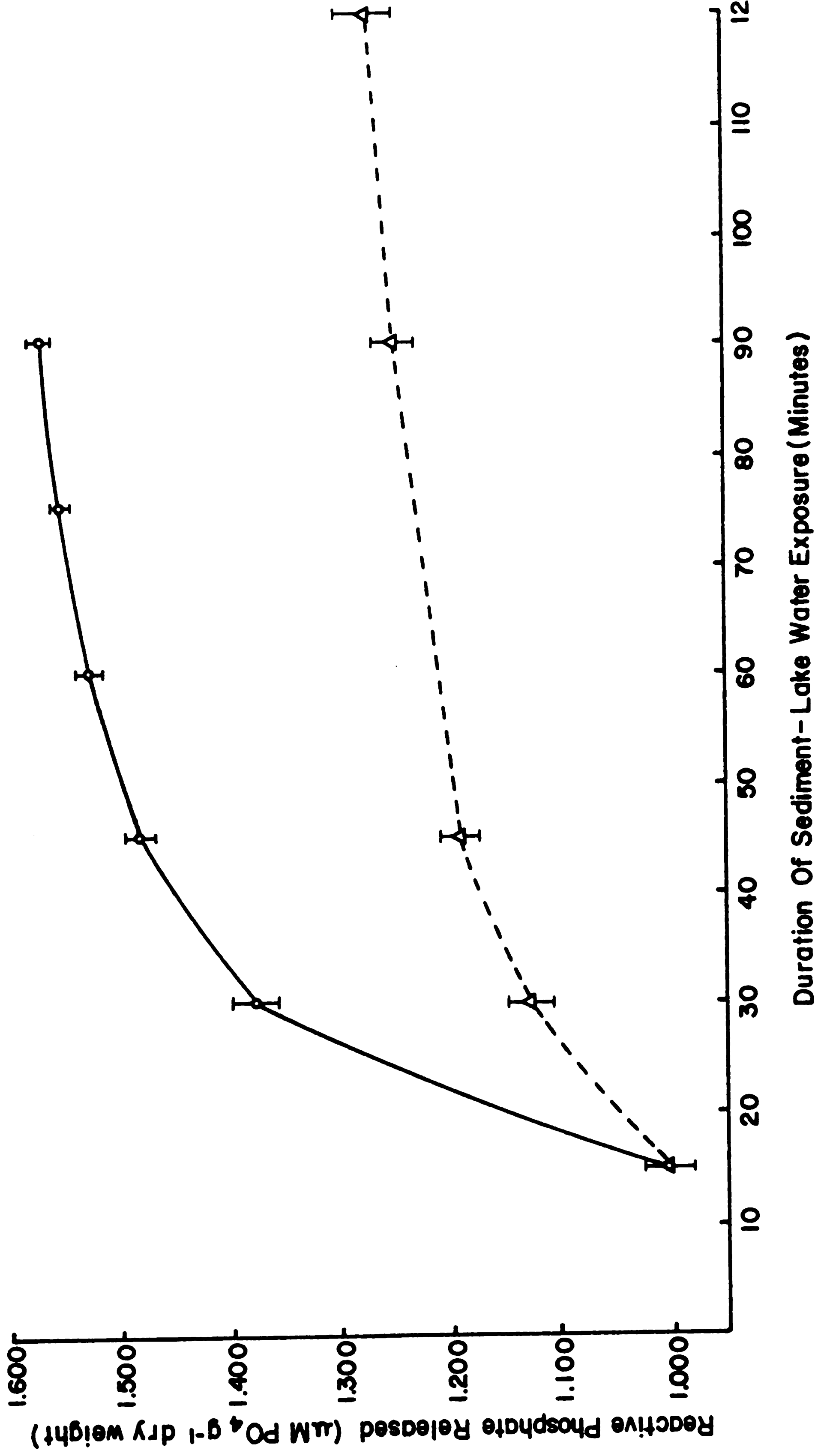
Filterable iron content did not change measureably in the sediment-lake water system (Appendix 3), suggesting that redox potentials did not fall below a critial level for chemical reduction of phosphate-binding iron oxides. While observed levels of soluble iron were low relative to analytical precision, they were high relative to predicted concentrations based on solubilities of iron oxides and hydroxides. Assuming particulate iron passing the 0.5 μm filter was minimal, the observed iron levels may reflect presence of naturally occurring metal chelating compounds in solution.

The reciprocal nature of phosphate exchange implies, for example, that the extent of particulate release of phosphate, in response to a reduction in ambient levels, is modified by the correspounding increase in solution phosphate. This suggests the importance of water movement characteristics on the extent of phosphate release from sediment particulates. Turbulent displacement of sediment particles to the relatively phosphorus-poor water column could maximize phosphate release from particle surfaces.

Figure 7 shows that phosphate release from fine sediments was greater when ambient phosphate was maintained at relatively low levels by lake water replacement. The dashed line of the figure indicates that following 2 hours exposure to 100 ml lake water, 0.5 g sediment released approximately 1.28 μM PO_4 g^{-1}; corresponding to an ambient phosphate level of 6.5 μM PO_4 l^{-1}. While sediment impact on ambient phosphate level was reduced from that observed with 1 g material per 100 ml (Figure 2) weight-normalized phosphate release was higher. This could indicate inhibiting effects of increased ambient phosphate on rate of net particulate release. Fine sediments released a total of approximately 1.57 μM PO_4 g^{-1} in response to ambient medium renewal.

Contrast in sediment response shown in Figure 7 was dominated by differences in phosphate release during the 15 - 30 minute exposure interval. Within the initial 15 minute exposure interval, sediments released 1.0 μM PO_4 g^{-1} resulting in ambient level near 5.1 μM PO_4 l^{-1}. Materials exposed to renewed medium, containing 0.1 μM PO_4 l^{-1}, released an additional 0.38 μM PO_4 g^{-1}, while continued exposure to 5.1 μM PO_4 l^{-1} restricted release to 0.13 μM PO_4 g^{-1}. The ratio of differences in phosphate released to differences in ambient phosphate within

Figure 7. Net reactive phosphate released from fine sediments under conditions of ambient phosphate accumulation (Δ-Δ), and cumulative phosphate released from fine sediments to ambient lake water replaced at 15 minute intervals (O-O). Lake water initially contained 0.10 μM PO_4 l^{-1}. Values are expressed as a mean of six replicates ±1 standard error.


Reactive Phosphate Released (uM PO4 g-1 dry weight)
1.600
1.500
1.400
1.300
1.200
1.100
1.000
Duration Of Sediment-Lake Water Exposure (Minutes)
10
20
30
40
50
60
70
80
90
100
110
120

the 15 - 30 minute exposure period was:

$$\frac{0.38 - 0.13}{5.10 - 0.10} = 0.05 .$$

This ratio declined during subsequent exposure intervals, indicating effects of diminishing quantities of desorbable phosphate associated with particles exposed to renewed medium.

The cumulative total of phosphate released to renewed medium, 1.57 μM PO_4 g^{-1}, was considered an estimate of desorbable particulate phosphate at time 0; and measured release during exposure intervals as a reduction in that amount. The data conformed to first order kinetics.

The general form of phosphate exchange can be expressed as:

$$\text{particulate} - PO_4 \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{solution} - PO_4$$

where k_1 and k_2 are exchange rate constants. The rate of particulate -lake water phosphate exchange can be expressed by:

$$-\frac{dP}{dt} = k_1P - k_2S$$

where P is particulate PO_4 and S is solution PO_4. If solution phosphate is reduced to levels below those supporting steady state and maintained low through ambient replacement, then the rate of change of P in approaching equilibrium with phosphate-poor lake water may be approximated from:

$$-\frac{dP}{dt} = k_1P .$$

Applied here, the equation indicates that the rate of change of particulate desorbable phosphate, $\frac{dP}{dt}$, is equal to a constant times the amount on the particle, and

$$\frac{dP}{P} = -k_1 dt \quad .$$

Integrating both sides the equation becomes a linear expression,

$$\ln P = -k_1 t + P \; .$$

The intercept P is the estimated desorbable particulate phosphate at t = 0. Specifically, for the data presented here,

$$\ln(\mu M \; PO_4 \; g^{-1}) = -0.059 + 0.324 \; .$$

The linearity of the data obtained ($r^2 = 0.995$) implies that observed release rates were a function of particle content. The difference between the calculated intercept of 1.383 µM PO_4 g^{-1} ($e^{.324} = 1.383$) and estimated 1.57 µM may reflect error involved in the implicit assumption that phosphate release within the initial 15 minutes interval was negligibly affected by ambient phosphate levels. The slope, k_1 was an estimate of the rate of change of particulate phosphate and calculated as 0.059 min^{-1}. While the release rate was specific to particle and environmental characteristics, the suggestion that it was a function of the amount of desorbable phosphate associated with particles exposed to a phosphate-poor environment may be generally applicable when $\frac{k_2}{k_1}$ is small.

DISCUSSION

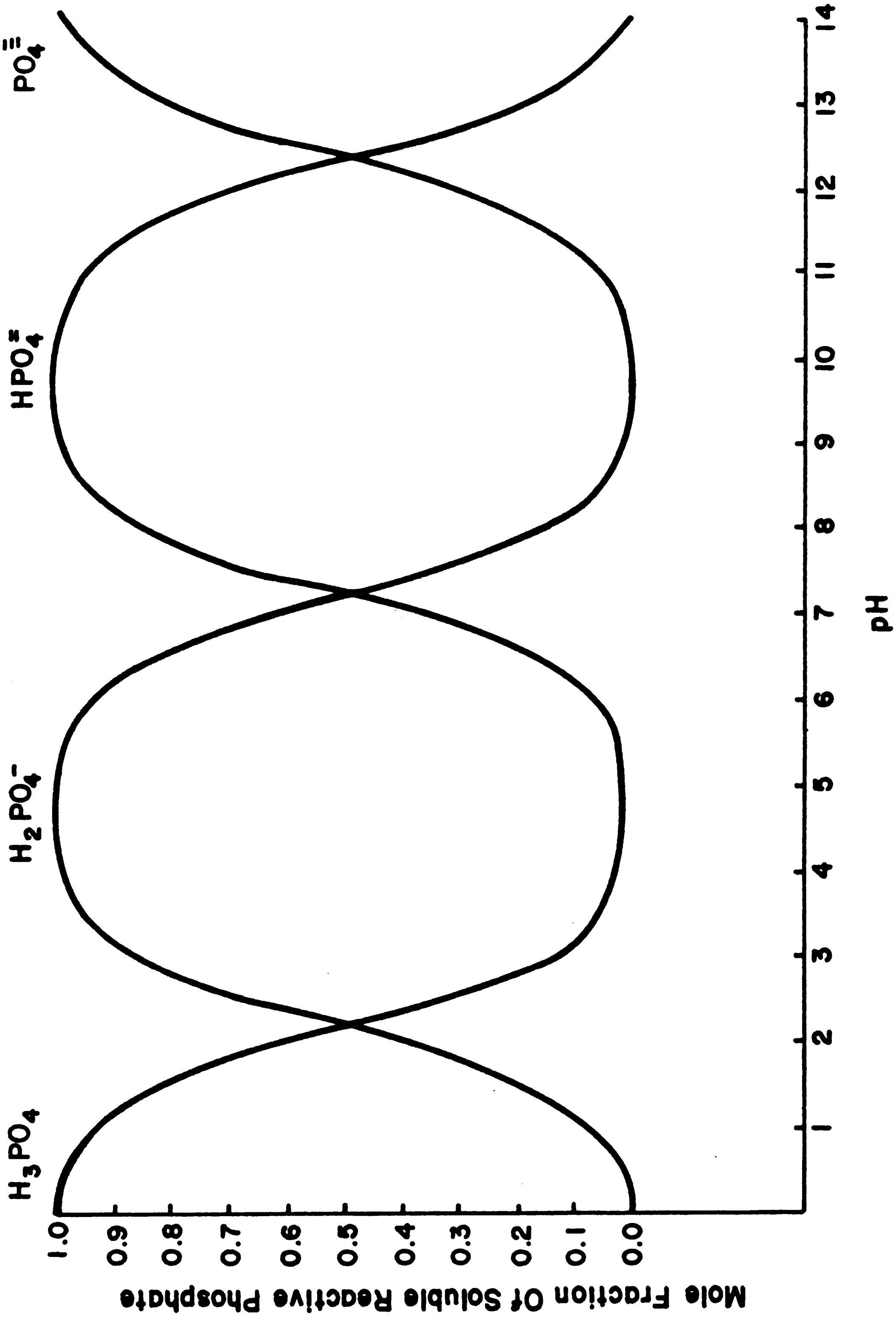
In contrast to overlying water, inorganic phosphorus frequently constitutes a major portion of total phosphorus in sediments (Sommers, et al. 1970). Phosphate originating from mineralization of sedimented organic matter or flux from deeper anaerobic sediment layers can result in interstitial phosphate levels greater than those of overlying water. Relatively high interstitial phosphate can result in gradients, such as the one measured here. Because phosphate gradients represent potential for release of sediment phosphate to overlying water, the nature of mechanisms involved in developing and maintaining gradients deserves attention.

Estimating the potential of phosphorus liberation from littoral sediments to overlying water can be approached by examining the effects of certain phosphate reactions between solid and solution sediment components. In addition to the impact of phosphate sorption/desorption reactions, equilibria characterized by solubility of solid Ca-phosphate precipitates can influence levels of interstitial phosphate, particularly in sediments of lakes that experience epilimnetic calcium precipitation (Stumm and Leckie, 1971). Evidence of a midsummer decline in Lake Lansing littoral and epilimnetic calcium, suggests presence of calcium in shallow sediments and warrants examination of the potential impact of Ca-phosphate solubility equilibria on observed phosphorus levels in sediment solution.

Since calcium phosphate equilibria expressions involve interactions between activities of specific ionic phosphate species and other soluble components of the aqueous medium, it is useful to consider factors influencing these variables with respect to the data presented. Soluble reactive phosphorus is considered to exist as one or more of the forms of phosphoric acid, ie. H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}. The forms dominating soluble phosphate levels depends on pH. Under pH conditions of the work discussed here, concern is with $H_2PO_4^-$ and HPO_4^{2-} (Figure 8). If soluble reactive phosphorus measurements used in this study are taken as estimates of ionic phosphate levels, the amount of each form present can be determined from measurements of ambient pH. An additional level of consideration is drawn from observations of physical chemistry that the reactivity of a given ion may not be entirely determined by its molar concentration. The concept is contained in the Law of Mass Action which states that 'at a given temperature, the rate of a chemical reaction is proportional to the active masses of the reactants', indicating that activity of soluble phosphate species is a relevant parameter when considering chemical reactions.

Concept of activity accounts for differences between observed and ideal behavior of solutes. When greater than 10^{-4} molar, the ionic strength of a given solution has been empirically determined to be an important factor modifying the effects of the concentration of the ion of interest.

Figure 8. Relation between pH and relative proportions of soluble reactive phosphate species. Calculations based on dissociation constants of phosphoric acid, mono-, and dihydrogen phosphate ions in dilute solution.


H_3PO_4
$H_2PO_4^-$
$HPO_4^=$
$PO_4^{\equiv}$
Mole Fraction Of Soluble Reactive Phosphate
1.0
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.0
pH
1
2
3
4
5
6
7
8
9
10
11
12
13
14

Quantification of this modifying factor, expressed in the activity coefficient, takes into account the concentration and valence of all ions in solution. For solutions of ionic strength less than 0.01 molar, the activity coefficient, γ, can be calculated from:

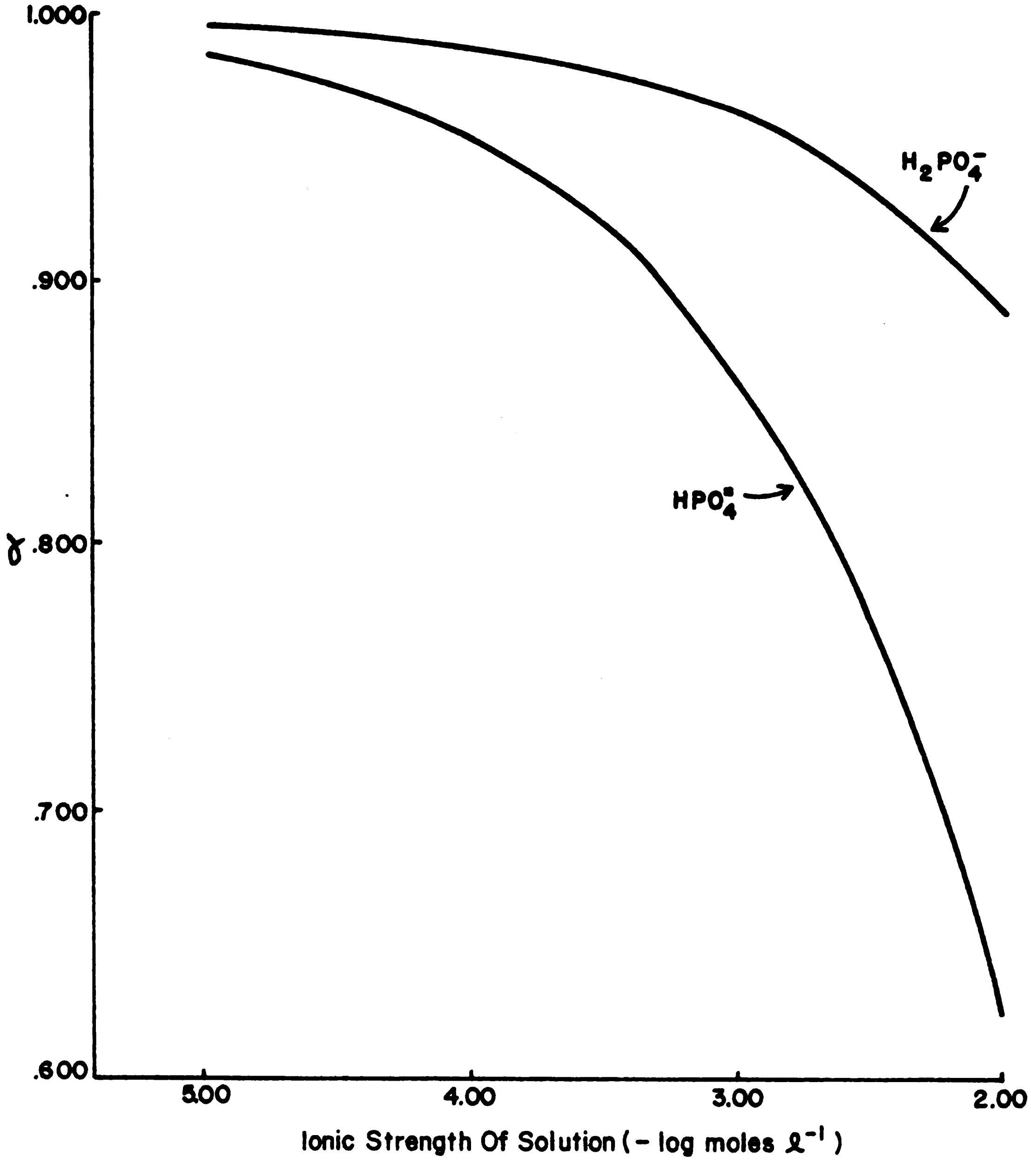
$$\log \gamma = -A\ z^2\sqrt{u}$$

where A is the temperature-dependent Debye-Huckel constant, equal to 0.5085 at 25°C, z is the valence of the ion of interest, and u is the ionic strength of the solution, $u = \frac{1}{2}(\sum_{i=1}^{n}$ molar concentration of ion i times the valence of ion i squared). Solute activity is equal to the concentration times the activity coefficient (Tinoco, et al. 1978).

Activity of soluble reactive phosphate is a function of pH dependent ionic distribution (Figure 8) and solution ionic strength (Figure 9).

Determination of ionic strength is most accurately made with knowledge of all ions of solution. However, it can be approximated with measurements of dominant forms (Stumm and Morgan, 1981). Ionic strength was approximated here as 3 x molar calcium levels (after Lindsay and Moreno, 1960). Based on measurements of soluble calcium of Lake Lansing epilimnion, ionic strength was taken as 3×10^{-3} molar. Griffin and Jurinak (1973), working with 124 river water samples and 27 soil extracts, found an excellent correlation ($r^2 = 0.992$) between ionic strength and electrical conductance, u = 0.013 EC, where EC is expressed as millimhos cm^{-1}. Electrical conductance of Lake Lansing epilimnion varied around a mean of 0.26 millimhos cm^{-1}, indicating

Figure 9. Influence of ionic strength (u) on activity coefficient (γ) of mono- and dihydrogen phosphate for solutions of ionic strength less than 0.01 molar. γ was calculated from: $\log \gamma = -0.5085\ z^2 \sqrt{u}$.

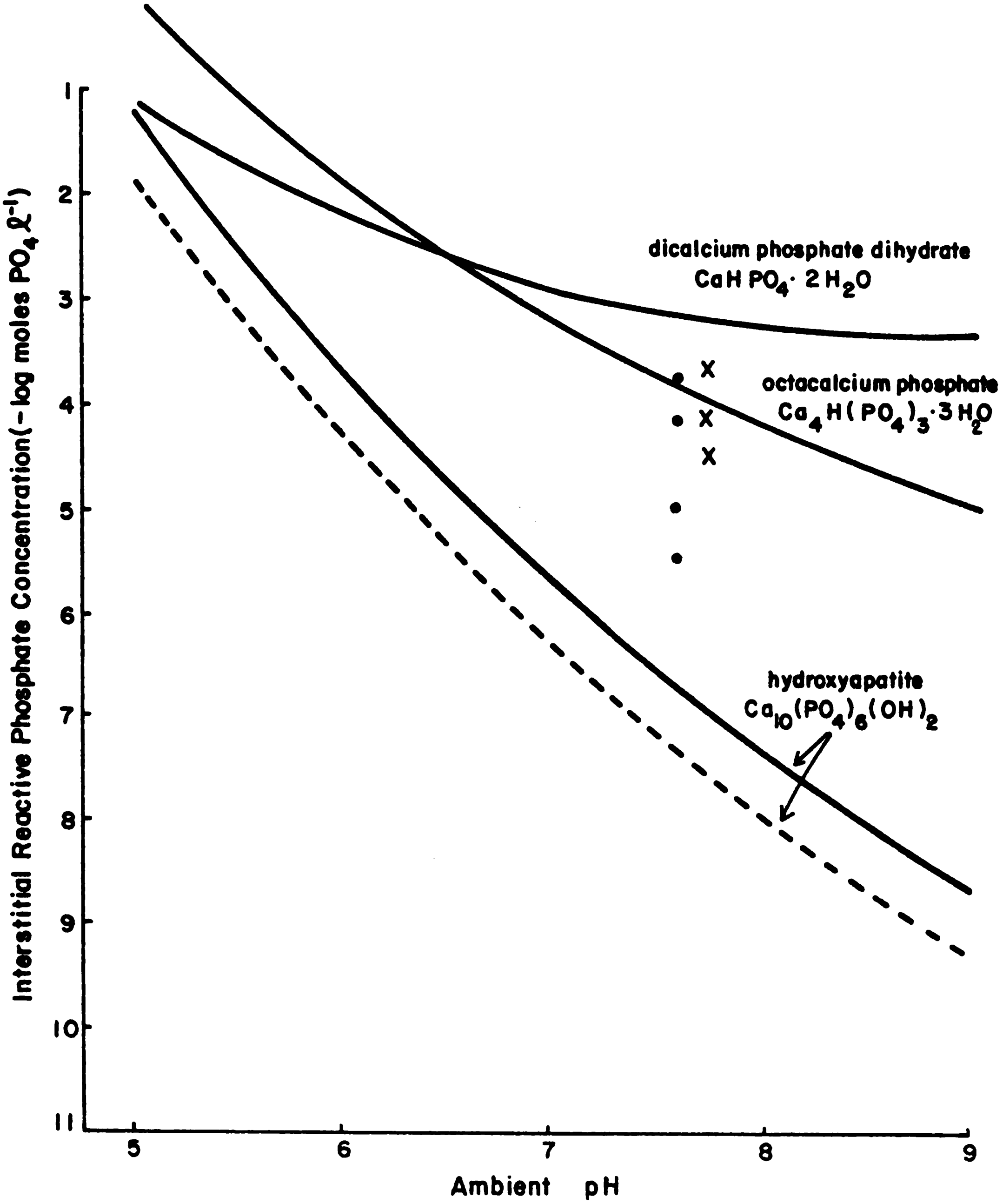

1.000
.900
.800
.700
.600
γ
5.00
4.00
3.00
2.00
Ionic Strength Of Solution (– log moles ℓ^{-1})
$H_2PO_4^-$
$HPO_4^=$

an ionic strength estimate near that made with calcium.

Incorporating information presented above and appropriate solubility expressions, the expected levels of total soluble reactive phosphorus in equilibrium with dicalcium phosphate, octacalcium phosphate, and hydroxyapatite can be calculated (Figure 10; also cf. Appendix 4). Calculations yield activities of soluble phosphate which have been converted to concentrations (using assumptions presented above) for comparison with data collected in this study. Although calcium phosphates other than those presented in Figure 10 may form in sediments, lack of information concerning their solubilities precludes inclusion in the Figure. Fluoroapatite which generally has a lower solubility than hydroxyapatite in the pH range of interest, has been excluded for lack of information concerning solution levels of fluoride ion.

Significance of the solubility diagram of Figure 10 stems from the potential of sediment interstitial water phosphorus levels to approach equilibrium with the stable calcium phosphate minerals considered. Measured soluble phosphate values falling above a given line indicate supersaturation with respect to that compound and suggest that precipitation is possible. Soluble phosphate levels below the line indicate undersaturation and that the corresponding compound would dissolve. Figure 10 suggests that dicalcium phosphate and octacalcium phosphate form or remain stable only at high levels of soluble phosphate. If soluble phosphate levels decreased, as a result of diffusion, biogenic uptake, or association with hydroxyapatite, these

Figure 10. Solubility diagram for certain calcium phosphate compounds in sediments at 25^{o}C. Levels of soluble reactive phosphate were calculated by considering appropriate solubility equilibria and assuming calcium levels maintained at 1 x 10^{-3} molar (solid lines) and 3 x 10^{-3} molar (dashed line). (•) refer to ambient reactive phosphate levels following 48 hours exposure to whole sediments to high initial levels of ambient phosphate. (X) same, but for fine sediment exposure. Phosphate activities were converted to concentrations for comparison with observed levels of total interstitial phosphate of south basin sediments.


Interstitial Reactive Phosphate Concentration(-log moles PO_4 ℓ^{-1})
1
2
3
4
5
6
7
8
9
10
11
5
6
7
8
9
Ambient pH
dicalcium phosphate dihydrate
$CaHPO_4 \cdot 2H_2O$
octacalcium phosphate
$Ca_4H(PO_4)_3 \cdot 3H_2O$
hydroxyapatite
$Ca_{10}(PO_4)_6(OH)_2$
X
X
X

minerals would tend to dissolve. Using measured levels of total interstitial phosphorus of sediments as an estimate of soluble reactive phosphate, surficial sediment solution levels ranged from about 0.581 to 3.871 $\mu M\ l^{-1}$, corresponding to 6.24 and 5.41, respectively, on the vertical scale. Based on the assumptions used to calculate the isotherms, sediments would experience dissolution of any dicalcium or octacalcium phosphate present and precipitation of hydroxyapatite at pH levels above 7. Calcium increases above 1×10^{-3} molar would have the effect of shifting the lines parallel (to the ones indicated) and downward (cf. predicted hydroxyapatite isotherm under conditions of 3×10^{-3} molar calcium, dashed line of Figure 10). In general, solution pH, calcium, and ionic strength can greatly influence equilibrium phosphate levels. Observed variability in interstitial phosphorus could result from differences in the magnitude of these parameters over short distances within the sediment.

Considerations of interstitial water buffering of soluble phosphate imposed by calcium phosphate equilibria suggest that equilibrium levels can be highly influenced by physicochemical parameters. In the dynamic environment of shallow water sediments, an important variable modifying sediment impact on soluble phosphate is the rate of response to ambient changes. In general, only the most soluble phosphate compounds react fast enough to determine solution phosphate activity under environmental conditions that may change within short time intervals. Kinetic information concerning the approach of ambient phosphate to equilibria with calcium phosphate minerals in sediments is, at best, qualitative. Dicalcium phosphate is considered the most reactive of the compounds discussed here, with reaction kinetics suggesting that equilibrium could be obtained within hours of ambient phosphate perturbation (Moreno, et al. 1960). Hydroxyapatite is the most insoluble of the forms presented. The pH and temperature dependent rate of formation involves slow transformation of amorphous calcium phosphate into crystalline form. Reported rates of apatite formation vary from two weeks (Stumm and Leckie, 1971) to over three months (Moreno, et al. 1960). It appears that at pH levels greater than 7, apatite phosphate may influence the direction and endpoint of ambient phosphate changes. However, attainment of equilibrium levels will likely be restricted to largely undisturbed systems where slow dissolution and precipitation reactions have adequate time to dominate ambient phosphate levels.

Laboratory work reported here shows that under aerobic conditions a major portion of sediment-induced change from initial phosphate levels occurred within 30 minutes of exposure. The rate of change following 2 hours exposure to all initial phosphate levels examined was greatly reduced. Quasi-equilibrium phosphate levels observed in the laboratory following 2 and 48 hours exposure to high initial levels of ambient phosphate are plotted at the corresponding mean final pH (Figure 10). Solution ionic strength, calcium, and temperature in experiments were similar to those assumed when calculating the isotherms. While a few points fall near predicted phosphate levels in equilibrium with octacalcium phosphate, viewed as a set, the data appear to be independent of the isotherm. Moreno, et al. (1960) observed that approximately one month was required for formation of the mineral under a similar pH and temperature regime. In the laboratory work presented here, calcium and phosphate activities did not exceed the solubility product of the more responsive dicalcium phosphate mineral. These observations indicate that 2 and 48 hour ambient phosphate concentrations stabilized at levels other than those predicted by solubility equilibria of calcium phosphate minerals considered and implicate other controlling mechanisms.

Sediment induced changes in ambient reactive phosphate have been attributed to phosphate association with pre-existing solids rather than through formation of insoluble precipitates. The Langmuir adsorption isotherm has been commonly used to quantitatively describe particulate induced changes in ambient reactive phosphate for soil (cf. Ellis and Knezek, 1972) and sediment (cf. Syers, et al 1973) systems. In contrast to solubility equilibria, Langmuir analysis describes the net effect of participating particulate-solution phosphate associations.

The Langmuir equation was originally based on the kinetic theory of gases. The same equation has been applied to adsorption of ions from solution by solids (Olsen and Watanabe, 1957). The analysis stems from the general consideration that observed solution levels result from the net effect of desorption and sorption reactions acting simultaneously (Shapiro and

Fried, 1959). Individually, the rate of release of phosphate from sediments is a function of sorbed particulate phosphate, $\frac{x}{m}$:

$$\text{rate of release} = k_1(\frac{x}{m})$$

where k_1 is a constant. Rate of phosphate sorption on particulate surfaces is a function of solution phosphate activity, (P), and the difference between phosphate sorbed and a sediment-specific sorption maximum, B:

$$\text{rate of sorption} = k_2(P)(B-\frac{x}{m}) \ .$$

At equilibrium, the rate of release equals the rate of sorption:

$$k_1(\frac{x}{m}) = k_2(P)(B-\frac{x}{m}) \ .$$

A linear transformation of the equilibrium expressions yields:

$$\frac{(P)}{\frac{x}{m}} = \frac{1}{KB} + \frac{(P)}{B}$$

where K is a sediment-specific constant, equal to $\frac{k_2}{k_1}$, and is related to the binding of particulate surfaces for sorbed phosphate.

The Langmuir constants, B and K, can be used to quantitatively describe the relationship between sorbed and equilibrium ambient phosphate for a given sediment-solution system. Values for the constants can be obtained from experimental observations if a plot of $\frac{(P)}{\frac{x}{m}}$ versus (P) is linear. The slope and intercept are equal to $\frac{1}{B}$ and $\frac{1}{KB}$, respectively.

Since $\frac{x}{m}$ of the Langmuir relationship refers to amount of phosphate sorbed, measurements of solution phosphate losses should be adjusted for the amount sorbed prior to sediment-solution exposure. In laboratory work with whole sediments, this adjustment was taken as the amount released following long-term exposure to phosphorus-poor lake water (0.305 μM PO_4 g^{-1}). This was added to measured solution phosphate losses to estimate $\frac{x}{m}$. Corresponding ambient phosphate activity was estimated by assuming ionic strength to be 3 x 10^{-3} molar (ie. 3 x observed soluble calcium) and pH of 7.6 . Under these conditions, measured concentrations of soluble reactive phosphate can be converted to activities by multiplying by 0.82 . A plot of values obtained following long-term whole sediment exposure to the three highest levels of initial ambient phosphate resulted in a straight line with a slope of 0.058, B = 17.179 μM PO_4 g^{-1}; and an intercept of 2.125, K = 0.027 liters per μM PO_4.

Estimation of the constants K and B for fine sediment material was made by adding 1.38 μM PO_4 g^{-1}, the quanitity of desorbable phosphate estimated from analysis of PO_4 released to renewed ambient medium, to measured solution phosphate losses. At an ambient pH of 7.75 and ionic strength of 3 x 10^{-3} molar, the conversion factor used to obtain ambient phosphate activity was 0.81 . The constant B, indicating sorption maximum, was estimated as 47.091 μM PO_4 g^{-1}. The constant K, related to phosphate binding energy, was 0.002 liters per μM PO_4.

The sorption maximum of fine material was over twice that calculated for whole sediments, and may reflect the greater proportion of small particles (< 227 μm in diameter). The larger surface area per unit weight of material implies a greater number of sites for phosphate sorption. An interesting feature of the analysis is the apparent ten fold reduction in the value of the constant related to the binding energy of processed fine sediments. This may indicate that expected carbonate precipitation on particulate surfaces during preparation of fine sediments altered phosphate sorption characteristics. Green, et al. (1978) found a negative correlation between value of the sorption energy parameter and calcite content of Maumee River sediments.

Figure 11 illustrates the relationship between sorbed phosphate and ambient activity, based on experimental estimates of Langmuir constants B and K. The sediment-specific relationships suggest that particulate-solution phosphate exchange would result from perturbation of equilibrium ambient phosphate activity (resulting from infusion of epilimnetic water through surficial sediments, for example). The direction and extent of particulate response would depend on phosphate activity of infusing medium, and sediment weight/solution volume ratio.

An equation that quantitatively describes sediment response to perturbation from equilibrium ambient phosphate can be obtained from the Langmuir expression:

$$\frac{(P)}{\frac{x}{m}} = \frac{1}{KB} + \frac{(P)}{B}$$

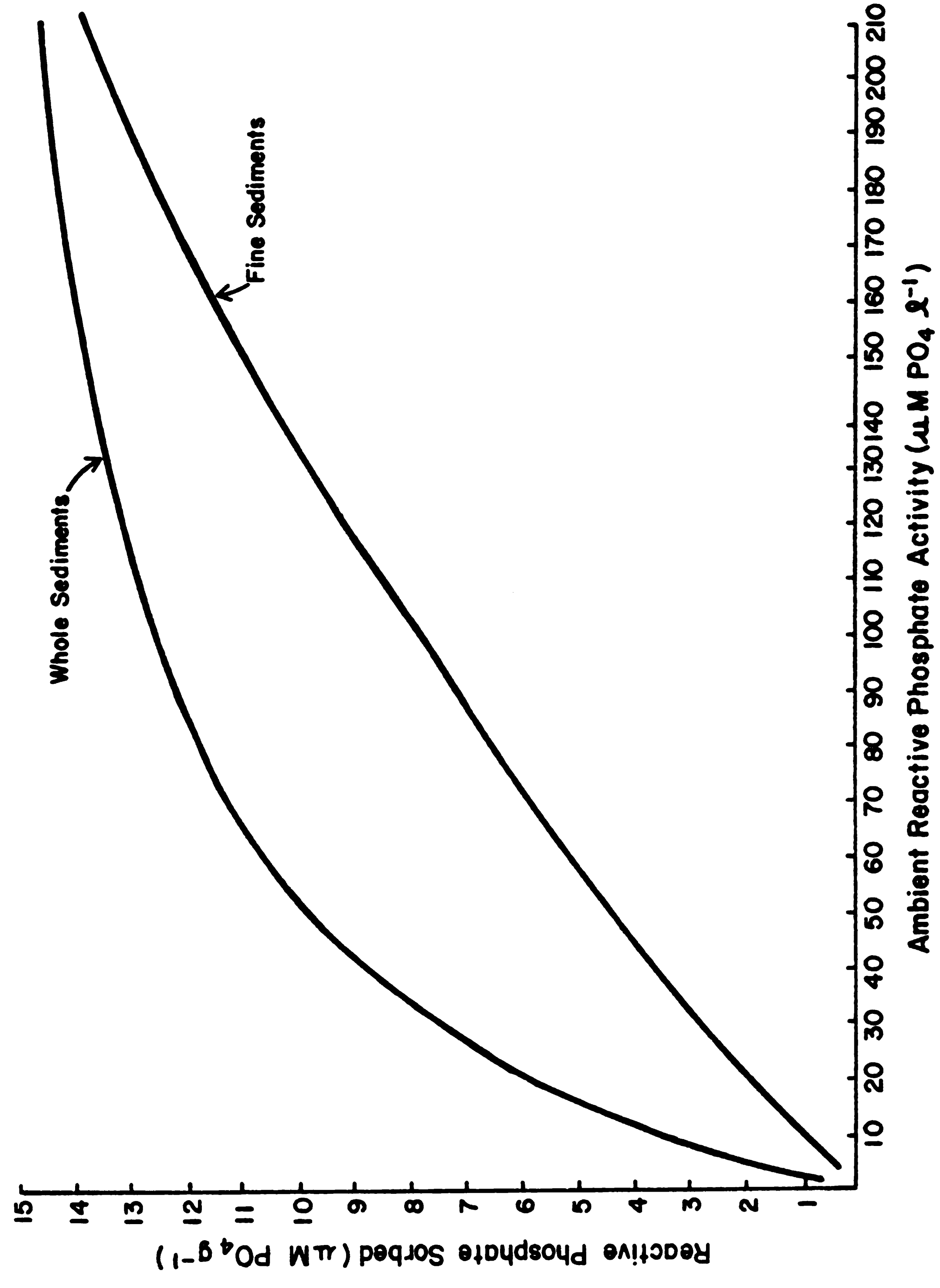
$$= \frac{1}{B}\left(\frac{1}{K} + P\right)$$

$$\frac{1}{\frac{x}{m}} = \frac{1}{BP}\left(\frac{1}{K} + P\right)$$

$$\frac{x}{m} = \frac{B(P)}{\frac{1}{K} + (P)} \qquad \text{(Equation 1).}$$

If y is taken as the net quantity of phosphate exchanged with sediment, then $\frac{x}{m} - y$ is the level of sorbed sediment

Figure 11. Calculated relationship between phosphate sorbed by whole and fine sediments and ambient phosphate activity. Each isotherm was developed from estimations of Langmuir constants B and K. Ionic strength 3 x 10^{-3} M and equilibrium with respect to particulate-solution phosphate exchange were assumed. The pH was taken as 7.60 and 7.75 for whole and fine sediments, respectively.


Reactive Phosphate Sorbed (μM PO4 g-1)
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
10
20
30
40
50
60
70
80
90
100
110
120
130
140
150
160
170
180
190
200
210
Ambient Reactive Phosphate Activity (μM PO4 ℓ-1)
Whole Sediments
Fine Sediments

phosphate following exchange. Ambient phosphate in equilibrium with $\frac{x}{m} - y$ will depend on impact of phosphate mass exchanged on solution activity:

$$\frac{x}{m} - y = \frac{B(P_1 + \Delta P)}{\frac{1}{K} + (P_1 + \Delta P)} \qquad \text{(Equation 2)}$$

where P_1 is the phosphate activity of infusing medium, and ΔP is a function of the solid : solution following perturbation and a conversion factor relating phosphate exchanged to resultant ambient phosphate activity.

Laboratory results obtained with whole sediments can be used to illustrate an application of these considerations. Estimated phosphate activity at crossover, 2.624 $\mu M\ PO_4\ l^{-1}$ (ie. 3.20 x 0.82 = 2.624) reflected an estimated sorbed phosphate level, $\frac{x}{m}$, of 1.137 $\mu M\ PO_4\ g^{-1}$ (from Equation 1). Perturbation of the sediment system by introduction to phosphate-poor lake water ($P_1 = 0.13 \times 0.82 = 0.107\ \mu M\ PO_4\ l^{-1}$) resulted in net phosphate release from sediments. At the solid : solution of 0.8 g dry weight per 100 ml lake water, each $\mu M\ PO_4$ released per gram would increase ambient phosphate activity by 6.56 $\mu M\ PO_4\ l^{-1}$ (ie. 8 $\mu M\ PO_4\ l^{-1}$ x 0.82 = 6.56). For this example, ΔP of Equation 2 is equal to 6.56 $g\ \ell^{-1}$ times y; where y is expressed in $\mu M\ PO_4\ g^{-1}$. Expected weight-normalized phosphate release, y, can be calculated from:

$$1.137 - y = \frac{17.179\ (0.107 + 6.56y)}{37.037 + (0.107 + 6.56y)}\ .$$

Expected phosphate release is 0.28 $\mu M\ PO_4\ g^{-1}$.

In general, calculated net phosphate exchange resulting from whole sediment exposure to initial phosphate activities examined agree reasonably well with observations of net exchange (Table 1).

Employing analogous considerations to results obtained with fine sediment, calculated net release following exposure to initial phosphate activities used is somewhat less than that observed (Table 2). This may reflect error in the estimated crossover value since points used for its estimation were widely separated (cf. Figure 2).

Influence of solid : solution on net phosphate exchange is indicated from measurements of phosphate desorption from 0.5 g fine sediment under conditions of ambient medium renewal. In this experiment, 100 ml lake water was renewed six times and considered similar to a solid : solution of 0.83 g l^{-1}. Assuming pre-disturbed ambient activity of 18.63 μM PO_4 l^{-1}, the calculated net release of 1.58 μM PO_4 g^{-1} is comparable to measured cumulative release of 1.57 μM PO_4 g^{-1}. Similarly, calculated desorption from 0.5 g to 100 ml lake water is 1.22 μM PO_4 g^{-1} and comparable to observed release of 1.26 μM.

A few limitations of the preceded analysis should be noted. Care should be exercised when applying constants. Any experimental error experienced when obtaining data could lead to serious deviations between calculated and operational values of B and K. Further, an implicit assumption of Equation 2 is that phosphate sorbed is entirely releaseable. This may not be true. If sorbed phosphate forms metastable associations with the particulate sorbent, hydrated ferric oxides for example,

Table 1. Calculated and measured net phosphate exchange ($\mu M\ PO_4\ g^{-1}$) between whole sediments and infusing lake water of different initial phosphate activity ($\mu M\ PO_4\ l^{-1}$). Values assume equilibrium conditions with ionic strength $3 \times 10^{-3}M$ and pH 7.60 . Negative sign indicates net sediment sorption of phosphate.

Initial Phosphate Activity	Calculated Exchange	Measured Exchange
0.107	0.28	0.30
1.246	0.15	0.16
5.108	-0.27	-0.31

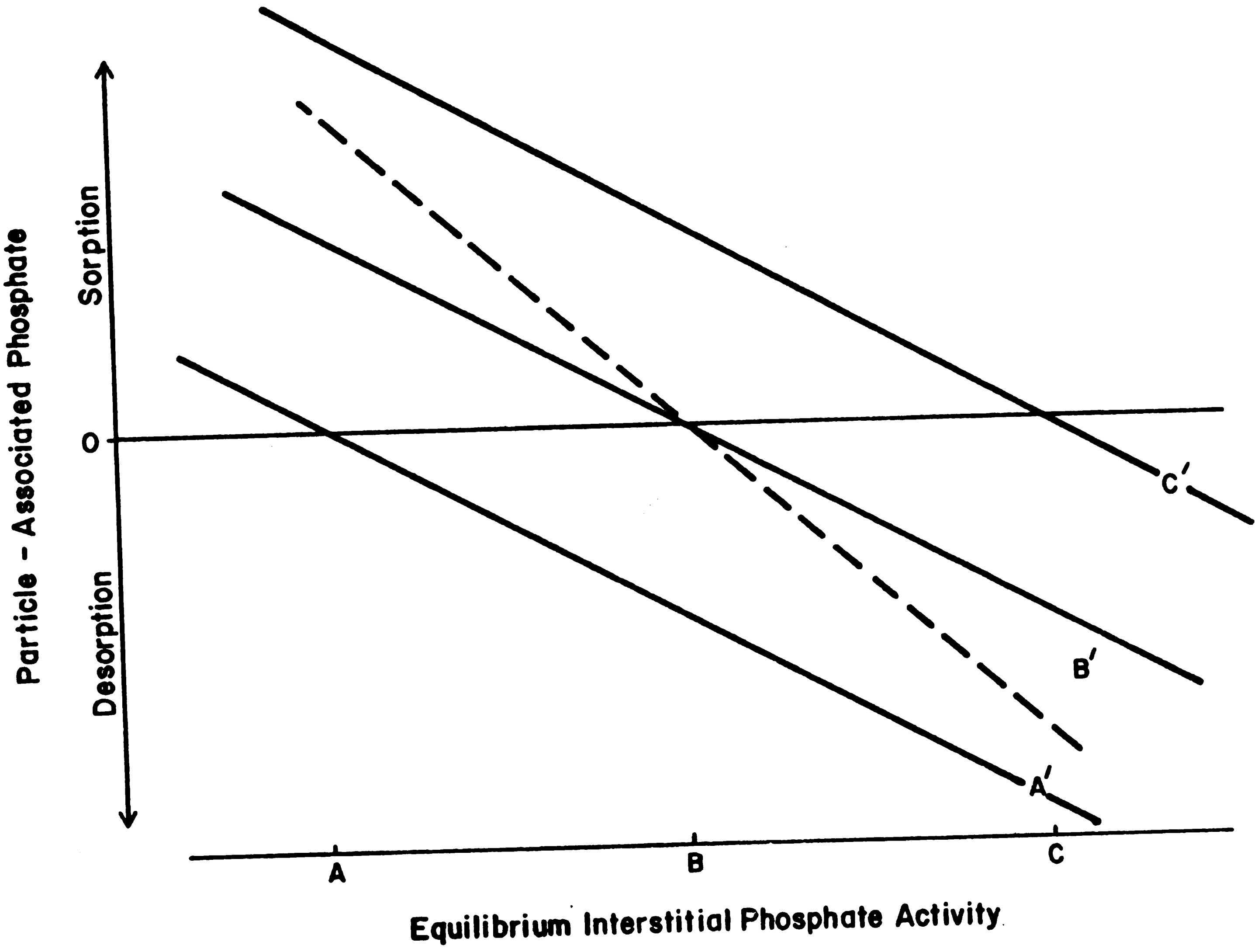
Table 2. Calculated and measured net phosphate exchange ($\mu M\ PO_4\ g^{-1}$) between fine sediments and infusing lake water of different initial phosphate activity ($\mu M\ PO_4\ l^{-1}$). Calculated exchange is based on experimentally estimated ambient crossover activity of 18.63 $\mu M\ PO_4\ l^{-1}$ (A), and on a hypothetical crossover activity of 22 $\mu M\ PO_4\ l^{-1}$ (B). Values assume equilibrium conditions with ionic strength 3×10^{-3} M and pH 7.75.

Initial Phosphate Activity	Calculated Exchange A	Calculated Exchange B	Measured Exchange
0.057	0.96	1.14	1.18
1.284	0.90	1.07	1.08
4.965	0.71	0.87	0.82

changes in the sorbent over time may affect its ability to release phosphate following perturbation. While these considerations suggest that modifications of Equation 2 may be required for quantitative predictions, the expression may be used to qualitatively envision response of a sediment-solution system to ambient perturbation.

A generalized representation of sorption/desorption concepts discussed is presented in Figure 12. Based on observations of this study, the figure illustrates hypothetical interactions between sediment particulates, characterized by phosphate binding energy (K) and sorption capacity (B), and infusing media. The direction and extent of phosphate exchange depends on equilibrium interstitial phosphate activity (A<B<C), phosphate activity of infusing medium (A´<B´<C´), and solid : solution of the disturbed system. For example, under conditions of constant solid : solution, particulate release of phosphate would be expected following infusion of medium of activity A´ into sediments previously resting under an interstitial equilibrium phosphate level of B. A new interstitial equilibrium could result and would be expected to fall somewhere between A and B. On the other hand, if medium C´ disturbed sediments resting at B, phosphate sorption would be predicted, and a new interstitial equilibrium expected between B and C. No net exchange is expected if interstitial and infusing medium phosphate activities are equal. The Figure also suggests that the extent of particle-solution phosphate exchange is expected to increase with increasing difference between infusing medium and

Figure 12. Net exchange of particle associated phosphate as a function of phosphate activity of infusing medium and of interstitial water in an idealized sorption-desorption exchange system. Letters indicate phosphate activity level (A<B<C) and superscripts indicate infusing media. The dashed curve indicates sediment response to infusing phosphate activity level (B´) if sediment : solution is reduced as result of perturbation.


Particle - Associated Phosphate
Sorption
0
Desorption
C′
B′
A′
A
B
C
Equilibrium Interstitial Phosphate Activity

interstitial phosphate activity levels.

The dashed line of Figure 12 indicates expected particulate response if infusion of medium B′ resulted in a sediment : solution lower than that of the sediment environment. For example, if the movement of infusing medium (with activity B′) were great enough to lift surficial sediment particulates (previously resting at C) from the interface, phosphate release would be greater than that expected if particulates were not displaced.

Literature estimates of sediment contribution of phosphate to overlying water are largely limited to estimates of diffusive flux (Burns and Ross, 1972; Holdren, et al. 1977). They represent a largely static relationship between lake and sediment compartments in that the potential impacts of water movement are not considered. Limnological thought is pervaded by the idea that summer density stratification results in stagnation of large lake-strata. There is little basis for this view. Even deep water sediments are disturbed from several millimeters to several centimeters (Davis, 1968, 1973; Wetzel, et al. 1972). Considerations drawn from the data of this study suggest that particle-solution chemical equilibria can interact with hydromechanics at the shallow sediment-water interface to influence rate and extent of sediment phosphate flux. Shallow sediments must be considered a particle-solution phosphate exchange system that functionally interacts with water movements to influence phosphorus dynamics.

LITERATURE CITED

American Public Health Association. 1976. Standard Methods for the Examination of Water and Wastewater 14th ed. Washington, D. C., American Public Health Association, 1193 pp.

Bache, B.W. 1963. Aluminum and iron phosphate studies relating to soil. I. Solution and hydrolysis of variscite and strengite. J. Soil Sci., 14: 113-123.

Batterson, T.R. 1980. Arsenic in Lake Lansing, Michigan. Ph.D. Diss., Michigan State University, East Lansing, Michigan.

Burns, N.M., and C.W. Ross. 1972. Oxygen-nutrient relationships within the central basin of Lake Erie. In H.E. Allen and J.P. Kramer, eds. Nutrients in Natural Waters. New York, Wiley-Interscience. 457 pp.

Carignan, R., and R.J. Flett. 1981. Postdepositional mobility of phosphorus in lake sediment. Limnol. Oceanogr., 26: 361-366.

Carritt, D.E., and S. Goodgal. 1954. Sorption reactions and some ecological implications. Deep-Sea Res., 1: 224-243.

Chen, Y.S., J.N. Bulter, and W. Stumm. 1973. Phosphate adsorption reactions with clay minerals. J. Colloid Interface Science, 43: 421-436.

Clesceri, N.L. and G.F. Lee. 1965. Hydrolysis of condensed phosphate -I: Non-sterile environment. Int. J. Air Wat. Poll., 9: 723-742.

Davis, M.B. 1968. Pollen grains in lake sediments. Redeposition caused by seasonal water circulation. Science, 162: 796-799.

Davis, M.B. 1973. Redeposition of pollen grains in lake sediment. Limnol. Oceanog., 18: 44-52.

Edzwald, J.K. 1977. Phosphorus in aquatic systems: the role of the sediments. In I.H. Suffet, ed. Fate of Pollutants in the Air and Water Environments, Vol. 8. New York, Wiley-Interscience. 214pp.

Ellis, B.G., and B.D. Knezek. 1972. Adsorption reactions of micronutrients in soils. In J.J. Mortvedt, P.M. Giordano, and W.L. Lindsay, eds. Micronutrients in Agriculture. Madison, Wisconsin, Soil Sci. Soc. Amer., Inc., Chapter 4.

Fitzgerald, G.P. 1970. Aerobic lake muds for the removal of phosphorus from lake waters. Limnol. Oceanogr., 15: 550-555.

Golterman, H.L., C.C. Bakels, and J. Jakobs-Mogelin. 1969. Availability of mud phosphates for growth of algae. Verh. Internat. Verein. Limnol., 17: 467-479.

Green, D.B., T.J. Logan, and N.E. Smeck. 1978. Phosphate adsorption-desorption characteristics of suspended sediments in the Maumee River Basin of Ohio. J. Environ. Qual., 7: 208-212.

Griffin, R.A., and J.J. Jurinak. 1973. Estimation of activity coefficients from the electrical conductivity of natural aquatic systems and soil extracts. Soil Sci., 116: 26-30.

Harter, R.D. 1968. Adsorption of phosphorus by lake sediment. Soil Sci Soc. Amer. Proc., 32: 514-518.

Hayes, F.R. 1964. The mud-water interface. Oceanogr. Mar. Biol. Ann. Rev., 2: 121-145.

Hayes, F.R., J.A. McCarter, M.L. Cameron, and D.A. Livingstone. 1952. On the kinetics of phosphorus exchange in lakes. J. Ecol., 40: 202-216.

Holdren, G.C., D.E. Armstrong, and R.E. Harris. 1977. Interstitial inorganic phosphorus concentrations in Lakes Mendota and Wingra. Water Res., 11: 1041-1047.

Hutchinson, G.E. 1957. A Treatise on Limnology. I. Geography, Physics, and Chemistry. New York, John Wiley and Sons, Inc., 1015 pp.

Johnson, D.L. 1971. Simultaneous determinations of arsenate and phosphate in natural waters. Environ. Sci., Technol., 5: 411-414.

Latterell, J.J., R.F. Holt, and D.R. Timmons. 1971. Phosphorus availability in lake sediments. J. Soil and Water Cons., 26: 21-24.

Li, W.C., D.E. Armstrong, J.D.H. Williams, R.F. Harris, and J.K. Syers. 1972. Rate and extent of inorganic phosphate exchange in lake sediments. Soil Sci. Amer. Proc., 36: 279-285.

Lindsay, W.L., and E.C. Moreno. 1960. Phosphate phase equilibria in soils. Soil Sci.Soc. Amer. Proc., 24: 177-182.

Mayer, L.M., and S.P. Gloss. 1980. Buffering of silica and phosphate in a turbid river. Limnol. Oceanogr., 25: 12-22.

McCallister, D.L., and T.J. Logan. 1978. Phosphate adsorption-desorption characteristics of soils and bottom sediments in the Maumee River Basin of Ohio. J. Environ. Qual., 7: 87-92.

Moreno, E.C., W.E. Brown, G. Osbern. 1960. Stability of dicalcium phosphate dihydrate in aqueous solutions and solubility of octacalcium phosphate. Soil Sci. Soc. Amer. Proc., 24: 94-98.

Mortimer, C.H. 1941. The exchange of dissolved substances between mud and water in lakes (Parts I and II). J. Ecol., 29: 280-329.

Mortimer, C.H. 1942. The exchange of dissolved substances between mud and water in lakes (Parts III, IV, summary, and references). J. Ecol., 30: 147-201.

Mortimer, C.H. 1971. Chemical exchanges between sediments and water in the Great Lakes - speculation on probable regulatory mechanisms. Limnol. Oceanogr., 16: 387-404.

Oloya, T.O., and T.J. Logan. 1980. Phosphate desorption from soils and sediments with varying levels of extractable phosphate. J. Environ. Qual., 9: 526-531.

Olsen, S.R., and F.S. Wateranabe. 1957. A method to determine phosphorus adsorption maximum of soils as measured by the Langmuir isotherm. Soil Sci. Soc. Amer. Proc., 21: 144-149.

Pomeroy, L.R., E.E. Smith, and C.M. Grant. 1965. The exchange of phosphate between estuarine water and sediments. Limnol. Oceanogr., 10: 167-172.

Ponnamperuma, F.N. E.M. Tianco, and T. Loy. 1967. Redox equilibria in flooded soils : I. The iron hydroxide system. Soil Sci., 103: 374-382.

Ruttner, F. 1963. Fundamentals of Limnology. (Translat. D.G. Frey and F.E.J. Fry.) Toronto, Univeristy of Toronto Press, 295 pp.

Ryden, J.C., J.K. Syers, R.F. Harris. 1973. Phosphorus in runoff and streams. Adv. in Agron., 25: 1-45.

Shapiro, J. 1973. Determination of dissolved reactive phosphate in natural waters. In E.J. Griffith, A. Beeton, J.M. Spencer, D.T. Mitchell, eds. Environmental Phosphorus Handbook. New York, Wiley-Interscience. 357 pp.

Shapiro, R.E. and M. Fried. 1959. Relative release and retentiveness of soil phosphates. Soil Soc. Amer. Proc., 23: 195-198.

Skukla, S.S., J.K. Syers, J.D.H. Williams, D.E. Armstrong, and R.F. Harris. 1971. Sorption of inorganic phosphorus by lake sediments. Soil Sci. Soc. Amer. Proc., 35: 244-249.

Sommers, L.E., R.F. Harris, J.D.H. Williams, D.E. Armstrong, and J.K. Syers. 1970. Determination of total inorganic phosphorus in lake sediments. Limnol. Oceanogr., 15: 301-304.

Sonzoni, W.C., S.C. Chapra, D.E. Armstrong, and T.J. Logan. 1981. Bioavailability of phosphorus imputs to lakes: Significance to management Great Lakes Environmental Planning Study, Contribution No. 40., 30 pp.

Stumm, W., and J.O. Leckie. 1971. Phosphate exchange with sediments; Its role in the productivity of surface waters. London, Proc. 5th Int. Wat. Pollut. Res. Conf. Pergamon Press. III, 26: 1-16.

Stumm, W., and J.J. Morgan. 1981. Aquatic Chemistry. An Introduction Emphasing Chemical Equilibria in Natural Waters. Second Edition. New York, Wiley-Interscience, 780 pp.

Syers, J.K., R.F. Harris, and D.E. Armstrong. 1973. Phosphate Chemistry in lake sediments. J. Environ. Qual., 2: 1-14.

Taylor, A.W., and H.M. Konishi. 1971. Phosphate equilibria on stream sediment and soil in a watershed draining an agricultural region. J. Agr. Food Chem., 19: 827-831.

Taylor, A.W., and H.M. Kunishi. 1974. Soil adsorption of phosphates from wastewater. In factors Involved in Land Application of Agricultural and Municipal Wastes. Beltsville, Maryland, U.S. Department of Agric., 195 pp.

Tinoco, I., K. Saucer, and J.C. Wang. 1978. Physical Chemistry. Principles and Applications in Biological Sciences. Englewood Cliffs, N.J., Prentice-Hall, Inc., 624 pp.

Turner, R.C. and J.S. Clark. 1956. The pH of calcareous soils. Soil Sci., 82: 337-341.

United States Environmental Protection Agency. 1979. Methods for Chemical Analysis of Water and Wastes. Environ. Monitoring and Support Lab. (O.R.D.), Cincinnati, Ohio, EPA-600 4-79-020.

Vollenweider, R.A. and J.J. Kerekes. 1980. Background and summary results of OECD cooperative program on eutrophication. pp. 25-36. Proc. International symposium on inland waters and lake restoration. Washington, D.C., U.S. EPA 440/5-81.

Wetzel, R.G. 1970. Recent and postglacial production rates of a marl lake. Limnol. Oceanogr., 15: 491-503.

Wetzel, R.G. 1971. The role of carbon in hard-water marl lakes. In G.E. Likens, ed. Nutrients and Eutrophication: The Limiting-Nutrient Controversy. Special Symposium, Amer. Soc. Limnol. Oceanogr., 1: 84-91.

Wetzel, R.G. 1975. Limnology. Philadelphia, W.B. Saunders Co., 743 pp.

Wetzel, R.G., P.H. Rich, M.C. Miller, and H.L. Allen. 1972. Metabolism of dissolved and particulate detrital carbon in a temperate hard-water lake. Mem. Ist. Ital. Idrobiol., 29: 185-243.

Wier, D.R., and C.A. Black. 1968. Mineralization of organic phosphorus in soils as affected by addition of inorganic phosphorus. Soil Sci. Soc. Amer. Proc., 32: 51-55.

Williams, J.D., J.K. Syers, R.F. Harris, and D.E. Armstrong. 1970. Adsorption and desorption of inorganic phosphate by lake sediments. Soil Sci. Soc. Amer. Proc., 35: 250-255.

Williams, J.D. J.K. Syers, S.S. Shukla, R.F. Harris, and D.E. Armstrong. 1971. Levels of inorganic and total phosphorus in lake sediments as related to other sediment parameters. Environ. Sci. Technol., 5: 1113-1120.

Williams, J.D., H. Shear, and R.L. Thomas. 1980. Availability to *Scenedesmus quadricauda* of different forms of phosphorus in sedimentary materials from the Great Lakes. Limnol. Oceanogr., 25: 1-11.

Winter, T.C. 1978. Ground-water component of lake water and nutrient budgets. Verh. Int. Ver. Limnol., 20: 438-444.

Woodruff, J.R. and E.J. Kamprath. 1965. Phosphorus adsorption maximum as measured by the Langmuir isotherm and its relationship to phosphorus availability. Soil Sci. Soc. Amer. Proc., 29: 148-150.

Appendix 1. Effects of solution arsenate on phosphate determinations and effectiveness of arsenate reductant in eliminating interference.

Table A-1. Effect of measured additions of arsenate (added as $Na_2HAsO_4 \cdot 7H_2O$) on determinations of phosphate in standard (KH_2PO_4) preparations.[1]

As Concentration (μM AsO_4 l^{-1})	P Concentration (μM PO_4 l^{-1})	P:As (μM PO_4 l^{-1}/ μM AsO_4 l^{-1})	Increase in Measured P (μM PO_4 l^{-1})	% Increase
0.33	0.00	-	0.03	-
	0.81	2.42	0.19	24.10
	1.61	4.84	0.23	14.00
	8.07	24.22	0.32	4.00
1.33	0.00	-	0.16	-
	0.81	0.60	0.74	92.10
	1.61	1.21	1.00	62.00
	8.07	6.05	1.15	14.30

[1] Activity coefficients for AsO_4 and PO_4 assumed equal to 1.

Figure A-1. Percent over-estimation of phosphate concentration as a function of the ratio of phosphate to arsenate in solution.

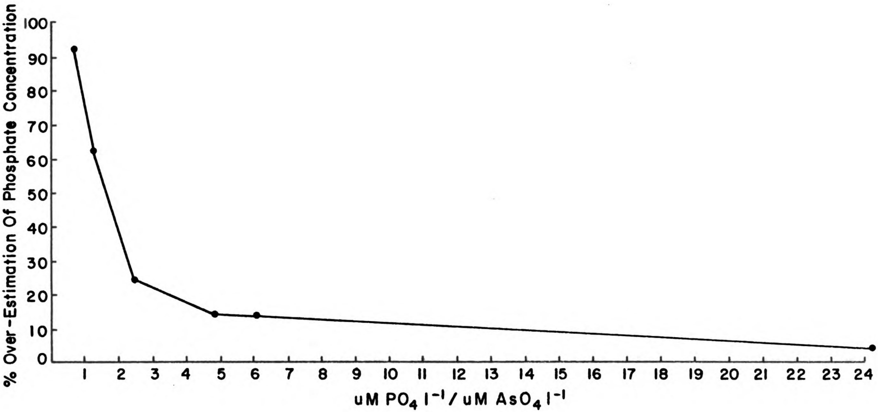

% Over-Estimation Of Phosphate Concentration
100
90
80
70
60
50
40
30
20
10
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
uM PO_4 l^{-1} / uM AsO_4 l^{-1}

Table A-2. Effects of addition of arsenate reductant on determinations of phosphate in distilled water solutions containing measured additions of phosphate and arsenate.

Concentration (μM l^{-1})		Measured PO_4 Concentration (μM l^{-1})	
PO_4	AsO_4	w/o Reductant	with Reductant[1]
0.00	0.00	0.00	0.00
	0.33	0.03	0.00
	1.33	0.16	0.00
0.81	0.00	0.84	0.74
	0.33	1.00	0.77
	1.33	1.55	0.77
1.61	0.00	1.61	1.58
	0.33	1.84	1.58
	1.33	2.68	1.71
8.07	0.00	8.07	8.07
	0.33	8.39	8.07
	1.33	9.29	8.03

1. 5 ml of arsenate reductant containing $Na_2S_2O_5$ and $Na_2S_2O_3 \cdot 5H_2O$ were added to samples and standards (cf. Johnson, 1971).

Appendix 2. Estimates of phosphorus, iron, and calcium added to fine sediment particulates during the evaporation and drying treatment.

Table A-3. Concentration of soluble reactive and total phosphate, iron, and calcium in shallow sediment collections and lake water used in processing fine sediment. Corresponding values represent estimates of the amount of each component deposited during drying (at 80°C) of 96 g of sediment material[1].

Soluble Component	Lake Water		Collected Sediment		Total
	(μM l^{-1})	(μM)	(μM l^{-1})	(μM)	(μM)
Reactive Phosphate	0.16	2.42	1.39	6.68	9.10
Total Phosphate	0.48	7.26	2.19	10.58	17.84
Total Iron	0.89	13.43	2.06	9.94	23.37
Total Calcium	798	11976	1267	6113	18089

1. Dry weight of fine sediment fraction (<227 μm in diameter) was 40% of whole sediment dry weight. Approximately 28% of fine sediment dry weight was lost following combustion at 550 °C for 1 hour.

Appendix 3. Total iron content of filtrate following exposure of sediment particulates to different initial levels of ambient phosphate.

Table A-4. Filterable iron (μM l^{-1}) in lake water of different initial phosphate levels following 0.5, 2.0, and 48 hours exposure to whole sediments[1]. Lake water, prior to sediment addition, contained 0.734 μM Fe l^{-1}.

Initial Lake Water Phosphate (μM l^{-1})	Duration of Exposure (hours) 0.5	2.0	48
0.13	0.895	0.985	0.985
1.52	0.698	0.985	0.842
6.23	0.734	0.842	0.842
31.29	0.734	0.842	0.806
122.30	0.734	0.842	0.734
302.90	0.859	0.895	0.698

---

[1] Estimated contribution of filterable iron from aqueous of whole sediment is 0.1 μM Fe l^{-1}.

Table A-5. Filterable iron ($\mu M\ l^{-1}$) in lake water of different initial phosphate levels following 0.5, 2.0, and 48 hours exposure to fine sediments. Lake water prior to sediment addition contained 0.842 μM Fe l^{-1}.

Initial Lake Water Phosphate ($\mu M\ l^{-1}$)	Duration of Exposure (hours) 0.5	2.0	48
0.07	0.985	0.734	0.842
1.58	0.913	0.985	0.734
6.13	0.842	0.842	0.985
32.26	0.842	0.734	0.842
122.30	0.985	0.842	0.734
302.60	0.967	0.842	0.842

Appendix 4. Solubility and dissociation expressions, and calculations used in the development of the calcium phosphate solubility diagram of Figure 10.

Table A-6. Solubility products of calcium phosphate compounds and dissociation constants of phosphoric acid species and water at 25°C used in the development of the solubility diagram of Figure 10[1].

Compound	Chemical Formula	Solubility Expression	pK^1
Dicalcium phosphate dihydrate	$CaHPO_4 \cdot 2H_2O$	$pK = pCa + pHPO_4$	6.56
Octacalcium phosphate	$Ca_4H(PO_4)_3 \cdot 3H_2O$	$pK = 4pCa + pH + 3pPO_4$	46.91
Hydroxyapatite	$Ca_{10}(PO_4)_6(OH)_2$	$pK = 10pCa + 6pPO_4 + 2pOH$	113.70
Phosphoric acid	H_3PO_4	$pK_1 = pH + pH_2PO_4 - pH_3PO_4$	2.12
Dihydrogen phosphate	$H_2PO_4^-$	$pK_2 = pH + pHPO_4 - pH_2PO_4$	7.20
Monohydrogen phosphate	HPO_4^{2-}	$pK_3 = pH + pPO_4 - pHPO_4$	12.32
Water	H_2O	$pK = pH + pOH$	14.00

1. cf. Lindsay and Moreno, 1960.

CALCIUM PHOSPHATE SOLUBILITY CALCULATIONS

The following calculations of soluble reactive phosphate concentration in equilibrium with calcium phosphate compounds at pH 7 and 25°C illustrate the development of Figure 10. Here, calcium concentration was taken as 1×10^{-3} molar, and ionic strength as 3×10^{-3} M. Activity coefficients, γ , were calculated from:

$$\log \gamma = -A\ z^2 \sqrt{u}$$

where A is a Debye-Huckel constant equal to 0.5085 at 25°C, and z is the charge of the ion of interest. Accordingly, $\gamma Ca^{2+} = 0.774$, $\gamma H_2PO_4^- = 0.938$, $\gamma HPO_4^{2-} = 0.774$, and $\gamma PO_4^{3-} = 0.561$. 'p' indicates negative log of the activity. For example, if Ca^{2+} concentration = 1×10^{-3} M, Ca^{2+} activity = 1×10^{-3} (0.774) = 7.74×10^{-4}; and pCa = 3.11.

A. Dicalcium phosphate dihydrate - $CaHPO_4 \cdot 2H_2O$

$$\begin{aligned} 6.56 &= pCa + pHPO_4 \\ 6.56 &= 3.11 + pHPO_4 \\ 3.45 &= pHPO_4\ . \end{aligned}$$ (cf. Table A-6)

Equilibrium levels of $H_2PO_4^-$ in solution at pH 7 can be obtained from:

$$\begin{aligned} 7.20 &= pH + pHPO_4 - pH_2PO_4 \\ 7.20 &= 7.00 + 3.45 - pH_2PO_4 \\ 3.25 &= pH_2PO_4\ . \end{aligned}$$

$pHPO_4^{2-} = 3.45 = 3.55 \times 10^{-4}$ M $HPO_4^{2-}\ l^{-1}$, and $pH_2PO_4^- = 3.25 = 5.62 \times 10^{-4}$ M $H_2PO_4^-\ l^{-1}$.

Molar concentration x γ = activity; activity/γ = molar concentration.

ion	activity (M l^{-1})	γ	concentration (M l^{-1})
HPO_4^{2-}	3.55×10^{-4}	0.774	4.59×10^{-4}
$H_2PO_4^-$	5.62×10^{-4}	0.938	5.99×10^{-4}

$$\begin{aligned} \text{p(reactive phosphate concentration)} &= \text{p}(5.99 \times 10^{-4} + 4.59 \times 10^{-4}) \\ &= 2.98\ . \end{aligned}$$

B. Octacalcium phosphate - $Ca_4H(PO_4)_3 \cdot 3H_2O$

$$\begin{aligned} 46.91 &+ 4\text{pCa} + \text{pH} + 3\text{pPO}_4 \\ 46.91 &= 4(3.11) + 7.00 + 3\text{pPO}_4 \\ 9.16 &= \text{pPO}_4\ . \end{aligned}$$

Equlibrium levels of HPO_4^{2-} can be obtained from:

$$\begin{aligned} 12.32 &= \text{pH} + \text{pPO}_4 - \text{pHPO}_4 \\ 12.32 &= 7.00 + 9.16 - \text{pHPO}_4 \\ 3.84 &= \text{pHPO}_4\ . \end{aligned}$$

($H_2PO_4^-$) can be obtained from:

$$\begin{aligned} 7.20 &= 7.00 + 3.84 - \text{pH}_2\text{PO}_4 \\ 3.64 &= \text{pH}_2\text{PO}_4\ . \end{aligned}$$

ion	activity (M l^{-1})	γ	concentration (M l^{-1})
PO_4^{3-}	6.92×10^{-10}	0.561	1.23×10^{-9}
HPO_4^{2-}	1.45×10^{-4}	0.774	1.87×10^{-4}
$H_2PO_4^-$	2.29×10^{-4}	0.938	2.44×10^{-4}

p(reactive phosphate concentration) = 3.26 .

C. Hydroxyapatite - $Ca_{10}(PO_4)_6(OH)_2$

ion	activity (M l^{-1})	γ	concentration (M l^{-1})
HPO_4^{2-}	3.55×10^{-4}	0.774	4.59×10^{-4}
$H_2PO_4^-$	5.62×10^{-4}	0.938	5.99×10^{-4}

$$\begin{aligned} \text{p(reactive phosphate concentration)} &= \text{p}(5.99 \times 10^{-4} + 4.59 \times 10^{-4}) \\ &= 2.98\ . \end{aligned}$$