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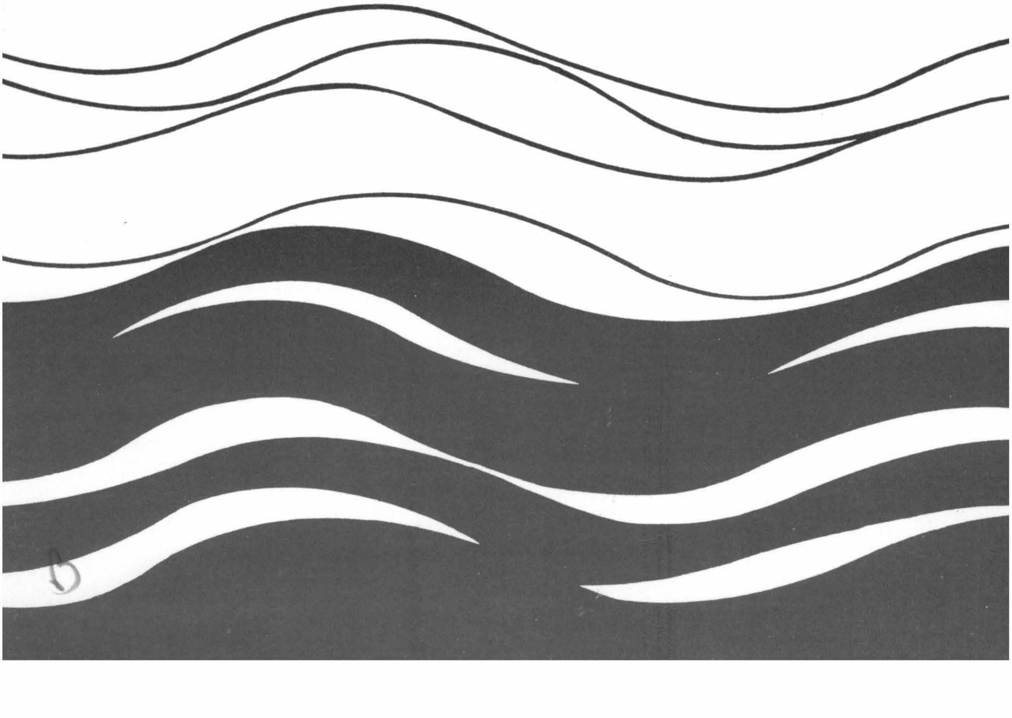
Carol A. Lake & William G. MacIntyre



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ABSTRACT

This investigation sought to provide additional needed information on overenrichment of estuarine areas by examining the extent to which phosphate nutrients are taken up by clay sediments in estuarine and marine environments. Examined specifically was the adsorption of orthophosphate and tripolyphosphate by the four clay minerals most commonly found in Virginia estuaries. A factorial analysis was applied to the design of the experiments in order to examine statistically the effect of pH, salinity, temperature, and initial phosphate concentration on orthophosphate adsorption. The main effects of pH and initial phosphate concentration were statistically important to orthophosphate adsorption. The amount of orthophosphate adsorbed by each of the clays increased in the following order: montmorillonite < kaolinite < illite < chlorite. The orthophosphate adsorption by synthetic clay demonstrated the generality of the adsorption experiments, for similar amounts were adsorbed by both synthetic and natural clays. When the source of phosphorus was tripolyphosphate rather than orthophosphate, each clay adsorbed more phosphorus under similar reaction conditions.

Key words: Phosphate, Adsorption, Clays, Sediment

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INTRODUCTION

Concentration of population and urbanization along seashores and estuaries has created sewage disposal problems. The discharge of domestic sewage and agricultural drainage into estuaries has accelerated nutrient enrichment. This overenrichment or eutrophication has been attributed to the presence of excess nutrients in the aquatic environment. Addition of excess nutrients can stimulate production of organic matter, algal blooms, and aquatic plant growth beyond the oxidative capacity of the system, thereby deteriorating the aesthetic and recreational qualities of our estuaries and nearshore waters. Interest in the role that phosphorus plays in the eutrophic process has led to increasing research on the exchange of phosphorus at the sediment-water interface in lakes, rivers, and estuaries. In natural systems, the sediment acts as a reservoir for phosphorus. Hayes and Phillips [1958] depict the dynamic interaction in the water and sediment system as:

P in aqueous phase	$\rightleftharpoons$	P in solid phase
(a small fraction of total P in system)		(a large fraction of total P in system)

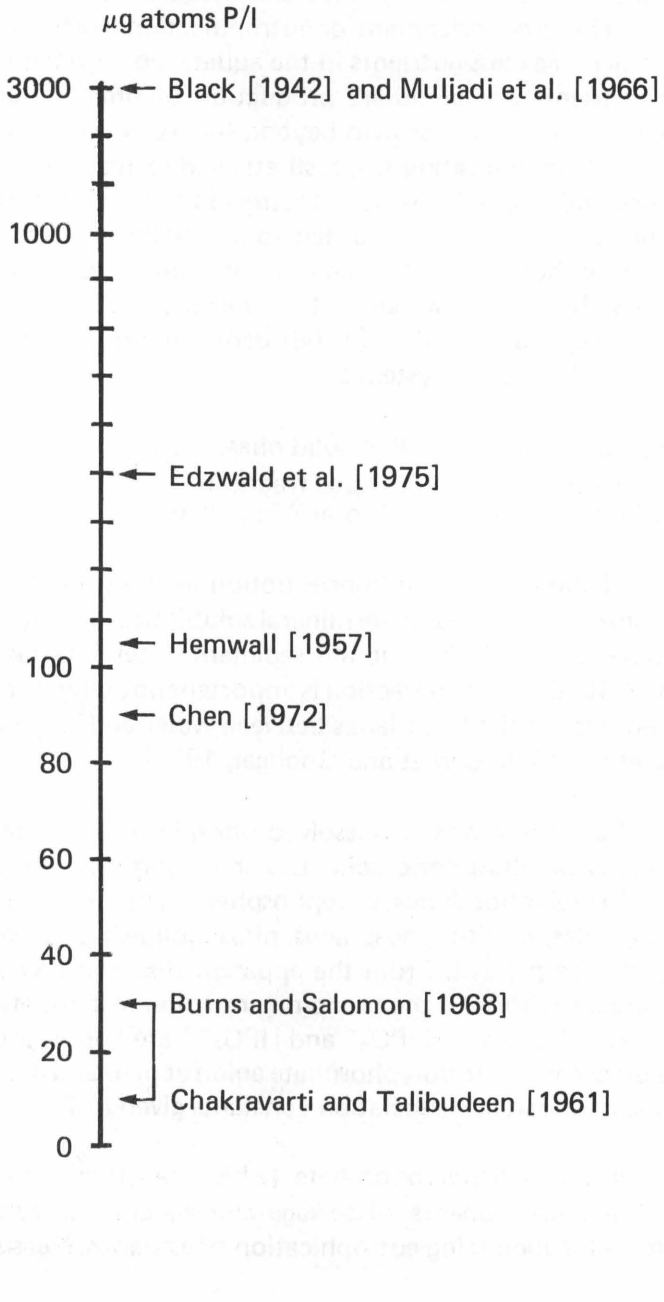
Regulation of the phosphorus concentration in the water by this interaction is controlled by phosphate mineral solubilities, and by adsorption or ion exchange equilibrium at the sediment-water interface [Stumm and Morgan, 1970]. This interaction is important not only at the bottom interface but also at the boundaries between water and suspended solids [Pomeroy et al., 1965; Carritt and Goodgal, 1954].

The most abundant forms of dissolved phosphorus in estuarine water are the anions of phosphoric acid. Lesser amounts of the condensed phosphates (tripolyphosphates, pyrophosphates) and organic phosphates (sugar phosphates; inositol phosphates, phospholipids, phosphoproteins, etc.) may also be present. From the apparent dissociation constants of phosphoric acid *(Table 1),* the predominant anion in synthetic seawater is HPO_4^{-2} at pH 8; both $H_2PO_4^-$ and HPO_4^{-2} are important species at pH 6. The predominant tripolyphosphate anion at pH 6 and 8 is $HP_3O_{10}^{-4}$ on the basis of apparent dissociation constants given in *Table 1.*

Othophosphate and tripolyphosphate (which can hydrolyze to orthophosphate) are components of sewage and agricultural runoff which contribute to the increasing eutrophication of estuaries. Measurement of

FIGURE 1

Phosphate Concentrations Used by Previous Workers



the exchange of phosphate with estuarine sediment is needed in order to describe quantitatively the role of sediments in regulation of phosphorus concentration in estuarine waters. Numerous workers [Frink, 1969; Shukla et al., 1971; Pratt, 1949; Rittenberg et al., 1955; Rochford, 1951; Williams et al., 1970; Armstrong et al., 1971; Jitts, 1959] have indicated the importance of clay minerals in the exchange of phosphate at the sediment-water interface and have considered clays to be signficant sites for the phosphate adsorption displayed by whole sediment samples. The study of both phosphate and polyphosphate adsorption by the clay minerals found in estuarine sediment permits evaluation of one mechanism of phosphate concentration regulation in overlying water. The present work is directed to this task, with the understanding that several other phosphorus uptake mechanisms must be studied by other research efforts. Only then can phosphorus uptake by a sediment be completely accounted for.

Although the adsorption of phosphate by sediment, soil and clay minerals has been extensively studied during the past thirty years, adsorption of phosphate and tripolyphosphate by major clay minerals under estuarine conditions has not been systematically investigated. In general, adsorption has been measured at much higher phosphate concentrations than those found normally in estuarine waters *(Figure 1).* The phosphate concentration in seawater is variable, averaging about 2.3 μg atoms P/l with a range from 0 to 5 μg atoms P/l [Griffith et al., 1973]. The concentration in estuarine waters ranges from zero to 50 μg atoms P/l [Adams et al., 1974; Ferguson and Simmons, 1974; Smith et al., 1977]. Extrapolation from high phosphate concentration data would be tenuous since the mechanism of phosphate adsorption onto clay minerals, particularly kaolinite, oftens varies with phosphate concentration [Muljadi et al., 1966; Kafkafi et al., 1967; Chen, 1972]. Also, most adsorption studies have been carried out in low salinity and low pH solutions.

The present study examines the amount of phosphate and tripolyphosphate adsorbed by clay minerals under estuarine conditions and the effect of environmentally important parameters (pH, phosphate concentration, temperature, salinity) upon this amount. Phosphate adsorption experiments also were conducted on sediments from Elizabeth River Estuary, Virginia. The Elizabeth River, a tributary of the James River, has five influent domestic sewage treatment plants. Frequent overflows from the treatment plants, toxic industrial wastes, and discharges from ships and docking facilities contribute to the apparent poor quality of the river. Little flushing of the river occurs due to the low freshwater inflow. Both eutrophication and general industrial pollution contribute to the deterioriating condition of the Elizabeth River. The Elizabeth River was chosen as a sample site since the authors have extensively studied the phosphorus concentration in its sediment and overlying water.

PREVIOUS PHOSPHATE-CLAY INTERACTION RESEARCH RELATING TO ESTUARIES

Research in the estuarine and inner continental shelf zone [Pratt, 1949; Rittenberg et al., 1955; Rochford, 1951] had demonstrated the importance of clay in the uptake and release of phosphate. Seshappa [1953] observed that increases in phosphate concentrations in the waters off the Malabar Coast of West India were correlated with agitation and suspension of phosphate-rich muds.

Carritt and Goodgal [1954] examined the adsorption of $P^{32}O_4^{-3}$ on suspended sediment in natural waters at various acidities. From the heat of reaction, variation in adsorption with temperature data, and considerations of Arrhenius's equation, they concluded the initial phosphate-solids complex was of limited stability. They also attempted to measure the effect of particle size and mineral composition on the adsorptive properties of the sediments, but results were inconclusive. Pomeroy et al., [1965] also used P^{32} to trace the exchange of phosphate between estuarine water and sediments. They concluded that sediments acted as a buffer for phosphate, because a final concentration of about 1 μ mole PO_4^{-3}/liter was obtained from phosphate-sediment solutions of varying phosphate concentrations (i.e., zero to 8.4 μ mole/liter). Burns and Salomon [1969] studied the reaction of phosphate with kaolinite under varying conditions of temperature, pH, salinity, and phosphate/kaolin ratio. In general, low salinity and pH, and high temperature and clay/phosphate ratio increased the percent phosphate adsorbed. Davis [1968] measured a significant mass transport of phosphorus from estuarine water, gravity-fed through troughs of estuarine muds. Jitts [1958] studied the effect of pH, phosphate concentration, particle size, iron and organic matter on the adsorption of phosphate by Australian estuarine sediment. He proposed that silt acted continuously as a trap for phosphate, and the phosphate adsorbed by the clay minerals was largely irreversibly fixed. More recently, Upchurch [1972] examined the amount of "available" phosphorus in sediments from the Pamlico Estuary, North Carolina, at the zone of transition from fresh to estuarine water. A strong correlation existed between the amount of "available" phosphorus and the oxalate-extractable iron in sediments of low salinity regions. As the salinity increased, the correlation decreased. This decrease in correlation suggested than an iron-phosphate complex formed in the sediment and that the complex was destabilized by increased ionic strenth.

Edzwald et al. [1976] studied the adsorption of phosphate by the clay minerals: kaolinite, montmorillonite, and illite. Some of the adsorption experiments were done in 0.498 M NaCl solution, approaching that found in seawater, i.e. about 0.7 ionic strength. They found that illite adsorbed more than montmorillonite which adsorbed more than kaolinite. The presence of salt did not affect the adsorption of phosphate by illite and montmorillonite but enhanced adsorption by kaolinite.

The adsorption of phosphate [Black, 1942; Hemwall, 1957; Chakravarti and Talibudeen, 1961; Muljadi et al., 1966; Chen, 1972; Edzwald et al., 1974] and of polyphosphates [Hashimoto et al., 1969; Bidwell et al., 1958; Philen and Lehr, 1967; Michael, 1958; Lyons, 1964] by clay minerals has been studied by numerous soil scientists. Though experimental conditions differ from those used in this study, comparison of the amount of phosphate adsorbed by the clay will be made with data obtained here.

EXPERIMENTAL METHODS

The dominant clay minerals in Virginia and North Carolina estuaries are kaolinite, illite, montmorillonite, and chlorite [Nichols, 1972; Nelson, 1958; Upchurch, 1972]. Specimens of clays used in these experiments were obtained from Ward's Natural Science Establishment, Inc. Two of the clays, kaolinite no. 5 and montmorillonite no. 25, are standard clay minerals from American Petroleum Institute Project No. 49. The illite is purified from shale occurring near Fithian, Illinois. The chlorite is a diabentite according to Hey's classification [Ross, 1969] which is labelled thuringite, collected in Donna Ana County, New Mexico. Two synthetic clay species similar to these natural clay minerals were used in the adsorption experiments. A comparison of the phosphorus adsorption ability of synthetic clays with no hydrous oxide (Fe or Ca) and natural clay minerals containing hydrous oxides may give an insight into adsorption mechanism. The synthetic minerals: kaolinite, montmorillonite, beidellite, hectorite, and saponite were supplied by Baroid Division of NL Laboratories, Inc., Houston, Texas. Their chemical composition is given in *Table 2.*

During initial washing with the synthetic seawater [Lyman and Fleming, 1940], the natural clay minerals, except chlorite, released phosphate at concentration levels greater than those used in the study. Chen [1972] found a similar release from illite at concentrations less than 6×10^{-5} M HPO_4^{-2}. The minerals were washed by shaking in synthetic seawater. After approximately a week of shaking, the suspension was filtered and the clay oven dried at 30° C. The washed clays were then resuspended in synthetic seawater, and the suspension was checked again for phosphate release. The clays were rewashed if necessary. In most cases, only one washing was required.

Six grams of clay were added either to 400 ml of synthetic seawater (salinity: 35 ppt) or to 200 ml synthetic seawater and 200 ml distilled water (salinity of 17.5 ppt). The suspension was shaken in a one liter, polypropylene volumetric flask and pH was initially adjusted to 6.0 with 1.0 M HCl solution, pH was measured on a Corning Model 12 meter fitted with a Radiometer combination electrode (GK 2322C). A few drops of Hg_2Cl_2 solution were added to retard bacterial growth. The pH had to be continually readjusted downward for a few days until a constant pH was maintained. This rise in pH was similar to that found by Kafkafi [1968], who explained the increase in pH as the result of hydration of aluminum oxides in the clay structure: $Al\text{-}OH + H_2O \rightarrow Al\text{-}OH_2^+ + OH^-$. Such a rise in pH might also be indicative of the partial decomposition of the clay structure [Chakravarti and Talibudeen, 1961]. Some adsorption experiments were conducted at the pH of the synthetic seawater, i.e., about pH 8.

In each experiment, the volumetric flasks were continuously agitated by a wrist-action shaker while immersed to the graduation mark in a constant temperature (± 0.5° C) water bath. After the clay was equilibrated in synthetic seawater at pH 6 or pH 8 for a week, a few milliliters of a known concentrated solution of NaH_2PO_4 were added to the clay-seawater suspension. Aliquots of the suspension were removed immediately and at various later times using a polyethylene syringe. The aliquot was centrifuged to remove large clay particles and then filtered through a 0.45 μ (Millipore Type HA) membrane filter. The filtrate was analyzed for phosphate [Strickland and Parsons, 1967] by measuring the concentration of a reduced molybdenum-phosphate complex at $\lambda = 810$ nm on a Beckman DU Spectrophotometer.

Experimental values were selected to determine the effect of temperature, salinity, pH, and phosphate concentration on phosphate adsorption by the four clay minerals. The values chosen were within the range likely to occur in estuarine or coastal waters. Temperatures of 5° ± 0.5° C, and 25° ± 0.5° C, and salinities of 17 ppt and 35 ppt were used. The concentration of phosphate ranged from about 4 μg atoms P/l (0.13 ppm) to about 50 μg atoms P/l (1.6 ppm), a range found in estuarine and coastal waters [Griffith et al., 1973; Adams et al., 1974; Ferguson and Simmons, 1974; MacIntyre and Lake, unpublished data]. Since pH 6 was common in estuarine water and sediments [Beck, 1972 and Nichols, 1972 in the James River, Virginia], two acidities were used, pH 6 and pH 8, the latter approximating the pH of seawater, thereby covering the range found in coastal waters.

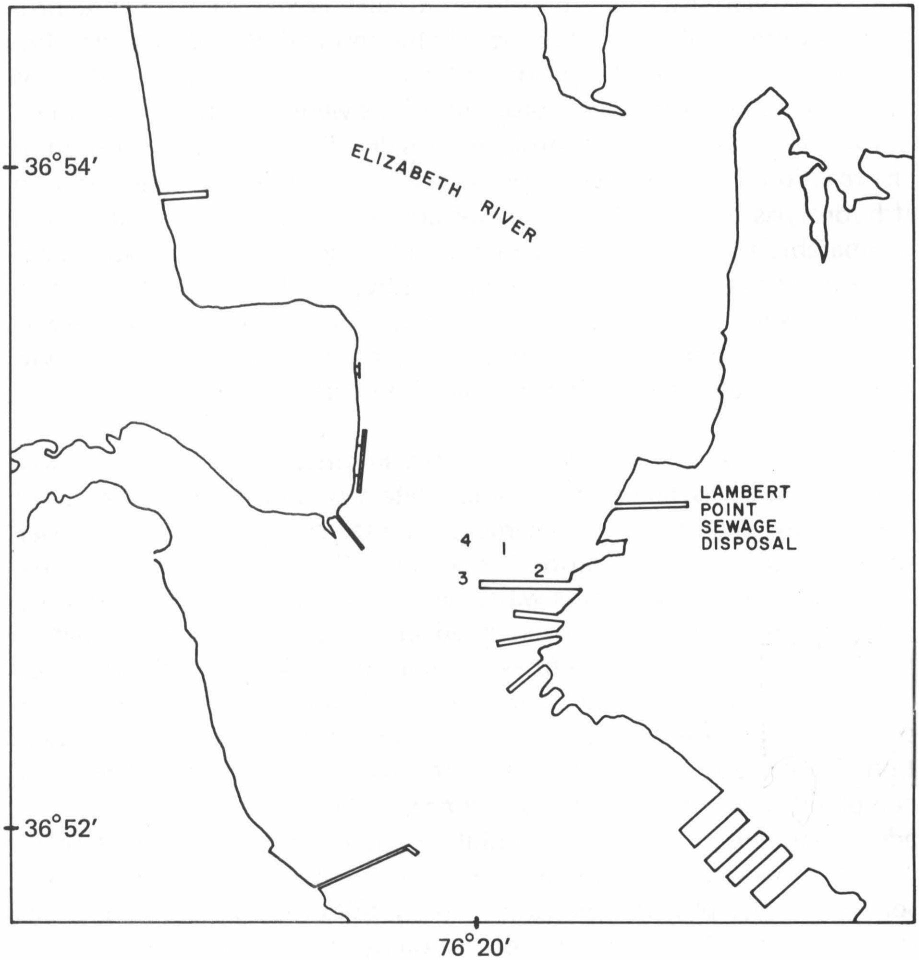
The adsorption of phosphate by the synthetic clays was studied by the same experimental procedure used for the natural clays. Washing the clays was unnecessary since their suspensions in synthetic seawater were nearly phosphate free. Conditions for adsorption experiments with synthetic clays were: pH 6; salinity, 35 ppt; 6 g of clay/400 ml solution; initial phosphate concentration, about 20 μg atoms P/l; temperature, 25° C.

The clay minerals used in this work were also examined for their tripolyphosphate (TPP) adsorption ability. These adsorption experiments were run at pH 6 and pH 8 under the following conditions: 35 ppt salinity, 25° C, and about 21 μg atoms P/l (7 μmoles TPP/l). Experimental procedures were identical to those used in the adsorption studies with orthophosphate except that a solution of $Na_5P_3O_{10}$, a tripolyphosphate, was added as the source of phosphorus. Solutions were prepared immediately before use to minimize hydrolysis of TPP. The TPP concentration in the reaction suspension would produce 21μmoles PO_4^{-3}/l concentration if hydrolysis to orthophosphate was complete. This concentration was comparable to that used in the previously described orthophosphate adsorption studies. Orthophosphate and polyphosphate concentration in solution were followed as a function of time. Polyphosphate was analyzed by hydrolysis to orthophosphate and spectrophotometric determination of phosphate as described in Strickland and Parsons [1967].

Phosphate adsorption experiments were also run on four Elizabeth River sediment samples taken with a small Petersen grab that obtained only the top few centimeters of sediment. The sampling locations were near the Hampton Roads Sanitation District outfall at Lambert Point *(Figure 2).* In the laboratory, excess water was decanted and filtered from the sediment which was then oven dried at 30° C. Desorption of native phosphate from the sediment was determined by adding six grams of dried sediment to 400 ml of synthetic seawater. The suspension was shaken for one week at 25° C, and then analyzed for phosphate in solution. Since the amount of phosphate released by the sediment was small compared to the initial phosphate concentration used in the subsequent adsorption experiments, a few milliliters of a concentrated solution of NaH_2PO_4 were added directly to this sediment suspension and the adsorption of phosphate by the sediments was followed by the experimental procedure described above for adsorption by clay minerals.

In order to obtain composition information on the clays and sediments used in experiments, acid extractable iron and calcium were determined by the method of Upchurch [1972]. In this method, 0.500 g of clay or sediment was added to 50 ml of a solution, prepared by diluting 12 ml of concentrated hydrochloric acid and 9 ml of concentrated sulfuric acid to 3 liters with distilled water. The solution had a pH of about 1.1. The clay-acid suspension was stirred for 2 hours, then filtered through a

FIGURE 2
Sample Sites on the Elizabeth River



0.45 micron type HA Millipore filter. Iron and calcium on the filtrate were analyzed on a Varian Techtron Atomic Absorption Spectrometer, Type AA-5.

RESULTS

I. Statistical Analysis in Reporting Results

The amount of phosphate adsorbed by clay and sediments depends on certain variables such as salinity, temperature, pH, and clay/phosphate ratio. In order to systematically investigate effects of these parameters, a factorial design is applied to the phosphate adsorption experiments.

A 2^k factorial design [Hunter, 1970] is used to estimate the effect of each k variable (e.g. temperature, salinity, and initial phosphate concentration) on the adsorption of phosphate by each clay mineral. In a 2^3 factorial design, each variable is examined at two levels, a high (+) and a low (–), and the variables are studied simultaneously in 2^3 experiments, run in random order. The notation of the factorial design used in this paper is given in *Table 3,* which also shows the high and low levels for each variable and the level of each variable in specific experiments. The results for total phosphorus uptake/gm of clay at pH 6, and the primary effects derived from factorial analysis are presented in *Table 4.* Temperature variation from 5° to 25° C and salinity change from 17 ppt to 35 ppt do not appreciably affect the adsorption of phosphate on any of the clay minerals. With each clay mineral, x_1, the effect of temperature, and x_2, the effect of salinity, are as small or smaller than the $100\,(1-a)$ percent individual confidence limits calculated from a t distribution. Only initial phosphate concentration influences the degree to which a clay adsorbs phosphate, i.e. higher phosphate concentration results in more adsorption.

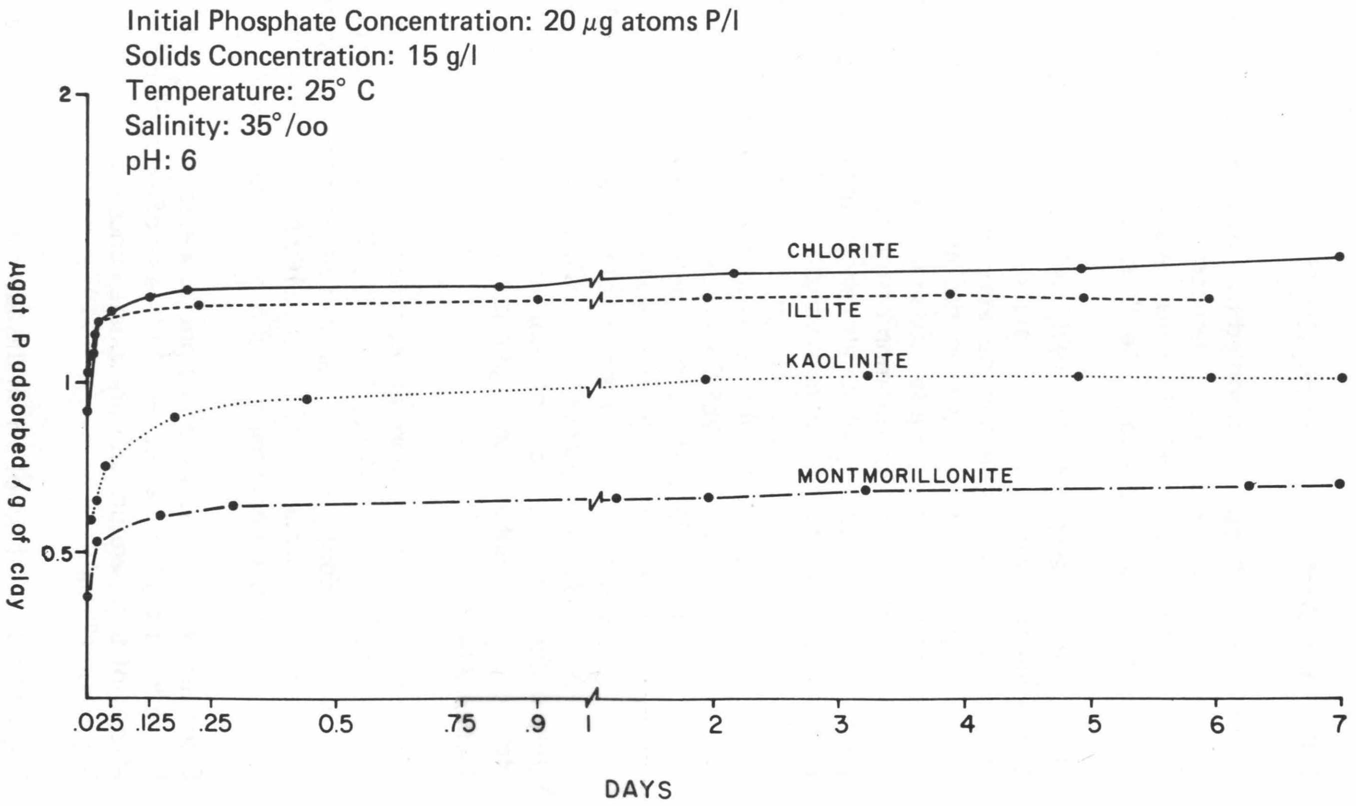
The variance of the primary effect shown is obtained from one set of experiments run in duplicate *(Table 5).* The variance, standard error, and 95 percent confidence limits are calculated from this design following the method of Hunter [1970]. It is tacitly assumed that these statistics are applicable to other experimental runs *(Tables 4* and *6).*

Since pH is known to influence phosphate adsorption, the adsorption by kaolinite at pH 8 was studied. In this set of experiments, the primary effects of termperature and phosphate concentration were statistically important *(Table 5).*

To estimate the effect of pH on the adsorption of phosphate by kaolinite, the results of *Table 4* and *Table 5* are combined into factorial designs

FIGURE 3

Adsorption of Orthophosphate on Estuarine Clay Minerals



Initial Phosphate Concentration: 20 μg atoms P/l
Solids Concentration: 15 g/l
Temperature: 25° C
Salinity: 35°/oo
pH: 6

at salinity 17 ppt and at salinity 35 ppt with the variables: temperature, pH, and phosphate concentration. Results of the two designs *(Table 6)* indicate the importance of all three variables on the phosphate adsorption. Concentration is still the most important factor affecting the adsorption with $x_3 = 0.72 \pm 0.07$ and 0.68 ± 0.07. In the range studied, the inverse relationship between temperature and adsorption and between pH and adsorption, is indicated by negative values for x_1 and x_2 at both salinity 17 ppt and 35 ppt *(Table 6).*

II. Phosphate Adsorption Capabilities

The clay minerals decreased in phosphate adsorption in this order: chlorite > illite > kaolinite > montmorillonite, as exemplified by *Figure 3.* With the exception of kaolinite, with a lower percent adsorbed (experimental μg atoms P adsorbed per g of clay ÷ theoretical μg atoms P adsorbed per g of clay x 100) at the initial phosphate concentration level of 50 μg atoms P/l, the percent of phosphate adsorbed did not vary substantially with initial phosphate concentration. Chlorite adsorbed phosphate nearly quantitatively, averaging about 98 percent adsorption. Illite was nearly as efficient with a 94 percent adsorption level. Kaolinite averaged about 79 percent adsorption at the two lower phosphate concentration levels and adsorbed 52.3 percent phosphate at the highest phosphate concentration. Montmorillonite adsorbed about 50 percent of the initial phosphate present. The general linear relationship, in this concentration range, between the initial phosphate concentration and phosphate adsorbed per gram of clay was illustrated in *Figure 4.*

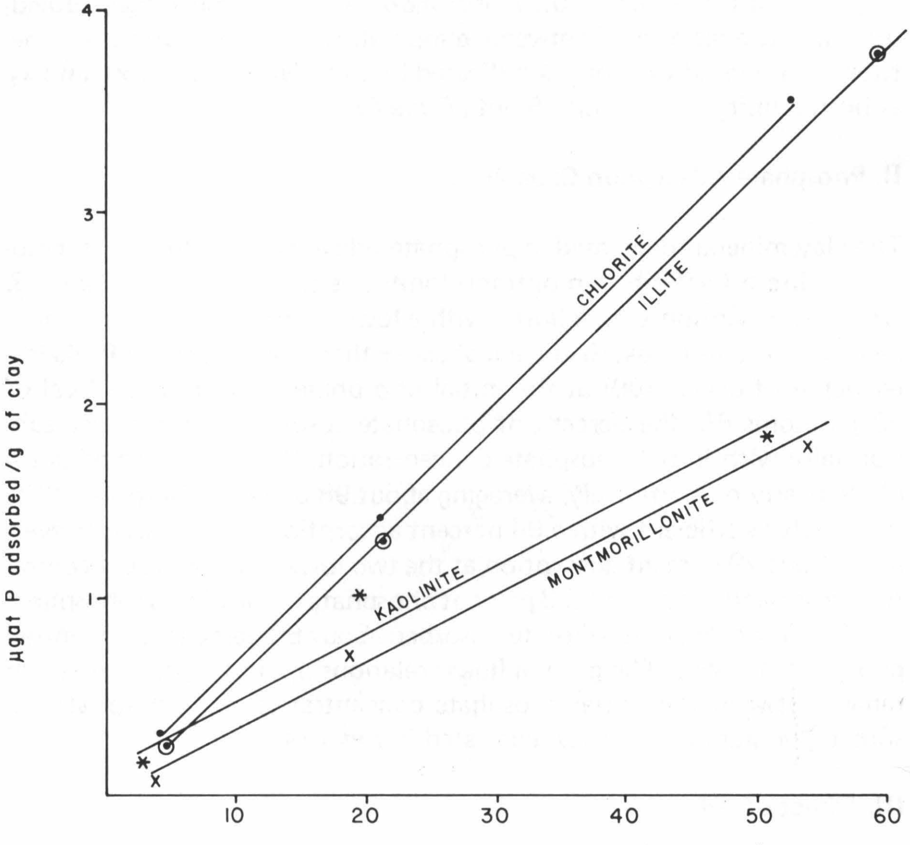
III. Effect of pH

The effect of pH on the adsorption of phosphate by clay minerals was determined by comparing the amount adsorbed at pH 6 *(Table 4)* and at pH 8 *(Table 7).* Increasing pH decreased the phosphate adsorption on all four clays. Montmorillonite and kaolinite adsorbed 21.8 percent and 13.7 percent, respectively, less phosphate at pH 8 than at pH 6. Illite adsorbed 14.4 percent less phosphate and chlorite was least affected by pH with a 9.7 percent decrease in phosphate adsorption.

IV. Adsorption Kinetic Data

Each phosphate-clay experiment was sampled for dissolved phosphate at several times, so that the time to reach a steady state could be deter-

FIGURE 4
Linear Relationship Between Initial Phosphate Concentration And Phosphate Adsorbed Per Gram of Clay



mined. In general, a steady-state ortho-phosphate concentration was reached in one day for the natural clays at pH 6 and pH 8, and for synthetic clays at pH 6 *(Tables 8-14).*

V. Tripolyphosphate Adsorption

In *Table 15,* the adsorption of polyphosphate by montmorillonite at pH 6 and 8 was shown. At pH 8, two hours after the addition of TPP, 4.99 μmoles/l of TPP remained in the solution. There was only a small amount of free phosphate present (0.18 μg atoms P/l) in solution, so the clay had adsorbed TPP at a level of 0.18 μmole TPP/g of clay. As the reaction continued, the concentration of the TPP in solution decreased with a simultaneous increase in orthophosphate concentration. The total phosphate in solution did not vary substantially after two days. At pH 6, after an initial rapid adsorption of TPP by montmorillonite, the total phosphorus and TPP in solution decreased with time.

The kinetic results *(Table 16)* for the adsorption of TPP by kaolinite at pH 8 were quite similar to those for montmorillonite at pH 8. After two hours, the uptake of TPP by kaolinite was 0.27 μmole TPP/g of clay. The TPP concentration in solution decreased and the free orthophosphate concentration increased with time.

At pH 8, adsorption of polyphosphate by illite and chlorite *(Tables 17* and *18)* was rapid and complete. After 2 hours, 98.3 percent of the TPP had adsorbed on illite and 97.4 percent had adsorbed on chlorite. As the reaction time increased, there was no substantial change in the free orthophosphate or the TPP concentration in solution.

When the pH was lowered to 6, the TPP was again adsorbed rapidly and nearly quantitatively by chlorite, 99.7 percent adsorption, illite 99.4 percent, and kaolinite 96.8 percent *(Tables 16, 17,* and *18).*

The hydrolysis of TPP in seawater at pH 6 and pH 8 was also measured to aid in interpretation of TPP adsorption data *(Table 19).* This hydrolysis can be described by a zero-order rate equation, as determined by linear regression, with variables: orthophosphate concentration in solution (c) and time (t). The equations for the hydrolysis were $c = 2.15 + 0.89\ t$ with a correlation coefficient of .926 at pH 8, and $c = 0.26 + 0.38t$ with a correlation coefficient of 0.997, at pH 6. Therefore, the rate equation was $dc/dt = k$ with k equal to 3.71×10^{-8} g atoms P/l/hr and 1.58×10^{-8} g atoms P/l/hr and 1.58×10^{-8} g atoms P/l/hr at pH 8 and 6, respectively.

VI. Results for Elizabeth River Sediments

Amounts of indigenous phosphate released to synthetic seawater by the sediments were: Sample 1, 0.11 μg atoms P/g; Sample 2, 0.27 μg atoms P/g; Sample 3, 0.28 μg atoms P/g; Sample 4, 0.16 μg atoms P/g.

The phosphorus kinetic data on these sediments *(Table 20)* indicated that the sediments were still removing phosphate from solution after two weeks, and a steady state was not reached in this series of experiments.

A gravimetric size analysis of the sediment samples was done. The results *(Table 20)* indicated that the particle size of 61-75 percent of the sample was greater than 62.5 μ.

If it is assumed that sand or silica in the sediments have very small phosphate adsorption capacity [Edzwald et al., 1976], the amount of phosphate adsorbed by the clay fraction of the Elizabeth River sediments was probably three to four times the value listed in *Table 20.* The $<62.5\ \mu$ fraction of these sediments was not analyzed by X-ray diffraction methods for clay minerals, so inferences as to the contribution of clay minerals to the total phosphate uptake by a sediment were not possible.

VII. Extractable Iron and Calcium Content of Clays

Natural kaolinite contained very small amounts of iron. The iron content increased in the following order: kaolinite, montmorillonite, illite, chlorite *(Table 21).* This data was in general agreement with that of Edzwald et al. [1976]. The natural clays used in the atomic absorption experiment had been previously washed with synthetic seawater; therefore, the iron and calcium contents reflected that which could be exchanged from seawater. The calcium content of the natural clays was similar except for montmorillonite, in which exchangeable Ca was higher by a factor of about two.

The Elizabeth River sediment contained relatively high concentrations of both Ca and Fe.

DISCUSSION

I. Amount of Phosphate Adsorbed

Phosphate adsorbed by the clay minerals used is qualitatively similar to the results of Chakravarti and Talibudeen [1961] and Burns and Salomon [1969]. Their data are shown for comparison purposes in *Table 22.* Burn's and Salomon's experiments in 19 ppt synthetic seawater closely simulate estuarine conditions, and their results for kaolinite are very close to those of the present work. Since Chakravarti and Talibudeen used a dilute (0.02 M) KCl solution of pH 5, their conditions are not quite estuarine. They did, however, use an initial phosphate concentration representative of polluted estuaries, and their values of adsorption by kaolinite and montmorillonite are close to those obtained here.

Black's [1942] data is also given in *Table 22.* He reports higher phosphate adsorption by kaolinite, montmorillonite and illite than is detected here. Aside from the dilute salt solution, his experimental conditions are representative of estuarine water. Black's methods of phosphate analysis is not stated and may not have been sensitive to low phosphate concentrations. This doubt is supported by his observation of zero phosphate adsorption at pH 8 for montmorillonite and illite.

The other authors quoted in *Table 22* worked at high phosphate concentration and/or low pH. Detailed comparison of these results with the present ones (summarized as the last entry in *Table 22)* is impossible, because the mechanism of phosphate fixation on kaolinite varies with phosphate concentration, as stated by Muljadi et al. [1969], Chen [1972], and Kafkafi et al. [1967].

The minimal effect of salinity on phosphate adsorption substantiates the results of Edzwald et al. [1976], Burns and Salomon [1969] and Carritt and Goodgal [1954]. Salinity becomes an important factor only when lack of turbulence permits flocs to form, thereby reducing the available clay surface area. The onset of floc formation is strongly dependent on salinity.

A decrease in phosphate adsorption on changing pH from 6 to 8 was expected and observed. The decrease was supported by the literature in that an adsorption maximum was found at pH 3-5 for kaolinite and at pH 5-6 for montmorillonite and illite [Black, 1942, Carritt and Goodgal, 1954; Chakravarti and Talibudeen, 1961; Muljadi et al., 1969; Hall and Baker, 1971, and Chen, 1972].

Edzwald et al. [1976] observed an opposite trend for montmorillonite, that is, more phosphate adsorbed at higher pH. He attributed this increase beyond pH 6 to the high acid extractable calcium (5.75 mg Ca/gm) in the clay. This calcium was presumed to participate in formation of a calcium phosphate solid phase. Edzwald's conclusion could not be supported by the data here; however, a similar calcium phosphate phase could have formed. The montmorillonite used was much lower in extractable calcium, but there should have been sufficient Ca^{++} from the synthetic seawater to initiate calcium phosphate formation. Edzwald's conclusion was made more doubtful by Chen's [1972] observation that calcium phosphate did not precipitate on kaolinite and aluminum oxide in a 10^{-4} M $CaCl_2$ solution until pH was > 10. Ionic equilibrium calculation of this precipitation could not be made because the identity of the calcium phosphate phase was unknown. If it became known, there would still be the problem of how nearly the system approached thermodynamic equilibrium.

Phosphate uptake by clays and sediment has often been related to their metal content, and particularly to iron oxides [Edzwald et al., 1976; Upchurch, 1972; Armstrong et al., 1971]. There is generally a direct correlation between iron content and phosphate adsorption. In the present work, illite and chlorite had high extractable iron contents, while montmorillonite and kaolinite were low *(Table 21).* Edzwald et al. [1976] determined quite similar concentrations of extractable iron in their clays and found a direct relation between this iron and the phosphate adsorbed. The present results do not yield such a good correlation, but a general trend was apparent, in accord with Jitts [1959]. Illite and chlorite had high extractable iron and adsorbed larger amounts of phosphate, while kaolinite and montmorillonite adsorbed less phosphate.

Adsorption of phosphate by clay minerals has been attributed to pH-dependent reaction of phosphate ions with the positive charged aluminate surface, and to pH-dependent precipitation of phosphate by Ca, Fe, and Al in the clay. The relation of high iron content with high phosphate adsorption may indicate the predominance of the precipitation mechanism for illite and chlorite.

Interaction of clay minerals and phosphate has been described by the

Freundlich equation, $x/m = kc^n$, where x/m is the amount adsorbed per gram of adsorbent, c is the equilibrium adsorbate concentration, and k and n are constants [Kuo and Lotse, 1974; Low and Black, 1950, and Russell and Low 1954]. Under the present experimental conditions, pH 6, 25° C, and phosphate concentrations of 4 to 50 μg atoms/liter, the Freundlich isotherm was apparently followed. The linear regression equations for the Freundlich isotherm are the following: for montmorillonite, $\log x/m = -1.68 + 1.38 \log c$; for kaolinite, $\log x/m = -0.66 + 0.71 \log c$; for illite, $\log x/m = -0.497 + 1.86 \log c$; for chlorite, $\log x/m = -0.469 + 0.60 \log c$. Linear regression plots of log x/m vs. log c had correlation coefficients of 0.866 to 0.999 for all four clays. The difficulty in establishing an adsorption isotherm from three data points is obvious, but the data from the experiments does permit a measure of linearity. Isotherm calculations were not a part of the experimental design, but were done because the form of the phosphate-clay isotherm had not previously been established under estruarine conditions.

II. Hydrolysis of Tripolyphosphate

Hydrolysis of polyphosphate has been measured in distilled water and lake water [Van Waser et al., 1952 and 1955; Crowther and Westman, 1954; McCullough et al., 1956; Strauss and Treitler, 1956; Shannon and Lee, 1966; Karl-Kroupa et al., 1957; Griffith, 1959 and Heinke, 1969]. No hydrolytic data is available in seawater. Hydrolysis occurs by the following reactions:

$$P_3O_{10}^{-5} + H_2O \overset{k_1}{\rightleftharpoons} P_2O_7^{-4} + PO_4^{-3} + 2H^+$$

$$P_2O_7^{-4} + H_2O \overset{k_2}{\rightleftharpoons} 2PO_4^{-3} + 2H^+$$

The rate constant measured in this study is for the sum of the two above equations, because tripolyphosphate and pyrophosphate were not differentiated in the reaction solution. Therefore, the rate constant describes the following reaction.

$$P_3O_{10}^{-5} + 2H_2O \overset{k_{sum}}{\rightleftharpoons} 3PO_4^{-3} + 4H^+$$

At high phosphate concentration in dilute solution, the hydrolysis followed a first order rate equation; however, Shannon and Lee [1966], working with a relatively low phosphorus concentration (17 μg atoms P/l), described the hydrolysis of tripolyphosphate as a zero-order rate reaction.

Their rate of hydrolysis, computed from the initial and final concentration of TPP, was 2.39×10^{-8} g atoms P/l/hr at 20° C in distilled water. This rate constant was quite close to that found here, 1.58×10^{-8} g atoms P/l/hr, and 3.71×10^{-8} g atoms P/l/hr at pH 6 and pH 8, respectively.

Since the hydrolysis of TPP in seawater was relatively slow, an adsorption study of TPP by clay minerals was feasible.

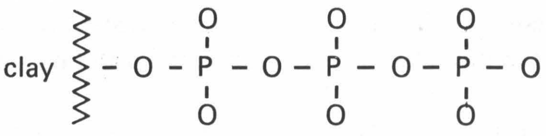
III. Tripolyphosphate Adsorption

Polyphosphates are introduced to estuaries as components of deflocculants and fertilizers and are sufficiently resistant to hydrolysis to persist near point sources. Since estuarine clays are exposed to polyphosphates, experiments on uptake of polyphosphate by clay minerals were conducted. Early research on polyphosphate-clay interaction was directed to polyphosphate use as fertilizers or detergent additives. Accordingly, either dense clay suspensions of 13 percent to 50 percent clay by weight or high polyphosphate concentration of 10^{-4} to 2 M were used [Hashimoto et al. 1969; Bidwell et al., 1970; Philen and Lehr, 1967; Michaels, 1958; and Lyons, 1964]. Comparison of these workers' results to the present ones is tenuous, because their experimental conditions are different from those of estuarine water. For example, tripolyphosphate (TPP) in the Elizabeth River water varies from zero to 2.1 μg atoms P/l [MacIntyre and Lake, unpublished data].

Several workers obtained information relevant to TPP adsorption on clays during investigation of catalytic hydrolysis of polyphosphate by clay minerals. Lyons [1964] proposed that TPP hydrolyzed rapidly to orthophosphate and pyrophosphate on kaolinite, and orthophosphate was displaced from the clay surface, leaving only pyrophosphate. This concept was supported somewhat by the observation that pyrophosphate competed more effectively than orthophosphate for surface sites on kaolinite [Hashimoto et al., 1969]. Lyons [1964] stated that only sixteen percent of the adsorbed phosphorus was orthophosphate. Displacement of orthophosphate, as proposed by Lyons, may have occurred at high TPP concentration; however, it did not occur significantly at the low TPP concentration used in the present work, because the consequent increase in orthophosphate concentration was not always observed. In the adsorption experiments on kaolinite at pH 6, and on chlorite and illite at pH 6 and 8, little or no dissolved phosphorus was in solution at any time, in agreement with Michael's [1958] results for the TPP-kaolinite system. Adsorption here was more rapid than hydrolysis, and if hydrolysis occurred on the clay surface, the products remained there.

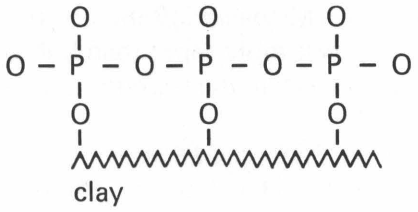
Orthophosphate concentration increased with time in kaolinite and montmorillonite suspensions at pH 8, but total dissolved phosphorus was relatively constant throughout these experiments. This situation could have resulted from either hydrolysis of dissolved TPP, since orthophosphate in solution was similar to amounts measured for hydrolysis of TPP in seawater without clay or clay surface hydrolysis to pyrophosphate followed by release of orthophosphate [Lyons, 1964]. The two processes (surface hydrolysis and homogeneous hydrolysis) probably occurred simultaneously and were not distinguishable by these experiments. In experiments with montmorillonite at pH 6, total phosphorus and polyphosphate concentrations decreased with time, but orthophosphate concentration concurrently increased. As found at pH 8, orthophosphate concentration in solution was consistent with that determined from hydrolysis of TPP in clay-free seawater of the appropriate pH (except for the 17 day value). Therefore, after a rapid initial adsorption of TPP, a slow, continued adsorption of TPP or pyrophosphate followed.

At both pH 6 and 8, adsorption by all four clay minerals was more rapid and greater when the source of phosphorus was tripolyphosphate rather than orthophosphate. This increased adsorption was especially evident for montmorillonite and kaolinite *(Table 23),* since adsorption by illite and chlorite was originally high in the orthophosphate experiments. If it was assumed that hydrolysis to orthophosphate was complete on the clay surface, the adsorption of phosphorus (stated as μg atoms P adsorbed per g of clay) would have been the same whether the source was TPP or orthophosphate, assuming the number of active sites remained the same. If the tripolyphosphate molecule remained intact on the clay mineral, the binding of TPP could have been either:



$$\text{clay} \wr - O - \underset{O}{\overset{O}{P}} - O - \underset{O}{\overset{O}{P}} - O - \underset{O}{\overset{O}{P}} - O$$

or



In the first type of binding, TPP bound to the same sites as orthophosphate and the clay could have theoretically accepted three times the amount of phosphorus (as TPP) per g of clay. In the second type TPP blocked active sites and the clay could have accepted only the same number of phosphorus atoms, whether from TPP or orthophosphate. The increased adsorption for TPP found here supports the first binding type, but more research is needed before a distinction could be made between the two types of binding of TPP and between adsorption with and without surface hydrolysis of polyphosphates.

IV. Phosphate-Sediment Interaction

The uptake of phosphate by sediments is regulated by:

1. organic matter that coats clay particles, thereby depressing phosphate adsorption [Jitts, 1959; Chen, 1972];
2. pH, which determines the clay surface charge and the ionic species of phosphoric acid and metal phosphates present;
3. quartz sand, which can comprise much of the mass, but little of the adsorption capacity of a sediment;
4. iron oxides, whose presence has been correlated directly with phosphate adsorption;
5. redox potential, which controls the oxidation state of iron and determines whether it forms soluble ferrous phosphate or slightly soluble ferric phosphate;
6. bacterial interconversion of inorganic and organic phosphate on sediment particles and in interstitial water. Adsorption of organophosphate by clays has not been investigated, but should be treated in future research, and
7. physical processes of bioturbation and wave-current action, which disturb bottom sediments and may cause release of phosphate to overlying water.

This study did not treat all the above factors, because phosphate adsorption was measured only when sediments were in a dispersed and aerated condition.

Phosphorus determinations were made in water and sediment of the Elizabeth River near the Lambert Point Sewage Treatment outfall. This work was done in support of the study of Neilson and Kuo [1974]. Since this information was available, sediment samples from the area were used in phosphate uptake experiments. The total phosphorus in these sediments varied from 8.7 to 33.8 μg atoms P/g of sediment, organic phosphorus varied from 2.5 to 12.3 μg atoms P/g and interstitial water orthophosphate concentration varied from 21.9 to 143.9 μg atoms P/l (determined under anoxic conditions). Another study [Huggett, 1971] found an average of total phosphorus of 19.2 ± 4.5 μg atoms P/g of sediment in cores taken along a transect in the Elizabeth River channel. Therefore, the minimal release of phosphate from the sediment sample (about 0.1 μg atoms P/g of sediment) into phosphate-free synthetic seawater substantiated the postulate of Jitts [1957], Muljadi et al. [1969], Kafkafi et al. [1967] that adsorbed phosphate could be irreversibly bound to clay minerals and to sediment.

The adsorption of phosphate by the sediments was slow and continuous throughout the two week experiment. Such a reaction rate may be indicative of precipitation of phosphate by metal ions present in the sediment. Sediment Sample No. 1, which adsorbed phosphate at the highest level, contained high concentrations of both calcium and iron. However, as with the clay minerals alone, phosphate adsorption was not directly related to their metal (Ca and Fe) content; other factors, e.g., organic content, also influenced phosphate adsorption.

SUMMARY AND CONCLUSIONS

The adsorption of phosphate by clay minerals was found to be related to pH and the initial phosphate concentration. The similarity of the amount of phosphate adsorbed by natural and by synthetic clays demonstrated the generality of the adsorption experiments. The organic, exchangeable cation and metal oxide contents of the synthetic clays differed from that of the natural clays, but the amount of phosphate adsorbed was similar.

Chlorite and illite, which predominate the clay fraction of the sediment from the lower James River estuary [Nichols, 1972], adsorbed phosphate and tripolyphosphate nearly quantitatively at phosphate levels (0-50 μg atoms P/l) and pH values (6-8) characteristic of the James and Elizabeth Rivers. The acid extractable metal content of the sediment and clay mineral was generally related to the amount of phosphate adsorbed, but there was no simple, direct relationship.

The importance of clay minerals in regulating the phosphate concentration of estuarine waters has been demonstrated by their ability to adsorb orthophosphate and tripolyphosphate under marine conditions. This information must be supported by the research on the other factors which affect phosphate adsorption so that a full description of phosphorus interaction with sediment can be achieved.

BIBLIOGRAPHY

Adams, D. D.; Wiesenburg, D. A.; Sauer, T. C., and Matthews, W. M., Jr., 1974. *Investigations and Monitoring of Hampton Roads Sanitation District Sewage Outfalls and the Receiving Waters, Norfolk.* Technical Report No. 15. Old Dominion University, Virginia. 83 p.

Arambarri, P., and Talibudeen, O., 1959. "Factors Influencing the Isotopically Exchangeable Phosphate in Soils." *Plant and Soil* 11:343-354.

Armstrong, D. E., Harris, R. F., and Syers, J. K., 1971. *Plant Available Phosphorus Status of Lakes.* The University of Wisconsin Water Resources Center, Wisconsin. 112 p.

Beck, K. C., 1972. *Sediment-Water Interactions in Some Georgia Rivers and Estuaries.* Georgia Institute of Technology, Georgia. 97 p.

Bidwell, J. I.; Jepson, W. B., and Toms, G. L., 1970. "The Interaction of Kaolinite with Polyphosphate and Polyacrylate in Aqueous Solutions—Some Preliminary Results." *Clay Minerals* 8:445-459.

Black, C. A., 1942. "Phosphate Fixation by Kaolinite and Other Clays as Affected by pH, Phosphate Concentration, and Time of Contact." In *Soil Science Society of American Proceedings* 7:123-133.

Bray, J. T.; Bricker, O. P., and Troup, B. N., 1973. "Phosphate in Interstitial Waters of Anoxic Sediments: Oxidation Effects During Sampling Procedure." *Science* 180:1362-1364.

Burns, P. A. and Salomon, M., 1969. "Phosphate Adsorption by Kaolin in Saline Environment." In *Proceedings of the National Shellfisheries Association* 59:121-125.

Carritt, D. E., and Goodgal, S., 1954. "Sorption Reactions and Some Ecological Implications." *Deep-Sea Research* 1:224-243.

Chakravarti, S. N. and Talibudeen, O., 1961. "Phosphate Interaction with Clay Minerals." *Soil Science* 92:232-242.

Chen, Y., 1972. "Phosphate Interaction with Aluminum Oxide, Kaolinite, and Sediments." Ph.D. dissertation. Harvard University, Massachusetts. 247 p.

Crowther, J. P. and Westman, A. E. R., 1954. "Hydrolysis of the Condensed Phosphates." *Canadian Journal of Chemistry* 32:42-48.

Davis, H. L., 1968. "The Net Exchange of Phosphorus by Estuarine Sediments in Flowing Waters." Master's thesis. North Carolina State University, North Carolina. 41 p.

Edzwald, J. K.; Toensing, D. C., and Leung, M. C., 1976. "Phosphate Adsorption Reactions with Clay Minerals." *Environmental Science and Technology* 10:485-490.

Ferguson, J. F., and Simmons, D., 1974. *The Fate of Nutrients in Back River.* CRC Publication No. 32. 27 p.

Frink, C. R., 1969. "Chemical and Mineralogical Characteristics of Eutropic Lake Sediments." In *Soil Science Society of America Proceedings* 33:369-372.

Griffith, E. J., 1959. "A Nomograph for the Hydrolytic Degradation of Pyro- and Tripolyphosphates." *Industrial and Engineering Chemistry* 51:240.

Griffith, E. J.; Benton, A.; Spencer, J. M., and Mitchell, D. T., 1973. *Environmental Phosphorus Handbook.* John Wiley and Sons. 718 p.

Hall, J. K., and Baker, D. E., 1971. "Phosphorus Fixation by Montmorillonite and Vermiculite Clays as Influenced by pH and Soluble Aluminum." In *Soil Science Society of America Proceedings* 35:876-881.

Hashimoto, K.; Hughes, J. D.; and Philen, O. D., Jr., 1969. "Reactions of Triammonium Pyrophosphate with Soils and Soil Minerals." *Soil Science Society of America* 33:401-405.

Hayes, F. R., and Phillips, J. E., 1958. *Lake Water and Sediments Limnology and Oceanography* 3:459-475.

Heinke, G. W., 1969. "Hydrolysis of Condensed Phosphates in Great Lakes Waters." In *Proceedings of the 12th Conference Great Lakes Research 1969.* p. 766-773.

Hemwall, J. B., 1957. "The Role of Soil Clay Minerals in Phosphorus Fixation." *Soil Science* 83:101-108.

Huggett, R., 1971. "Study of Channel Sediments, Baltimore Harbor, Norfolk Channel, York Entrance Channel." Submitted to the U.S. Army Corps of Engineers. Virginia Institute of Marine Science. 43 p.

Hunter, J. S., 1970. *Statistical Design of Engineering Experiments.* American Institute of Chemical Engineers. New York.

Jitts, H. R., 1959. "The Adsorption of Phosphate by Estuarine Bottom Deposits." *Australian Journal of Marine and Freshwater Research* 10:7-21.

Kafkafi, U., 1968. "Hydrogen Consumption and Silica Release During Initial Stages of Phosphate Adsorption on Kaolinite at a Constant pH." *Israel Journal of Chemistry.* 6:367-373.

Kafkafi, U..; Posner, A. M., and Quirk, J. P., 1967. "Desorption of Phosphate from Kaolinite." *Soil Science Society of America Proceedings* 31:348-353.

Karl-Kroupa, E.; Callis, C. F.; Seifter, E., 1957. "Stability of Condensed Phosphates in Very Dilute Solutions." *Industrial and Engineering Chemistry* 49:2061-2062.

Kuo, S., and Lotse, E. G., 1974. "Kinetics of Phosphate Adsorption and Desorption by Hematite and Gibbsite." *Soil Science* 116:400-406.

Low, P. R., and Black, C. A., 1950. "Reactions of Phosphate with Kaolinite." *Soil Science* 70:273-290.

Lyman, J., and Fleming, R. H., 1940 "Composition of Seawater." *Journal of Marine Research* 3:134-146.

Lyons, J. W., 1964. "Sodium Tri (poly) phosphate in the Kaolinite-Water System." *Journal of Colloid Science* 19:399-412.

McCullough, J. F.; Van Wazer, J. R., and Griffith, E. J., 1956 "Structures and Properties of Condensed Polyphosphates. XI Hydrolytic Degradation of Graham's Salt." *Journal of the American Chemical Society* 78:4520-4533.

Michaels, A. S., 1958. "Deflocculation of Kaolinite by Alkali Polyphosphates." *Industrial and Engineering Chemistry* 50: 951-958.

Muljadi, D.; Posner, A. M., and Quirk, J. P., 1966a. "The Mechanism of Phosphate Adsorption by Kaolinite, Gibbsite, and Pseudoboehmite. Part I. The Isotherms and the Effect of pH on Adsorption." *Journal of Soil Science* 17:212-229.

Nelson, Bruce W., 1958. "Clay Mineralogy of the Bottom Sediments, Rappahannock River, Virginia." In *Clays and Clay Minerals, Proceedings of the Seventh National Conference on Clay and Clay Minerals.* p. 135-147.

Nichols, M. M., 1972. "Sediments of the James River Estuary, Virginia." *The Geological Society of America, Memoir* 133:169-212.

Philen, O. D., Jr., and Lehr, J. L., 1967 "Reactions of Ammonium Polyphosphates with Soil Minerals." In *Soil Science Society of America Proceedings* 31:196-199.

Pomeroy, L. R.; Smith, E. E., and Grant, C. M., 1965. "The Exchange of Phosphate between Estuarine Water and Sediments." *Limnology and Oceanography* 10:167-172.

Pratt, D. M., 1949. "Experiments in the Fertilization of a Salt Water Pond." *Journal of Marine Science* 8:36-59.

Rittenburg, S. C.; Emery, K. O., and Orr , W. L., 1955. "Regeneration of Nutrients in Sediments of Marine Basins." *Deep-Sea Research* 3:23-45.

Rochford, D. J., 1951. "Studies in Australian Estuarine Hydrology. I. Introductory and Comparative Features." *Australian Journal of Marine and Freshwater Research* 2:1-116.

Ross, G. J., 1969. "Acid Dissolution of Chlorites." *Clay and Clay Minerals.* 17:347-354.

Russell, G. C. and Low, P. R., 1954. "Reactions of Phosphate with Kaolinite in Dilution Solution." *Soil Science Society of America Proceedings* 18:22-25.

Seshappa, G., 1953. "Phosphate Content of Mudbanks along the Malabar Coast." *Nature* 171:526-527.

Shannon, J. E., and Lee, G. F., 1966. "Hydrolysis of Condensed Phosphates in Natural Waters." *International Journal of Air and Water Pollution* 10:735-756.

Shukla, S. S.; Syers, J. K.; Williams, J. D. H.; Armstrong, D. E., and Harris, R. F., 1971. "Sorption of Inorganic Phosphate by Lake Sediments." In *Soil Science Society of America Proceedings.* 35:244-249.

Smith, C. L., MacIntyre, W. G., Lake, C. A., and Windsor, J. G., 1977. In *Effects of Tropical Storm Agnes on Nutrient Flux and Distribution in Lower Chesapeake Bay.* Johns Hopkins University Press. p. 636.

Strauss, U. P., and Treitler, T. L., 1956. "Degradation of Polyphosphate in Solution. I. Kinetics and Mechanism of the Hydrolysis at Bonding Points in Polyphosphate Chains." *Journal of the American Chemical Society* 78:3553-3557.

Strickland, J. D. H., and Parsons, T. R., 1968. *A Practical Handbook of Seawater Analysis.* Fisheries Research Board of Canada. Bulletin 167. 311 p.

Stumm, W., and Morgan, J. J., 1970. *Aquatic Chemistry.* Wiley-Interscience. 583 p.

Upchurch, J. B., 1972. *Sedimentary Phosphorus in the Pamlico Estuary of North Carolina.* Sea Grant Publication UNC-SG-72-03. Chapel Hill, North Carolina. 39 p.

Williams, J. D. H.; Syers, J. K., and Harris, R. F., 1970. "Adsorption and Desorption of Inorganic Phosphate by Lake Sediments in a 0.1 M NaCl System." *Environmental Science and Technology* 4:517-519.

Van Waser, J. R.; Griffith, E. J., and McCullough, J. R., 1952. "Hydrolysis of Condensed Phosphates." *Journal of the American Chemical Society* 74:4977-4978.

Van Waser, J. R.; Griffith, E. J., and McCullough, J. F., 1955. "Structure and Properties of the Condensed Phosphates. VII. Hydrolytic Degradation of Pyro- and Tripolyphosphate." *Journal of the American Chemical Society* 77:287-291.

TABLES

TABLE 1a

Dissociation Constants of Phosphoric Acid

(electrolyte: artificial seawater, $\mu = 0.68$, 20° C.)

$$\frac{\alpha_{H^+} (H_2PO_4^-)}{(H_3PO_4)} = K_1' = 10^{-1.63}$$

$$\frac{\alpha_{H^+} (HPO_4^{-2})}{(H_2PO_4^-)} = K_2' = 10^{-6.06}$$

$$\frac{\alpha_{H^+} (PO_4^{-3})}{(HPO_4^{-2})} = K_3' = 10^{-8.86}$$

TABLE 1b

Dissociation Constants of Tripolyphosphoric Acid

(electrolyte: TMA^+Cl^-, $\mu = 1.0$, 25° C.)

$$\frac{\alpha_{H^+} (H_4P_3O_{10}^-)}{(H_5P_3O_{10})} = K_1' \sim 10^{-.51}$$

$$\frac{\alpha_{H^+}\ H_3P_3O_{10}^{-2}}{(H_4P_3O_{10}^-)} = K_2' = 10^{-1.06}$$

$$\frac{\alpha_{H^+} (H_2P_3O_{10}^{-3})}{(H_3P_3O_{10}^{-2})} = K_3' = 10^{-2.11}$$

$$\frac{\alpha_{H^+} (HP_3O_{10}^{-4})}{(H_2P_3O_{10}^{-3})} = K_4' = 10^{-5.83}$$

$$\frac{\alpha_{H^+} (P_3O_{10}^{-5})}{(HP_3O_{10}^{-4})} = K_5' = 10^{-8.81}$$

Source: Griffith et al., 1973.

TABLE 2
Chemical Composition of Synthetic Clay Minerals

Kaolinite	$(Al_4)(Si_4)O_{10}(OH)_8$
Montmorillonite	$(Al_{3.33}Mg_{0.67})(Si_8)O_{20}(OH_{3.2}F_{0.8})\ 0.67NH_4^+$
Beidellite	$(Al_4)(Si_{7.33}Al_{0.67})O_{20}(OH_{3.27}F_{0.73})\ 0.67NH_4^+$
Hectorite	$(Mg_{5.33}Li_{0.67})(Si_8)O_{20}(OH_{3.33}F_{0.67})\ 0.67Li^+$
Saponite	$(Mg_6)(Si_{7.25}Al_{0.75})O_{20}(OH)_4\ 0.75Na^+$

TABLE 3
Factorial Design Notation

Run	Notation Values for Variables			Temperature	Salinity	PO_4^{-3} Concentration
	(x_1	x_2	x_3)	x_1	x_2	x_3
1	(+	+	+)	25° C	35 ppt	20 μg atoms P/l
2	(+	–	+)	25° C	17 ppt	20 μg atoms P/l
3	(–	+	+)	5° C	35 ppt	20 μg atoms P/l
4	(–	–	+)	5° C	17 ppt	20 μg atoms P/l
5	(+	+	–)	25° C	35 ppt	4 μg atoms P/l
6	(+	–	–)	25° C	17 ppt	4 μg atoms P/l
7	(–	+	–)	5° C	35 ppt	4 μg atoms P/l
8	(–	–	–)	5° C	17 ppt	4 μg atoms P/l

TABLE 4
Adsorption of Orthophosphate by Natural Clays at pH 6

Experiment			μg atoms-P/g Illite	μg atoms-P/g Kaolinite	μg atoms-P/g Montmorillonite	μg atoms-P/g Chlorite
Temperature,	Salinity,	PO_4^{-3}				
+	+	+	1.29	1.03	0.67	1.33
+	–	+	1.28	1.06	0.59	1.44
–	+	+	1.24	0.89	0.60	1.42
–	–	+	1.27	1.01	0.53	1.42
+	+	–	0.26	0.26	0.08	0.30
+	–	–	0.22	0.26	0.11	0.30
–	+	–	0.23	0.19	0.14	0.32
–	–	–	0.30	0.24	0.12	0.32
Main effect of temp. x_1			0.00	0.07	0.02	–0.02
	Main effect of Salinity x_2		0.02	–0.05	0.03	–0.03
		Main effect of Concentration x_3	1.02	0.76	0.49	1.10

TABLE 5

Adsorption of Orthophosphate by Kaolinite at Seawater pH

(duplicate runs)

Experiment			μg at-P/g of Clay	Average
Temperature,	Salinity,	PO_4^{-3}		
+	+	+	0.49	0.49
+	+	+	0.49	
+	–	+	0.43	0.39
+	–	+	0.35	
–	+	+	1.15	1.14
–	+	+	1.13	
–	–	+	1.03	1.09
–	–	+	1.15	
+	+	–	0.04	0.04
+	+	–	0.04	
+	–	–	0.18	0.17
+	–	–	0.16	
–	+	–	0.12	0.13
–	+	–	0.13	
–	–	–	0.16	0.18
–	–	–	0.20	

(continued)

TABLE 5 (Continued)

Main effect of temperature: $x_1 = -0.36 \pm 0.07$
Main effect of salinity: $x_2 = -0.004 \pm 0.07$
Main effect of concentration: $x_3 = 0.65 \pm 0.07$

Effect of temperature x concentration: $x_1 x_3 = -0.78 \pm 0.07$
Effect of temperature x salinity: $x_1 x_2 = -0.01 \pm 0.07$
Effect of concentration x salinity: $x_2 x_3 = 0.05 \pm 0.07$

Calculation of S.E.

$$s^2 \text{ pooled} = \frac{\Sigma d^2/2}{8} \quad \frac{0 + (\quad)^2 + (\quad)^2 + \ldots}{16} \quad = .00146$$

S.E. = $s^2/4 = 0.019$

at 5 percent of Student's t distribution:

$$(\bar{y}_+ - \bar{y})_- \quad \pm \quad t\,8,\alpha/2\sqrt{s^2/4} \quad = \quad (\bar{y}_+ - \bar{y}_-) \quad \pm \quad .07$$

TABLE 6
Adsorption of Orthophosphate by Kaolinite

Experiment Temperature,	 pH,	 PO_4^{-3}	μg at-P/gm Kaolinite at Salinity = 17 ppt	μg at-P/gm Kaolinite at Salinity = 35 ppt
+	+	+	0.39	0.49
+	–	+	1.06	1.03
–	+	+	1.09	1.14
–	–	+	1.01	0.89
+	+	–	0.16	0.04
+	–	–	0.26	0.26
–	+	–	0.18	0.13
–	–	–	0.24	0.24
Main effect of temperature:			–0.16	–0.14
Main effect of pH:			–0.19	–0.15
Main effect of concentration:			0.68	0.72

TABLE 7

Kinetic Data of Orthophosphate Adsorption at pH 8

(μg atoms P/g of clay)

Clay Time (days)	Kaolinite	Montmorillonite	Illite	Chlorite
0	0.13	0.19	0.42	0.75
0.01	0.22			
0.02	0.28	0.35	0.87	0.99
0.04	0.35	0.35	0.90	1.00
0.18	0.34			
0.31		0.40	0.94	1.16
1.04		0.47	0.99	
1.15				1.23
1.98	0.46			
2.22	0.49			
3.02		0.46	1.02	
3.13				1.29
3.93	0.50			
5.04		0.46	1.03	
5.15				1.30
6.00	0.49			
6.92		0.46	1.02	
7.02				1.31
% adsorbed	34.3	33.9	75.8	90.3

Initial phosphate concentration:	≈20 μg atoms P/l,
Solids concentration:	15 g/l, 25° C, and
Salinite:	35 ppt.

TABLE 8
Kinetic Data of Orthophosphate Adsorption (μg atoms P/g of clay) by Montmorillonite at pH 6

Experiment Time (days)	+++	+–+	–++	––+	++–	+––	–+–	–––
0	0.36	0.26	0.25		0	0	0	0
0.007							0.02	0.04
0.01	0.45	0.36	0.37	0.13	0.01	0.03		
0.013							0.04	0.03
0.02	0.50	0.42	0.36	0.16	0.03	0.02		
0.028							0.06	0.04
0.03			0.38	0.19				
0.04					0.03	0.05	0.07	0.04
0.06			0.44	0.30			0.06	0.05
0.08					0.03	0.05		
0.10							0.07	0.07
0.15	0.59	0.54						
0.17			0.45	0.30				
0.19							0.07	0.07
0.30	0.61	0.58						
0.34			0.50	0.32				
0.47					0.05	0.08	0.09	0.08
0.85			0.56	0.39				
0.98			0.57	0.45			0.10	0.09
1.25	0.64	0.59						
1.94					0.08	0.08		
1.96	0.64	0.58						
1.98							0.12	0.10
3.21	0.67	0.62						
3.96	0.69	0.64						
3.98							0.13	0.12
4.19			0.58	0.55				
4.27					0.08	0.11		
4.94					0.08	0.11		
5.19			0.59	0.54				
5.90					0.08	0.11		
6.29	0.68	0.64						
6.96	0.69	0.64						
7.19			0.60	0.53				
7.13							0.14	0.12
% adsorbed	55.7	50.9	51.3	40.6	26.3	62.2	57.5	45.0

TABLE 9

Kinetic Data of Orthophosphate Adsorption (μg atoms P/g of clay) by Kaolinite at pH 6

Experiment Time (days)	+++	+–+	–++	––+	++–	+––	–+–	–––
0	0.33	0.40	0.39	0.55	0.10	0.11	0.06	0.11
0.01	0.57	0.60	0.48	0.62	0.12	0.14	0.10	0.14
0.02	0.67	0.68	0.53	0.67	0.13	0.13	0.10	0.16
0.04	0.74	0.76	0.58	0.73	0.13	0.15	0.15	0.17
0.10					0.14	0.20		
0.13							0.13	0.19
0.17			0.68	0.82				
0.18	0.90	0.92						
0.42					0.15	0.16		
0.44	0.96	0.95						
0.46							0.15	0.20
0.52			0.77	0.90				
1.29							0.16	0.22
1.35			0.82	0.95				
1.88					0.15	0.16		
1.96	1.01	1.03						
2.13							0.17	0.22
2.19			0.87	0.99				
3.24	1.03	1.06						
4.16							0.18	0.22
4.20					0.15	0.16		
4.23			0.90	1.06				
4.24	1.02	1.05						
4.88					0.15	0.16		
4.90	1.02	1.06						
5.83					0.15	0.16		
6.96	1.02	1.06						
7.16							0.19	0.23
7.23			0.89	1.00				
14.33							0.19	0.24
14.39			0.89	1.01				
% adsorbed	78.0	80.4	76.7	82.7	72.8	78.6	77.6	84.3

TABLE 10
Kinetic Data of Orthophosphate Adsorption (μg atoms P/g of clay) by Illite at pH 6

Experiment Time (days)	+++	+−+	−++	−−+	++−	+−−	−+−	−−−
0	1.04	1.04	0.90	0.99	0.24	0.10	0.19	0.23
0.01	1.16	1.17	1.05	1.12	0.25	0.21	0.21	0.24
0.02	1.20	1.19	1.08	1.17		0.21	0.21	0.25
0.03						0.21		
0.04	1.21	1.21	1.14	1.20	0.25		0.21	0.34
0.19							0.22	0.26
0.21			1.20	1.23				
0.23	1.26	1.26						
0.25					0.26	0.22		
0.90	1.28	1.28						
0.92					0.26	0.22		
1.19							0.23	0.26
1.97	1.28	1.28						
1.98					0.27	0.22		
2.35			1.24	1.27				
3.90	1.29	1.29						
3.92			1.25	1.27	0.26	0.22		
3.94							0.23	0.27
4.85			1.25	1.28				
4.97	1.29	1.28						
4.98					0.26	0.22		
5.93			1.25	1.28				
5.95	1.29	1.28						
5.96					0.26	0.22		
6.94							0.23	0.27
% adsorbed	90.2	89.9	94.8	96.5	81.8	70.4	79.1	91.0

TABLE 11

Kinetic Data of Orthophosphate Adsorption (μg atoms P/g of clay) by Chlorite at pH 6

Experiment Time (days)	+++	+–+	–++	––+	++–	+––	–+–	–––
0	0.92	1.29	1.00	1.13	0.23	0.24	0.30	0.30
0.01	1.11				0.26	0.27		
0.014			1.27	1.24			0.31	0.32
0.02		1.39						
0.028	1.20		1.31	1.29			0.32	0.31
0.03					0.28	0.28		
0.04	1.24	1.41	1.33	1.30			0.32	0.32
0.1			1.36	1.36			0.32	0.32
0.13	1.27							
0.21	1.30							
0.22					0.29	0.30		
0.31		1.44						
0.83	1.32							
0.85					0.29	0.30		
1.15		1.44						
1.25			1.40	1.41			0.32	0.32
2.16	1.36							
3.13		1.45						
3.19					0.30	0.30		
3.21			1.41	1.42			0.32	0.32
4.19			1.42	1.42			0.32	0.32
4.92	1.38							
4.94					0.30	0.30		
5.04			1.42	1.42			0.32	0.32
5.15		1.45						
6.92	1.41							
6.94					0.30	0.30		
7.02		1.45						
7.92	1.42							
8.92	1.42							
% adsorbed	98.9	99.6	97.4	98.0	98.7	98.7	97.3	97.3

TABLE 12

Kinetic Data of Orthophosphate Adsorption (μg atoms P/g of clay) At Higher Initial Phosphate Concentration (50 μg atoms P/l)

Clay	Kaolinite	Clay Montmorillonite	Illite	Chlorite
Time (days)				
0				1.19
0.014	0.56		2.75	2.48
0.028	0.60			2.69
0.04	0.82		3.26	2.84
0.1	0.88			3.08
0.31		0.83	3.44	
0.60	1.20			
0.75			3.64	3.48
1.98	1.51			3.52
2.08		1.55	3.69	
3.81	1.59			3.54
3.92		1.60	3.68	
6.06	1.67			3.55
6.17		1.71	3.71	
8.13	1.73			3.55
8.23		1.80	3.74	
9.13				3.56
9.23			3.76	
18.04	1.79			3.56
18.13		1.79	3.77	
% adsorbed	52.3	49.4	95.2	100.0

Solids concentration = 15 g/l, temperature = 15° C, salinity = 35 ppt.

TABLE 13

Kinetic Data of Orthophosphate Adsorption (μg atoms P/g of clay) by Kaolinite at Seawater pH (Duplicate Runs)

	Experimnt															
Time (days)	+++		+–+		––+		–++		++–		+––		–+–		–––	
0	0.13	0	0	0	0.23	0.59	0.67	0.15	0	0	0.11	0.05	0	0	0.02	0.03
0.01	0.22	0.13	0.14	0.16				0.48	0.03	0.04	0.14	0.08	0.14	0.08		0.04
0.014					0.49	0.78	0.80						0.04	0.05	0.06	
0.02	0.28	0.24	0.20	0.18				0.55	0.04	0.05	0.15	0.09				
0.028					0.57	0.82	0.88									
0.03																0.07
0.035													0.06	0.07	0.08	
0.04	0.35	0.28	0.24	0.25	0.61	0.86	0.88	0.71	0.05	0.05	0.15	0.09				
0.13							1.01									
0.15			0.28	0.27												
0.17					0.76	0.98		0.88								
0.18	0.34	0.34														
0.21													0.08	0.09	0.11	0.11
0.97									0.03	0.06						
0.98											0.18	0.13				
1.26									0.04	0.04						
1.27											0.18	0.13				
1.29							1.03									
1.33					0.96	1.11										
1.96			0.42	0.35												
1.98	0.46	0.46														
2.19			0.42	0.37												

2.21								1.05					0.11	0.11	0.16	0.14
2.22	0.49	0.49														
2.92							1.16									
2.95					1.01	1.13										
2.97									0.04	0.05						
2.98											0.18	0.14				
3.93	0.50	0.49														
3.96							1.15									
3.97									0.04	0.04						
3.98											0.18	0.14				
4.09																0.15
4.10													0.12	0.13	0.17	
4.90			0.41	0.33												
5.13													0.12	0.13	0.18	
5.17																0.15
5.96								1.13								
6.00	0.49	0.49														
6.09																0.16
6.10													0.12	0.13	0.19	
6.13					1.01	1.14										
6.14							1.15									
6.96								1.13								
6.97			0.43	0.35												
7.00													0.12	0.13	0.20	0.16
7.04											0.18	0.14				
8.92							1.15									
8.95					1.05	1.15										
10.92							1.15									
10.95					1.03	1.15										

TABLE 14

Kinetic Data of Orthophosphate Adsorption (μg atoms P/g of clay) by Several Synthetic Clays

	Clay				
Time (days)	Hectorite	Kaolinite	Saponite	Beidellite	Montmorillonite
0	0.38	0.59	–	0.40	0.51
0.02		0.74	0.40	0.60	
0.04	0.53		0.47	0.72	0.66
0.05		0.85			
0.09	0.54				0.73
0.13		0.95			
0.31			0.74	0.75	
0.88	0.69				0.86
0.92		1.12			
1.15			0.82	0.83	
2.90	0.78				0.85
2.94		1.18			
3.13			0.91	0.93	
5.15			0.93	0.95	
5.96	0.76				0.83
6.00		1.20			
7.02			0.92	0.95	
9.90	0.78				0.85
9.94		1.21			
12.88	0.77				0.85
12.92		1.22			
% adsorbed	57.1	90.6	63.3	57.1	63.3

Initial phosphate concentration = ≈20 μg atoms P/l, solids concentration = 15 g/l, temperature = 25° C, and salinity = 35 ppt, pH = 6.

TABLE 15
Kinetic Data of Adsorption of Polyphosphate by Montmorillonite

(pH = 6, Initial TPP = 7.75 μmole/l)

Time (days)	o-PO_4^{-3} in solution (μg atoms P/l)	TPP in solution (μmole/l)	Total Phosphorus in solution (μg atoms P/l)
0.02	0		
0.04	0.04	4.34	13.05
1.15	0.61	1.81	6.05
2.96	2.20	2.23	8.90
8.15	3.43	0.64	6.35
17.06	3.46	0.76	5.75

(pH = 8, Initial TPP = 7.64 μmole/l)

Time (days)	o-PO_4^{-3} in solution (μg atoms P/l)	TPP in solution (μmole/l)	Total Phosphorus in solution (μg atoms P/l)
0.02	0		
0.08	0.18	4.99	15.15
0.81	0.91		
1.81	1.72	2.91	10.44
4.04	5.50	1.95	11.35
7.02	6.60	1.01	9.65
12.19	9.40	0.48	10.80

TABLE 16
Kinetic Data of Adsorption of Polyphosphate by Kaolinite

(pH = 6, Initial TPP = 7.75 μmole/l)

Time (days)	o-PO_4^{-3} in solution (μg atoms P/l)	TPP in solution (μmole/l)	Total Phosphorus in solution (μg atoms P/l)
0.02	0.04		
0.04	0.10	0.25	0.85
1.15	0.17	0.14	0.60
2.96	0.40	0.02	0.46
8.15	0.39	0.03	0.47
17.06	0.31	0.03	0.39

(pH = 8, Initial TPP = 7.64 μmole/l)

Time (days)	o-PO_4^{-3} in solution (μg atoms P/l)	TPP in solution (μmole/l)	Total Phosphorus in solution (μg atoms P/l)
0.02	0.35		
0.08	0.77	3.58	11.5
0.81	2.27		
1.81	3.87	1.44	8.2
4.04	3.77	1.47	8.19
7.02	8.18	0.67	10.20
12.19	11.20	0.43	12.50

TABLE 17

Kinetic Data of Adsorption of Polyphosphate by Illite

(pH = 6, Initial TPP = 7.75 μmole/l)

Time (days)	o-PO_4^{-3} in solution (μg atoms P/l)	TPP in solution (μmole/l)	Total Phosphorus in solution (μg atoms P/l)
0.02	0		
0.04	0	0.04	0.12
1.15	0	0.02	0.07
2.96	0	0.03	0.09
8.15	0	0.04	0.11
17.06	0	0.05	0.16

(pH = 8, Initial TPP = 7.64 μmole/l)

Time (days)	o-PO_4^{-3} in solution (μg atoms P/l)	TPP in solution (μmole/l)	Total Phosphorus in solution (μg atoms P/l)
0.02	0.25		
0.08	0.36	0.01	0.39
0.81	0.30		
1.81	0.42	0.02	0.49
4.04	0.52	0.03	0.62
7.02	0.50	0.06	0.68
12.19	1.25	0.01	1.27

TABLE 18
Kinetic Data of Adsorption of Polyphosphate by Chlorite

(pH = 6, Initial TPP = 7.75 μmole/l)

Time (days)	o-PO_4^{-3} in solution (μg atoms P/l)	TPP in solution (μmole/l)	Total Phosphorus in solution (μg atoms P/l)
0.02	0		
0.04	0	0.02	0.06
1.15	0	0	0
2.96	0	0.03	0.08
8.15	0	0	0
17.06	0	0	0

(pH = 8, Initial TPP = 7.64 μmole/l)

Time (days)	o-PO_4^{-3} in solution (μg atoms P/l)	TPP in solution (μmole/l)	Total Phosphorus in solution (μg atoms P/l)
0.02	0.04		
0.08	0.04	0.05	0.20
0.81	0.28		
1.81	0.12	0.02	0.18
4.04	0.09	0	0.09
7.02	0.07	0.07	0.30
12.19	0.08	0.04	0.20

TABLE 19
Hydrolysis of TPP in Seawater

pH 8; Initial TPP = 7.64 μmole/l = 22.92/μg atoms P/l

Time (days)	o-PO_4^{-3} in solution (μg atoms P/l)
0.02	0.02
0.08	0.12
0.81	0.71
1.81	1.31
4.04	7.18
7.02	11.05
12.19	17.45
14.81	19.45
19.19	21.40
28.81	21.50

pH 6; Initial TPP = 7.75 μmole/l = 23.25 μg atoms P/l

0.02	0.06
0.04	0.25
1.15	0.50
2.96	1.43
8.15	3.80
17.06	7.00
24.27	9.15

TABLE 20

Kinetic Data of Orthophosphate Adsorption (μg atoms P/g sediment) by Elizabeth River Sediments

Sediment Identified by Location Number and Percent Sand by Weight

Time (days)	Sediment No. 1 61 % Sand	Sediment No. 2 63 % Sand	Sediment No. 3 75 % Sand	Sediment No. 4 69 % Sand
0	0.32	0.09	0.29	0.38
0.04	0.58	0.44	0.42	0.61
0.08	0.67	0.50	0.66	0.78
0.29		0.55	0.64	
1.23	0.84	0.65	0.80	0.81
4.98	1.16	0.86	0.93	0.96
7.06	1.28	0.92	0.97	1.06
13.98	1.35	1.03	1.17	1.19
% adsorbed	82.8	63.1	71.7	72.9

Initial phosphate concentration: $\approx$20 μg atoms P/l; solids concentration: $\approx$15 g/l; temperature: 25° C; pH: $\approx$8, and salinity: 35 ppt.

TABLE 21

Atomic Absorption Analysis of Acid Extractable Iron and Calcium On Clay Mineral and Sediment

Clay	mg of Fe/g of clay	mg of Ca/g of clay
Kaolinite	.037	.197
Montmorillonite	.95	.460
Illite	6.35	.177
Chlorite	10.88	.197
Sediments from Elizabeth River		
No. 1	2.70	12.50
No. 2	2.45	0.305
No. 3	0.95	0.133
No. 4	3.07	1.63

TABLE 22

Experimental Conditions of Several Phosphate Adsorption Studies

Author	Clay	μg atoms P/l initial conc.	pH	μg atoms P adsorbed per g of clay	μ (ionic strength)
Black	kaolin	31	6	6.8	~0
	kaolin	31	8	2.9	~0
	mont	31	6	6.8	~0
	mont	31	8	0	~0
	illite	31	6	6.2	~0
	illite	31	8	0	~0
Hemwall	Na-kaolin	115	4	7.0	~0
	Al-kaolin	115	4	8.5	~0
	Na-mont	115	4	1.0	~0
	Al-mont	115	4	10.86	~0
Chakravarti & Talibudeen (1961)	kaolin	10	5	0.51	0.02
	kaolin	10	5	0.54	0.02
	mont	10	5	0.65	0.2
	glau	10	5	0.77	0.02
Burns & Salomon (1969)	kaolin	31	7	1.41	0.33
Chen (1972)	kaolin	90	6	4.8	0.01
	kaolin	90	8	1.8	0.01
Edzwald et al., (1974)	kaolin	500	7.5	4.5*	0.001
	mont	500	7.5	22.6*	0.0001
	illite	500	7.5	71.0*	0.001
This Study	kaolin	50	6	1.79	0.68
		20	6	1.02	0.68
		4	6	0.15	0.68
		20	8	0.49	0.68
	mont	50	6	1.79	0.68
		20	6	0.69	0.68
		4	6	0.08	0.68
		20	8	0.46	0.68
	illite	50	6	3.77	0.68
		20	6	1.29	0.68
		4	6	0.26	0.68
		20	6	0.26	0.68
	chlorite	50	6	3.56	0.68
		20	6	1.42	0.68
		4	6	0.30	0.68
		20	8	1.31	0.68

*Indicates adsorption capacities (Langmuir equation).

TABLE 23
Adsorption of Polyphosphates by Clay Minerals And Percent Increase over Adsorption of Orthophosphate

pH	Clay	μg atoms P adsorbed per g of clay*	Percent Increase
6	Illite	1.54	119.4
6	Chlorite	1.55	109.2
6	Kaolinite	1.52	149.0
6	Montmorillonite	1.16	168.1
8	Illite	1.44	141.1
8	Chlorite	1.51	115.3
8	Kaolinite	0.69	140.1
8	Montmorillonite	0.80	173.9

*μg atoms P adsorbed = TPP adsorbed x 3.

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