Assessment on the Stability and Speciation of Phosphorus in River Sediments

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Abstract: Sediments are heterogeneous mixtures of assorted soil separates and organic matter that serve as repositories of many pollutants. This study investigated phosphorus (P) stability in river sediments as controlled by P speciation and environmental conditions, such as temperature (T), dissolved oxygen (DO), redox conditions (Eh), and pH. It attempted to evaluate the experimental conditions under which P could potentially be tied-up in river sediments. Sediment cores samples were collected from James River, in Virginia, U.S.A. near a former dairy farm and analyzed for T, pH, Eh, carbon (C) and pertinent metal ions. Results indicated that high P concentration correlated well with Fe and had non-uniform correlations with clay, Al and Ca, which changed with depth of cores. At low pH, P concentration was higher in anaerobic than aerobic sediments and aluminum (Al) precipitation was highest at low pH, which indicated Al phosphate stability in reduced (anaerobic) conditions. Above pH 7, in aerobic environments, the Minteqa2 speciation model predicted a high stability for Al-OH species. The minerals variscite, vivianite, strengite hydroxyapatite, and two forms of magnesium hydroxide species were predicted to exist in the pH ranges used in this study. Elemental P distribution assessment using Scanning Electron Microscopy (SEM), Energy Dispersive X-ray (EDX) inferred that P could be bound either to C and Al, Fe or Mn depending on their relative abundances.

Keywords: River sediment, phosphorus, speciation, stability.

1. INTRODUCTION

Sediments could serve both as sinks and sources of P in surface waters. Elevated levels of P in surface waters result in eutrophication, which has negative effects on water quality [1]. Phosphorus cycling between the sediment and water systems is complex since P in the aquatic environment occurs in dissolved reactive form, which is in equilibrium with sediments. When the concentration of the dissolved reactive phosphorus (DRP) is higher in the epilimenion, P adsorption on sediment occurs. However, when the concentration of P in the sediment is higher than what is in the water, desorption occurs and P is lost as soluble P [2]. Phosphorus flux and mineral associations are influenced by physical and chemical parameters. Sediment-associated P can be sorbed onto particles or precipitated as secondary minerals [3]. For instance, vivianite formation is common in Fe-rich, acidic, and anoxic sediments, and it is linked to sewage effluents (House, 2003). The co-precipitation of P with calcite occurs at higher pH's possibly related to hard water or photosynthesis [4].

Manure applications on agricultural fields can result in soil P in excess of crop needs [5]. Phosphorus is transported by erosion, runoff, and subsurface drainage in dissolved or particulate form [6]. Particulate P (PP) includes primary and secondary minerals as well as organic P and is the major portion transferred from cultivated land [7]. Preferential erosion and transport of finer particles results in P enrichment of sediments relative to soil. River dynamics determine the deposition and re-suspension of particles, where in more quiescent waters finer particles settle out while in rapid water flow more suspended particles are carried away. This particle sorting influences the P content of sediments. Particulate P provides a long-term source of P into the aquatic ecosystem and becomes increaseingly available in reducing conditions.

The dynamics of P are sensitive to O_2 status; anaerobic conditions resulting in higher P flux [8]. For instance, reduced Fe^{2+} phosphates have a higher solubility than oxidized Fe^{3+} phosphates, particularly in acidic conditions [9, 10]. Metals and pH also influence P flux, Al and Fe exerting greater influence at lower pH and Ca and Mg under alkaline conditions [11]. Iron redox chemistry controls P flux from sediments with Fe^{3+} acting as a barrier to diffusive P flux. Anaerobic conditions favor ferrous iron (II) phosphate, which is more soluble than ferric iron (III) phosphate [12]. Microbial activity can have contradictory effects on P availability; biological assimilation can reduce availability while decomposition can liberate P [13]. High pore water P can lead to flux into the water

column [14]. Sediment-associated P can be adsorbed onto soil particles [15] or precipitated as secondary minerals [2]. Surface adsorption and solubility of P is controlled by P concentrations while mineral solubility is not influenced by the amount of P precipitate present [16, 12]. This suggests that P minerals may represent relatively immobile sinks for P in sediment systems. Vivianite [$Fe_3(PO_4)_2 8 H_2O$] formation is common in Fe-rich, acidic, anoxic sediments; and co-precipitation of P with calcite also occurs at higher pH [2]. Strengite and variscite can convert to vivianite; and vivianite suppresses P solubility in sediments [12]. Other studies have also indicated that P flux from sediment to water is sensitive to O_2 status and anaerobic conditions result in higher P flux [9]. Near the sediment surface, more oxidized conditions may exist while anaerobic conditions increase with increased depth of the sediment column. Reduced forms of Fe-phosphates have a higher solubility than oxidized forms, particularly in acidic conditions [9, 17]. Ferric iron (Fe^{3+}) and redox chemistry strongly influence sediment P movement to the water column [11]. House [13] also reported greater P flux in anaerobic than aerobic sediments, which he credited to greater availability of carbon and other organic ligands. Others [9, 10] have indicated that the interaction of metals and pH also influence P flux, whereby Al and Fe exert greater influences at lower pH and Ca and Mg at higher pH.

A combination of SEM, EDX element mapping, and GIS techniques provides a method for the spatial analysis of sediment chemistry [18]. SEM allows spatial processing of image samples, while being used to determine the morphology of mineral concretions on the soil fabric; however, it has rarely been used to spatially examine patterns in soil chemistry. Similarly, EDX has long been used as a point-based technique for deriving sample means and transect values of element densities and relationships to further the understanding of pedogenic processes, but it has been used less often to describe special relationships. Through the combination of SEM techniques and GIS analysis, a novel approach has been taken to examine phosphorus chemistry and dynamics in river sediments [19].

The objectives of this study were to (i) assess the presence of P in river sediments near an abandoned dairy farms; (ii) characterize chemical and physical parameters that affect P speciation in river sediments; and (iii) explore the combined utility of SEM, EDX, and Minteqa2 speciation model to determine P stability and precipitation in river sediments.

2. MATERIALS AND METHODS

2.1. Sediment Core Sampling and Characterization

Sediment core samples were obtained by a scuba diver from four sites on James River near Richmond, Virginia (Figure **1**). The sampling site was located
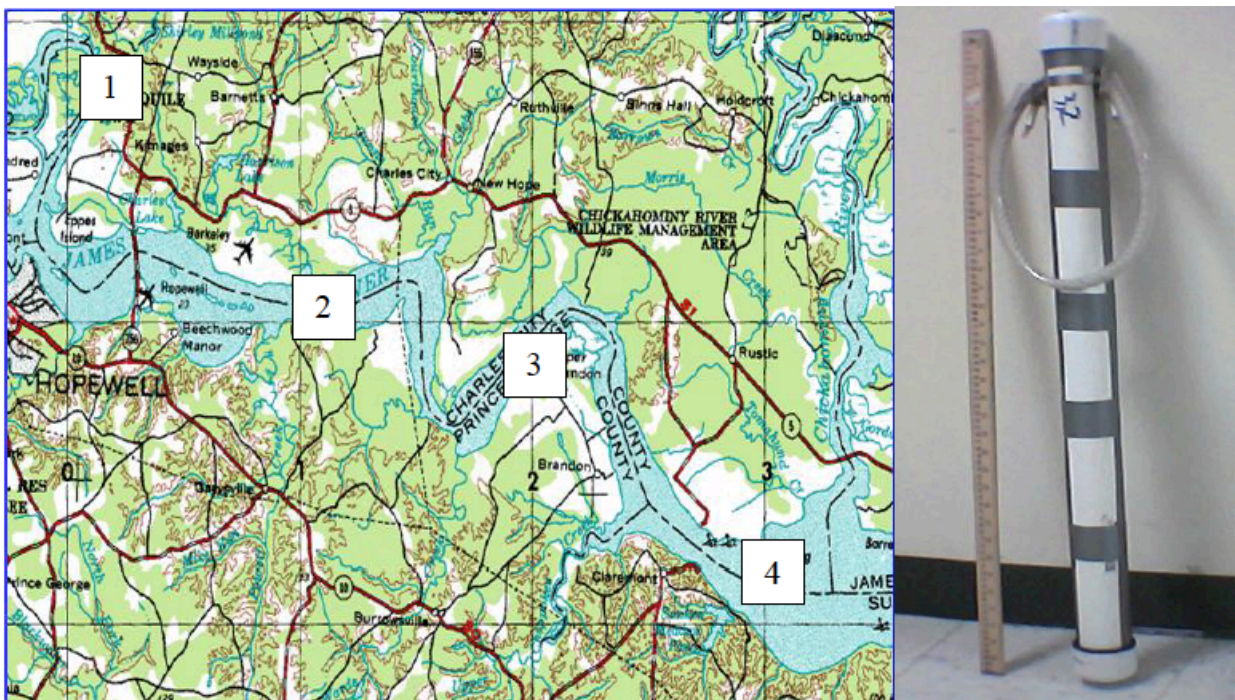
Figure 1: Sampling sites (numbered 1 through 4) and core sampler for sediments along the James River near Richmond, Virginia U.S.A.

downstream from a former Curlesneck Dairy Farm in Henrico County (37° 30'N, 77° 24'W), Virginia. Samples were obtained by inserting vertically cut 4 in. diameter PVC pipes into the sediment column to a depth of 1 meter. The pipes were then slowly pulled out with minimum disturbance after placing a cap in the bottom of the pipe. A second cap was placed on the top of the pipe and sealed to prevent sediment and pore water losses. All cores were stored vertically in a cooler and covered with crushed ice to maintain a temperature of <4°C. They were then transported to the laboratory following procedures described by Moore and Reddy [8]. The cores were opened under a nitrogen atmosphere inside a laminar flow hood and sectioned into 5cm segments. Several sub-samples were taken from each segment in an anoxic condition and analyzed for temperature, Eh and pH using 1:2.5 (sediment to deionized water ratio). Another set of sediment-samples were dried and analyzed for percent elemental abundance using scanning electron micrograph (SEM). Pore water was separated from sediments by placing samples in acid washed Teflon® tubes and centrifuged at 4500 rpm. The supernatant was decanted and filtered through 0.2μm filter paper and analyzed for P and other metals. The remainder of the sectioned core samples was air-dried, ground, acid digested, and analyzed for total metals using Inductively Coupled Plasma (ICP) following EPA Method 3050. Particle size and percent C of sediments were determined by the hydrometer and loss on ignition methods, respectively [19, 20].

2.2. Microcosm Suspension Experiment

Sediment samples taken from each site were sieved to pass through a 2mm screen and kept frozen until needed. A microcosm was prepared using 600ml deionized water and 300 g sediment, which was mixed in 2-liter Mason jars using magnetic stirrers. The mixture was maintained at temperatures between 25 and 30°C. Four holes were drilled on each jar lid and fitted with plastic tubes for introduction of gases, pH, Eh and DO sensors. The desired pH was maintained by adding either 1M HCl or NaOH solutions. Depending on the type of environment (aerobic or anaerobic) to be maintained inside the jars, either nitrogen or air was passed through the inlet tubes and allowed to bubble throughout the content of the jar. The microcosm was then allowed to equilibrate for 4 weeks by periodically monitoring dissolved oxygen, pH, Eh, and temperature.

2.3. SEM and EDAX Studies

Sediment samples were analyzed using SEM and EDX to create spectral maps of P for use in GIS.

Sediment particles were firmly pressed onto a double sticky tape mounted on aluminum stubs and carbon coated using EMS 950x Turbo Evaporator (Electron Microscopy Sciences). The carbon coat thickness typically measured 15-25nm; after coating samples were kept dry and stored in a dehumidifying chamber. Three stubs were derived from each sample and pH level, which was viewed in a Hitachi field emission scanning electron microscope (FESEM) at 20kV. Spectral mapping at several locations per stub was performed at 3,000x magnification using EDAX Genesis EDS software (AMERITEK, Mahwah, NJ) to determine percent elemental abundance for selected elements.

3. RESULTS AND DISCUSSION

Phosphorus flux into and out of sediments is controlled by P speciation and environmental conditions. This study was conducted to characterize chemical and physical parameters that affect P speciation in James River sediments and to evaluate experimental conditions under which sediment-bound P can become biologically available. Sediment cores were analyzed for pH, Eh, P, C and selected metals. Results indicated varying P concentrations with location and the highest P concentration occurred in cores samples near the location of a dairy farm (Figure **2**). The amount of P in sediment was significantly correlated with Al, Fe, Ca, C, clay and/or silt and depths within the cores. The influences of pH, oxygen, metals and organic matter all seem to interact to determine P flux. Under acidic yet aerobic conditions, iron phosphates tend to form while under alkaline conditions calcium phosphates were the predominant forms of P. More P immobilization was also evident under anaerobic conditions. SEM and EDX analyses suggest that P was associated with clay, organic matter, Fe and Mn under acidic and anaerobic conditions; which was consistent with Minteqa2 findings.

Sediment core samples from near Curlesneck Dairy Farm (site 1) contained higher concentration of sediment bound P, average concentration = 1050ppm than soluble P, average concentration = 125ppm, (Figure **1**). Both forms of P did not vary significant with depth, except for the core from site 4 which showed inconsistent values. The influence of the dairy farm operation near this site was suspected to be a major contributor to the observed high P concentrations in sediment and pore water samples. These samples also showed a wide range in concentration of metals. Iron
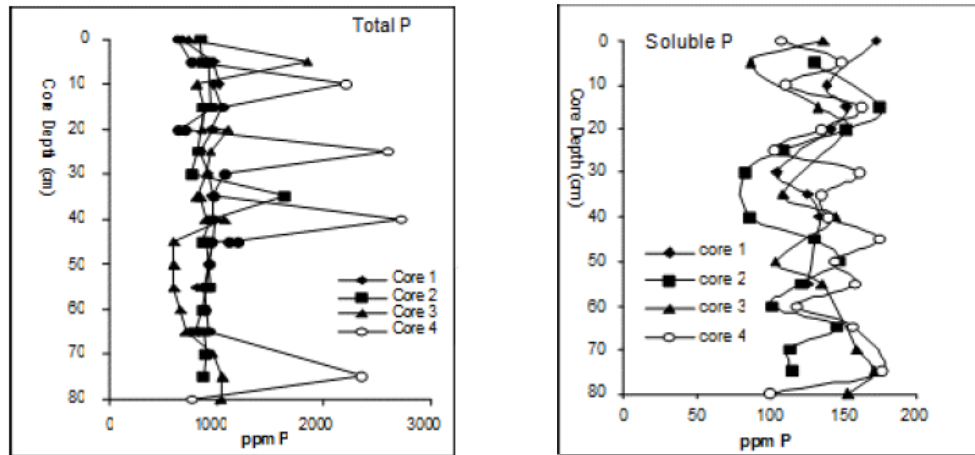
Figure 2: Variation in total P and soluble P concentrations with depth in sediment core samples obtained from James River near the former Curlesneck dairy farm.

was the predominant metal found (35,000 to 80,000ppm) in sediment core samples. The concentrations of other metals were comparatively lower, with Al ranging from 13,000 to 29,000ppm, and Ca from 3,000 to 9000ppm. It was assumed that if any precipitation of P were to occur, it would be primarily due to the high concentration of Fe, which could serve as a preferred companion ion. Sediment core samples from site 1 were also high in clay (25 to 69%), and sand (5 to 68%). The diverse silicate clay minerals could also serve as adsorption sites for P. There were also sections in the cores that were rich in organic matter. The organic layers from cores 1 and 2 at 70cm depth and cores 3 at 50cm depth corresponded to high carbon, and in some instances indicated high moisture and low pH conditions. Pore water samples taken from each core had low ortho-P levels except the top few centimeter layers that showed much higher ortho-P concentrations.

Results in Table **1** indicate that James River sediment from site 1 (Figure **1**) showed high correlation between Fe and P in all replicated samples. In core 1, P was negatively correlated with pH and positively correlated with Al and Fe, which could imply that P precipitation with Al and Fe was feasible. In core 2, P was positively correlated with C, Ca, and Fe. In this case organic matter, Ca, and Fe could potentially serve as ligands to precipitate P. Core 3 showed high correlation with Ca and Fe indicating P precipitation with Ca and Fe could be possible. Results from core 4 samples also showed significant correlations between P and clay, P and Ca, as well as P and Fe. The concentration of Fe was much higher than any other element found in sediment samples, which may partially explain the high correlation between Fe and P. Moreover, since the measured pH of the sediment was

low, P minerals could be predominantly associated with ferrous (Fe^{+2}) ion. Iron was strongly correlated with P in all cores, while Ca, C and clay were positively correlated with P in cores 1 and 4 (Table **1**). Layers of clay or organic debris resulted in high variability in clay or C levels within a core that resulted in stronger correlations between these properties and P concentrations in sediments. Samples from cores 1 and 4 showed high particle size variability with clay ranging from 25 to 70% in core 1 and from 27 to 56% in core 4. In these cores, P had better correlations with high clay variability than in cores with low clay variability. The low pH, C and Al concentrations along with the high clay content occurred in core 1 where Al was strongly correlated with P, and pH was negatively correlated with P suggesting that in finer grained and acidic sediments, Al may be a controlling factor in P immobilization than in coarser grained, less acidic sediments. The organic layers, in cores 2 at 70cm depth and core 3 at 50cm depth, corresponded to high C and in some instances high moisture or low pH. The
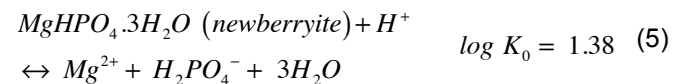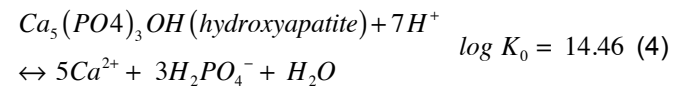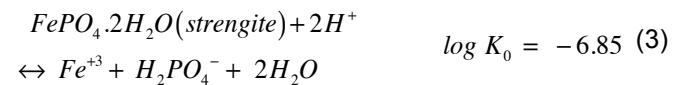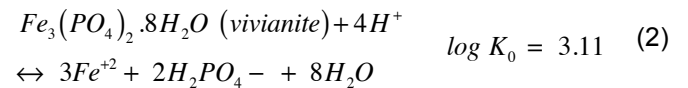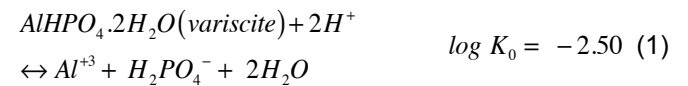
Table 1:   Phosphorus Correlations with metals in Sediment Core Samples Obtained from James River

Correlation	Core 1	Core 2	Core 3	Core 4
P:pH	-0.59*	0.10	-0.22	-0.16
P:Eh	-0.30	0.14	-0.01	0.16
P:Clay	0.41	-0.25	-0.11	0.70*
P:C	-0.19	0.52*	-0.21	-0.28
P:Ca	-0.32	0.66*	0.81*	0.88*
P:Al	0.73*	0.01	0.09	-0.08
P:Fe	0.54*	0.87*	0.85*	0.97*

*Implies existence of correlation.

strong positive correlation between P and Fe, Ca and clay in core 4 reflect the role of Ca or Fe as a bridge between the negatively charged clay and phosphates. In some instances layers of organic debris increased the correlation between C and P, such as in core 2. Moreover, sampling at site 2 was extremely difficult due to the rocky nature of the river bed. As the result, sediment samples could not be obtained with greater depth. Collected samples were sandy (ranging from 58 to 98%) with a few exceptions in sediment layers with high organic content. They were generally low in P both in pore water and sediment samples. Phosphorus concentration in the sediment reflected the physiographic influence of the region as reflected by the soil formation typically characterized by high Fe and Al contents. The flow of the river was more quiescent at site 3 with deep sediment layers. As the result, samples collected from sites 1, 2 and 3 were more clayey with some distinct layers showing dark sand and clay mixtures coated with organic materials at depths between 10 and 20cm. Surface sediments were very wet and loose, with sand content ranging from 15 to 95%. The cores had low P with the exception of a layer at about 5 to 10cm depth in core 2 that had high concentrations of P, Al and Fe. These concentrations varied with replicate samples, possibly due to inclusion of organic debris. In general, the characteristics of sediment core samples included loose and sandy, where sand ranged from 74 to 91%, with some clay layers in cores 2 and 3 between 10 and 15cm. Sediment layers (15 to 91cm depth) were very firm to brittle and difficult to penetrate with the corer. The sandy nature of the sediments was reflected by high variability in C content and low concentrations of Al, Fe and Ca.

Figure **3** shows solubility diagram for the most likely minerals that would form under the experimental conditions in the microcosm (temperature $25^{o}C$, aerobic or anaerobic). The figures were generated using the Minteqa2 speciation model software [1]. Results from the microcosm experiment were used as base data for the Minteqa2 chemical speciation model. The model predicted Fe and Al phosphate species to predominate in acidic conditions, and Ca and Mg in basic conditions. Mn-phosphate species were stable under both aerobic and anaerobic conditions. Based on the model predictions, strengite would form under aerobic and acidic conditions, while vivianite would form under anaerobic and acidic conditions. Equations that show the dissolution of these minerals under the laboratory conditions used in the study are shown here along with their equilibrium constants:

$$AlHPO_4.2H_2O(variscite)+2H^+$$
$$\leftrightarrow Al^{+3}+H_2PO_4^-+2H_2O \qquad log\,K_0=-2.50 \quad (1)$$

$$Fe_3(PO_4)_2.8H_2O\ (vivianite)+4H^+$$
$$\leftrightarrow 3Fe^{+2}+2H_2PO_4-\ +8H_2O \qquad log\,K_0=3.11 \quad (2)$$

$$FePO_4.2H_2O(strengite)+2H^+$$
$$\leftrightarrow Fe^{+3}+H_2PO_4^-+2H_2O \qquad log\,K_0=-6.85 \quad (3)$$

$$Ca_5(PO4)_3OH\,(hydroxyapatite)+7H^+$$
$$\leftrightarrow 5Ca^{2+}+3H_2PO_4^-+H_2O \qquad log\,K_0=14.46 \quad (4)$$

$$MgHPO_4.3H_2O\ (newberryite)+H^+$$
$$\leftrightarrow Mg^{2+}+H_2PO_4^-+3H_2O \qquad log\,K_0=1.38 \quad (5)$$

Variscite and strengite are common in soils and freshwater sediments [3]. FePO4(s) (strengite) and AlPO4 (s) variscite) are stable solid phases if P precipitates in the low-pH range. In neutral to alkaline
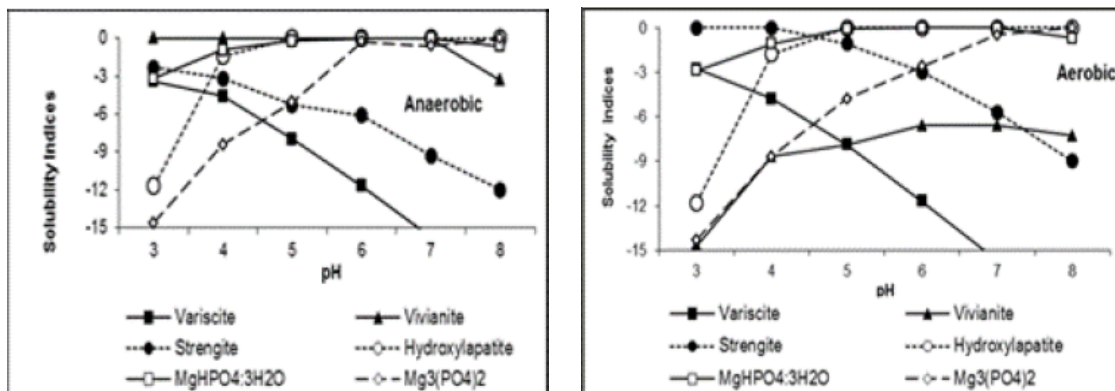

Figure 3: Solubility/stability diagram for phosphate minerals in sediment core samples as predicted by the Mintequa2 speciation model both in aerobic and anaerobic conditions.

pH ranges, metastable hydroxophosphate containing [Al(III) or Fe (III)] precipitates can be formed. Other Ca-P and Mg-P species, such as newberryite and hydroxyapatite also precipitate at much higher pH ranges in sediments [22]. Figure **3** also shows that under both aerobic and anaerobic conditions, Mg- and Ca-bearing minerals [$MgHPO_4.3H_2O$, $Mg_3(PO_4)_2$, and $Ca_5(PO_4)_3OH$] were more soluble (as indicated by increasing solubility index) with increasing pH. In the aerobic situation steady increase in solubility index for vivianite formation with pH would indicate this Fe-phosphate mineral might not be stable. Strengite and variscite showed the most decrease in solubility in both aerobic and anaerobic situations perhaps implying more stability of these Fe- and Al-phosphates. The solubility and/or stabilities of these compounds in sediments is specific to the experimental conditions imposed by this study.

Elemental analysis results obtained in the laboratory and chemical model prediction using Miteqa2 indicated that P would be soluble along with most of the elements at pH 4, Table **2**.

Table 2: Minteqa2 Speciation Model Predictions for Phosphate Precipitation at pH 4 and pH 8

| Element	pH 4	pH 8
Fe	Fe^{2+} dissolved (100%) Fe^{3+} dissolved (100%)	Fe^{2+} precipitated (100%) Fe^{3+} dissolved (100%)
Ca	Dissolved (100%)	Precipitated (99%)
Al	Precipitated (100%)	Precipitated (100%)
Mn	Mn^{2+} precipitated (100%) Mn^{3+} dissolved (100%)	Mn^{2+} precipitated (100%) Mn^{3+} dissolved (100%)

However, at pH 8, it would precipitate with Fe^{+2}, Ca, Al, and Mn^{+2}. While the literature would support P precipitation with Al and Ca at high pH, the Minteqa2 prediction for Mn^{+2} and Fe^{+2} precipitation would indicate specific environmental conditions at the sampling site where Mn^{+2} and Fe^{+2} were present at predominantly higher concentrations than the other ions (Table **2**). Aluminum could be a major ion in competing with other ligands for P precipitation in James River sediments. Similarly ferric ion (Fe^{+3}) might also be a preferred ligand for P precipitation in the sediment core samples, since this ligand was predicted to dissolve at both pH conditions (Table **2**). Minteqa2 also predicted that P would precipitate with Al and Mn^{+2} at pH 4 and 8, making Al a more likely companion ion for P precipitation. Since Mn is not present at high

concentrations in assayed sediment core samples, it is unlikely that Mn-bearing phosphate species would be able to form under the selected experimental conditions.

Figure **4** depicts results of the microcosm study when the system was kept under aerobic conditions and varying pH ranges. At all pH ranges, Fe is the predominant metal ligand that would be expected to bind P in sediments. The abundance of Fe in James River sediments is primarily due to the iron-rich Triassic parent materials of the Piedmont and Coastal Plain residuals through which the river flows. The next abundant element is Al followed by Ca, Mg, and Mn. The distribution of these elements was similar in the
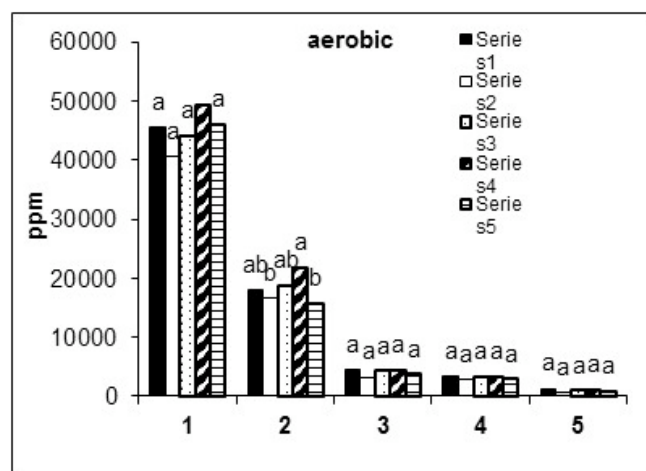
Figure 4: Availability of metal ligands for P binding by the same letter for each metal are not significantly different from each other.
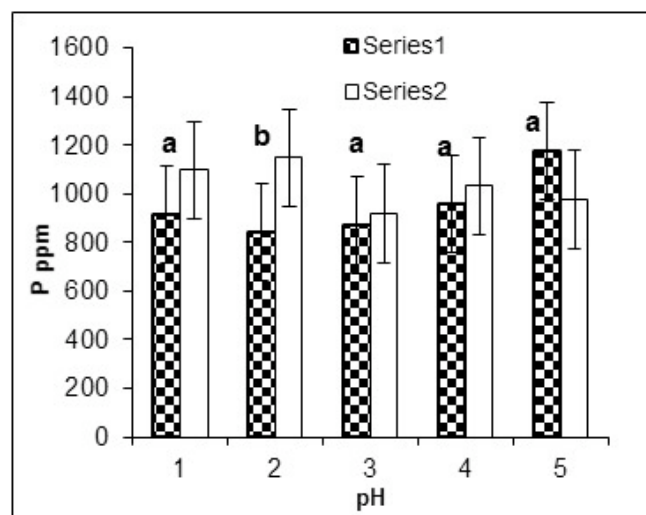
Figure 5: Sediment-bound P released from sediments at various equilibrium pH ranges under aerobic or anaerobic conditions.

anaerobic experimental setting. Data in Figure **4** suggest that P availability might be governed by Fe^{+2}/Fe^{+3} equilibria at all pH conditions. Results from the laboratory experiment in which sediment samples were maintained in aerobic or anaerobic conditions at varied pH indicated that P was lower in anaerobic sediments at pH 4 and 5 (Figure **5**). It appears that P availability is higher when the system was kept under anaerobic and low pH conditions. At alkaline pH more P was detected under aerobic than anaerobic conditions. In both anaerobic and aerobic conditions obtained data also showed considerable variability in Al concentration. High concentrations of iron in sediments and significant correlations between Fe and P suggest that Fe has an important influence on P dynamics in James River sediments. Aluminum phosphate ($AlPO_4$) is stable around pH 5 and $FePO_4$ increases in stability below pH 5 with decreasing stability at lower pH values [12]. The decrease in P, Ca, Fe and Al at low pH possibly relates to the generally higher P solubility, a transition from hydroxyphosphates of Fe and Al at higher pH to Fe and Al phosphates at lower pH. Variscite and strengite are common phosphate minerals in acidic and aerobic environments [9]. House [18] has reported a close relationship between P, Ca, Fe and organic matter in river sediments, and stated that sediments are influenced by redox conditions, and Fe-phosphates can form in oxidized conditions [9]. Iron and P can be released in reducing, particularly acidic conditions; and Al and Fe phosphates are more stable at low pH while Ca phosphates are more stable at high pH [12].

Phosphorus flux and mineral associations are influenced by physical and chemical parameters. Near the surface, at the sediment-water interface, more oxidized conditions exist while deeper in the sediment column reduced (anaerobic) conditions would be expected to dominate [11]. Surface sediment characteristics could be highly variable due to mixing during turbulent water flow. This was apparent in the measured surface pH values, where readings were inconsistent. The influence of pH on P flux was more important at lower than at higher pH values. The negative correlation between P and pH in the first core samples from the selected site suggested that some degree of P concentration was controlled by pH, particularly at lower pH ranges. This was supported by positive correlations observed with P and Al as well as P and Fe. Sediment core samples taken from site 4 had the highest pH values and displayed a strong correlation with Ca and Fe. This could be due to input from nearby agricultural operations that use lime for soil conditioning.

4. CONCLUSIONS

Phosphorus in river sediments exists in highly buffered medium bound to companion ions, both alkaline and acidic earth metals, such as Ca, Mg, K, Fe, Mn, and Al; and to organic carbon. The solubility or release and precipitation or adsorption of P in the sediment water system is controlled by its immediate environment, such as pH, temperature and dissolved oxygen. All of these parameters seem to be affected by the turbulence generated by the water current. At low pH or reduced conditions, P associates more with acidic cations; therefore its stability might be controlled by the Fe^{+2}/Fe^{+3}, Mn^{+2}/Mn^{+3}, and Al equilibria. Consequently, at low pH, P bearing minerals would be enriched with Fe^{+2}, Mn^{+2}, and Al; and at higher pH, they would be enriched with Ca^{+2}, Mg^{+2}, Fe^{+3}, and Mn^{+3}. Understanding the factors that control P stability in the sediment water system would help control conditions under which the element may be retained in sediments to prevent its desorption into the water column.

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