THE ROLE OF IRON-RICH SEDIMENT IN THE BIOGEOCHEMICAL CYCLING OF PHOSPHORUS IN GEORGIA PIEDMONT IMPOUNDMENTS

by

AMANDA KAYE PARKER

(Under the direction of M. Bruce Beck)

ABSTRACT

Phosphorus cycling in lake systems can be significantly affected by the iron cycle. Iron oxides bind inorganic phosphorus via ligand exchange. Bt horizon soil in the Georgia Piedmont is high in oxidized metals, especially iron and manganese. Impoundments in the Georgia Piedmont receive sediment laden with phosphorus and iron from tributary flow. We present here studies that explore the role of transported sediment in the biogeochemical cycling of phosphorus in Lake Lanier, a Georgia Piedmont impoundment. X-ray diffraction analysis of Lake Lanier surface water demonstrate that newly formed iron oxides are present in surface water samples. Experiments to investigate the capacity of iron oxyhydroxide, Piedmont soil from the Bt horizon, and Lake Lanier sediments to adsorb phosphate were conducted in a series of treatments. Lake Lanier sediments had the greatest capacity to sorb phosphate in all treatments, and sorbed all the phosphate in solution in most experiments. We conducted laboratory investigations to determine if sediment bound phosphorus would be available for uptake by natural cultures of lake phytoplankton. Biological uptake of radiolabelled P in the sediment treatment was not evident. Alkaline desorption experiments were conducted with Bt horizon soil. Desorption of phosphate occurred at pH values greater than 8. The higher the pH the greater the
desorption of phosphate from Bt horizon soil. Transported sediment plays a more significant role in the phosphorus cycle in impoundments of the Georgia Piedmont than in the north temperate systems where the traditional phosphorus cycling paradigm was developed. The photosynthetic elevation of the local pH may increase local phosphate availability by releasing phosphate from oxidized metal complexes, and thus may be a mechanism for niche construction by phytoplankton in poorly buffered surface waters.

INDEX WORDS: Phosphorus, Nutrient Cycling, Lake Lanier, Iron, Phosphate, Nutrient Availability, Oxidation-Reduction, Iron-Phosphorus Interactions
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DEDICATION

This dissertation is dedicated to the friends and family that have been so supportive and helpful during the time I have spent working on my dissertation. Thank you.
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CHAPTER 1. INTRODUCTION

This dissertation seeks to investigate the cycling of phosphorus and the role of iron in impoundments in the Georgia Piedmont. Phosphorus is the primary nutrient of concern for eutrophication. Eutrophication brings with it increases in nuisance phytoplankton and increases in bacterial biomass in the warm waters of the southeastern United States. Eutrophication also leads to increased organic matter cycling, and can increase problems with pathogenic bacteria. Increases in biomass of phytoplankton and bacteria in the surface waters that typically accompany eutrophication, may also lead to increases in organic carbon delivery to the sediments, which can lead to reduction of oxidized iron in the sediments and release of bound phosphate. The role of iron in the phosphorus cycle has been previously explored, but as national regulatory programs are developed for management of nutrients in surface waters (USEPA 1998), regional differences in the cycling of nutrients become important to identify the most appropriate concentrations of nutrients for surface waters, and the most appropriate management actions needed to achieve those nutrient concentrations.

Phosphorus Cycle in Lakes

The scientific basis for the conventional paradigm of phosphorus cycling in lakes was developed with data primarily from high alkalinity (< 20 mg/L), north-temperate systems (Hutchinson 1957, Rodhe 1969, Carlson 1977). This paradigm involves the sinking of inorganic particles and organic material from the surface (epilimnnetic) waters to the hypolimnnetic waters of lakes during stratification. The depletion of oxygen and anoxic respiration in the hypolimnion creates reducing conditions in the
buffered waters and sediments of north-temperate lakes in the Midwestern US. Iron can play an important role in the cycling of phosphate by sequestering it in the oxygenated waters, and then releasing it as oxidized iron is reduced in the sediments. Oxidized iron complexes with phosphate and may precipitate, aggregate and/or sorb to other particles as they sink to the sediments. Iron-phosphorus compounds are reduced and organic matter is decomposed in the anoxic hypolimnion and reduced sediments resulting in a steady increase in DIP (dissolved inorganic phosphorus) which is circulated to the lake at mixis. (Hutchinson 1957; Wetzel 2001; Goldman and Horne 1994). This phosphorus cycling paradigm fails to explain phosphorus cycling in Southeastern Piedmont lakes.

The climate in north-temperate regions creates ice-covered lakes in winter that stratify thermally, with the colder water at the surface. These climatic conditions produce dimictic lake systems; lakes that stratify in both summer and winter and mix twice in the annual cycle, at fall overturn and at spring ice-out. The north temperate regions on which the traditional P cycling paradigm was developed typically have high total alkalinity (> 20 mg CaCO$_3$/L), measurable concentrations of Ca and K, and low concentrations of Fe.

In contrast, the climate in the Southeastern Piedmont provides a longer growing season and warmer annual average temperatures than those found in north temperate regions. This difference in climate affects the length of time the lake is stratified, and the strength of disturbance needed to disrupt stratification. The lack of ice cover during the winter months is also important, creating warm-monomictic rather than dimictic lake systems in the southeast region of the US. The siliceous (or acid) geologic materials of the Southeastern Piedmont are rich in Fe, but have low total alkalinity (< 20 mg CaCO$_3$/L, unpublished data), and low concentrations, frequently below detection limit, of Ca and K, and thus little buffering capacity.
The lower buffering capacity, alkalinity, sulfur concentrations, and higher iron concentrations in lakes of the Southeastern Piedmont create conditions that prevent the accumulation of DIP in the anoxic hypolimnion and its subsequent circulation at fall mixis in Southeastern Piedmont lakes. Biogeochemical cycling of phosphorus in Southeastern Piedmont impoundments, and the role of iron and organic carbon in that cycle, are the central themes of this dissertation.

The Role of Phosphorus in Lakes

Phosphorus (P) is considered the nutrient most frequently limiting to algal production in lakes (Hutchinson 1957; Rodhe 1967; Carlson 1977; Carpenter et al. 1998). Hence, elevated concentrations of P generally lead to an increase in nuisance algal blooms and lake eutrophication. Phosphorus occurs in lakes in both organic and inorganic forms. The most common measurements of phosphorus, however, are those of the total phosphorus in unfiltered water, and dissolved inorganic phosphorus (DIP, orthophosphate), the fraction most easily consumed by the biota. Total particulate P (comprised of bacterial, animal, and plant P, and suspended inorganic P) is generally present in much larger quantities than soluble P in most aquatic environments. Particulate and dissolved forms of phosphorus are defined analytically as those which do not and do pass through a 0.45 μm filter. Dissolved organic P (DOP) low-molecular weight phosphate esters and organic and P absorptive colloids make up the bulk of total dissolved P (Wetzel 2001). The small DIP fraction primarily occurs as orthophosphate (PO$_4^{3-}$). A fraction of dissolved P is also found in colloidal form, but colloidal P does not usually comprise a significant fraction of total P (Goldman and Horne 1994).

Bioavailability of DIP is restricted by its tendency to precipitate in the presence of bivalent metal (Ca$^{2+}$, Mg$^{2+}$) and ferric (Fe$^{3+}$) ions at neutral to alkaline pH, and its tendency to sorb to clay and poorly crystalline inorganic particles such as aluminum and iron oxides (Reynolds and Davies 2002). The ratio
of precipitated to cycled phosphate is determined by water chemistry (such as pH and concentration of
cations which favor precipitation) and hydrological conditions (such as stratification, and internal
seiches) that may restrict or enhance the free movement of phosphate (Atlas and Bartha 1993; Wetzel
2001, Reynolds and Davies 2002). Turnover time for DIP in the epilimnion of stratified lakes as
demonstrated by radio-tracer studies is rapid (minutes to hours), and is bacterially mediated (Rigler
transformations can be viewed as transfers of inorganic to organic phosphate as DIP is incorporated
into bacterial and algal biomass. However, transfers of insoluble, immobilized forms to soluble or
mobile compounds and releases of DIP from the decomposition of organic matter are also microbially-
mediated phosphorus transformations (Reynolds and Davies 2002).

Phosphorus cycling in lake systems can be significantly affected by the iron cycle. Ferric oxides
sorb DIP via ligand exchange. These ferric-phosphorus complexes can be transformed by reduction to
the more soluble ferrous form, and by desorption at elevated pH; both transformations release sorbed
phosphate. Biochemical transformations of phosphorus in a lake then, can only be understood in the
context of redox potential or the development of reducing conditions and the related concentrations of
iron (Hutchinson 1957).

The Iron Cycle in Lakes

Iron can be delivered to waterbodies as ferrous (Fe$^{2+}$) and ferric (Fe$^{3+}$) ions, iron hydroxide
(Fe(OH)$_3$), iron oxides and oxyhydroxides (Fe$_2$O$_3$, FeOOH) with various crystallinity, or complexed to
calcium, phosphorus, and other anions. Once in a receiving waterbody, iron can be transformed via
reduction, oxidation, and precipitation or biological consumption. The mobilization of insoluble ferric
phosphates may occur when microorganisms reduce ferric ions to ferrous ions in soil or sediments under anaerobic conditions (Stumm and Morgan 1996).

The cycling of iron consists primarily of oxidation-reduction reactions that reduce ferric to ferrous ions and oxidize ferrous to ferric ions. Amounts of iron in solution, and the rate of oxidation of ferrous to ferric iron in oxygenated water, primarily depends upon the pH, Eh, and temperature. Ferrous ions are oxidized spontaneously in the presence of oxygen to the ferric form in alkaline to neutral conditions, and may be precipitated as ferric oxides and ferric oxide complexes in alkaline environments (Einsele 1948, Hutchinson 1957, Sumner 2000, Wetzel 2001); these reactions are important in both inorganic and organic iron-containing compounds. Iron complexes with certain organic molecules altering thus its solubility and availability. Elevated concentrations of complexed soluble iron are associated with high levels of humic acids, tannic acids, and other lignin derivatives which can act as chelating agents for ionic and charged colloidal iron (Hutchinson 1957; Wetzel 2001).

Ferric hydroxide in oxygenated waters has low solubility, but may be found as a flocculent (particle sizes < 500 nm), or as a finely divided precipitate of ferric hydroxide that has the properties of a colloid (particle sizes from 1 to 500 nm, charged). Colloidal particles of Fe(OH)$_3$ commonly are positively charged, although a negative charge can occur at high pH. Ions in solution (including PO$_4^{3-}$) and negatively charged clay particles, organic colloids, and other suspended solids can neutralize the charges on the hydroxide colloidal particles. The uncharged aggregates join to form a rapidly settling precipitate. As pH increases (> 8), the colloidal Fe(OH)$_3$ particles may lose their positive charge and thus any complexed anions (Stumm and Morgan 1996). This release of anions may be important in waters where algal photosynthesis elevates the local pH.
In environments of limited oxygen diffusion and significant heterotrophic microbial activity, anaerobic conditions may decrease the redox potential sufficiently (<200 mV) to allow ferric iron to act as an electron sink and be reduced to Fe$^{2+}$, or precipitated as ferrous sulfide in the presence of H$_2$S (Hutchinson 1957; Atlas and Bartha 1993; Wetzel 2001). Iron is more soluble in the ferrous state than in the ferric state, hence reduction of ferric-phosphate complexes solubilizes both iron and phosphorus. The reduction of ferric to ferrous forms is the mechanism that leads to elevated phosphate concentrations in the anoxic hypolimnion of lakes in the traditional phosphorus cycling paradigm.

The high reactive iron content (~2 - 3 % by weight, see Chapter 3) in the soils and resident parent material of the Georgia Piedmont (Figure 1.1) results in significant transport of iron in runoff to receiving waterbodies (Figure 1.2). Bt horizon soil particles are easily transported in runoff and are iron-rich. Evidence from studies of agricultural runoff indicates that the mechanical working of these soil particles can decrease the size and increase the availability of reactive surfaces of transported soil particles (McDowell et al. 2002), and thus may enhance the sorptive capacity of these particles. Hence, in the circum-neutral pH of the surface waters of the Georgia Piedmont, the availability of inorganic phosphate is likely controlled by the iron cycle.

**Internal Phosphorus Loading**

Impoundments in the Georgia Piedmont receive sediment laden with phosphorus from tributary flow (Figure 1.2). Suspended sediment concentrations are quickly attenuated in most lakes as sediments are deposited, though may persist for relatively longer periods of time when the particles are small enough to have a slower settling rate (Kennedy and Walker 1990). Much of the phosphorus associated with sediment is complexed to oxidized metals and settles or precipitates out of solution into the sediments (Hayes and Phillips 1958; Tarapchak and Nalewajko 1986; Wetzel 2001).
Iron reduction proceeds spontaneously, but slowly as other electron acceptors are consumed under anoxic conditions (Table 1.1, after Cai et al. submitted). Iron reduction is known to be microbially mediated by a diverse group of bacteria collectively known as iron-reducing bacteria (FeRB) (Lovely and Phillips 1986). These bacteria use oxidized iron as an electron acceptor for carbon mineralization in anaerobic conditions. They have been found in marine and freshwater sediments, and compete with sulfate reducers and methanogenic bacteria for organic carbon (Roden and Gorby 2002). Roden et al. (2002) propose that microbially mediated iron reduction and oxidation form a coupled system in circumneutral, low-sulfate freshwater environments such as Lake Lanier, and could become the primary form of organic matter mineralization in these sediments.

Much of the P transported to waterbodies sinks to the sediments where it is consumed and chemically transformed. Sediment release of soluble inorganic phosphorus occurs when oxidized metals are spontaneously reduced in anaerobic conditions, or are used as electron acceptors for carbon mineralization by FeRB (Mortimer 1941, 1942; Roden et al. 2002). Soluble P released from the reduction of metals in the sediments can be inhibited by resorption to newly formed iron oxides in less reduced conditions above the sediment water interface. The release of inorganic phosphate from reduced sediments to the water column is known as internal loading.

The internal loading of phosphorus can contribute significantly to the productivity of lake systems, and can result in significant water quality degradation. In a series of lakes targeted for water quality restoration in the Netherlands, water quality improvement was inhibited due to prolonged internal phosphorus loading. The water quality in these systems was not improved by nutrient load reduction, due to internal phosphate loading from the sediments (Boers et al. 1998). Consumption of organic matter in the sediments by metal reducing bacteria releases phosphate. Hence, reducing nutrient
loading without also reducing delivery of consumable organic matter to the sediments may result in internal phosphorus loading, and no improvement in water quality (Boers et al. 1998).

*The Role of Organic Carbon in Internal Phosphorus Cycling*

Organic matter loading and consumption are important to phosphorus cycling. Consumption of organic matter by metal reducing bacteria in the sediments and hypolimnetic waters leads to reduction of iron and hence release of phosphate from oxidized iron-phosphate complexes. Accordingly, microbial activity in the sediment plays an important role in carbon degradation and nutrient regeneration and cycling. Sediments with large amounts of consumable organic carbon and an abundant supply of oxidants will support metal reducing bacteria. The reduction of oxidized metals during bacterial carbon mineralization can lead to substantial release of sorbed or complexed anions, such as phosphate, at mixis. The amount of complexed anions released from oxidized metal complexes in the sediments is largely dependent upon the supply of oxidized metals and easily consumable organic carbon (Sposito 1994, Kotska 2002).

Easily consumable organic carbon can be delivered to lake sediments by loading from allochthonous nonpoint and point sources, and through autochthonous inputs, primarily via senescing phytoplankton and bacteria. Consumption of easily consumable forms of organic carbon can lead to iron reduction and release of inorganic phosphate in sediments. Allochthonous organic carbon inputs are generally thought to be primarily comprised of recalcitrant forms of organic carbon. Cole et al. (2002), however, demonstrated that allochthonous organic carbon is respired by lake bacteria, but is not incorporated into biomass, and thus, oxidation of terrestrial DOC can be the primary source of lake dissolved inorganic C. The respiration of allochthonous organic C inputs may also fuel reduction of iron oxides and the production of inorganic C in anoxic lake sediments.
Van Mooy et al. (2001) demonstrate tight coupling between cycling of particulate organic matter (POM) and active bacteria in Lake Michigan. The cycling of POM changes during the course of stratification due to changes in the source of POM from one at depth due to primary production in a deep chlorophyll layer to one of recycled production in surface waters. The cycling of POM at depth and the transference of cycling of POM to surface waters is indicative of the increased processing of organic matter over the course of summer stratification.

*Release and Re-oxidation of Reduced Metals: The control of P by re-oxidized metals*

In alkaline to neutral conditions, ferrous iron is inherently unstable in the presence of oxygen and is oxidized spontaneously to ferric iron (Stumm and Morgan 1996). Microorganisms do not usually extract energy from this oxidation reaction. Anaerobic conditions may be sufficient to allow ferric iron to act as an electron sink and be reduced to Fe$^{2+}$ in environments of limited oxygen diffusion and significant heterotrophic microbial activity (Atlas and Bartha 1993). Iron reduction also occurs nonenzymatically when reduced products of microbial metabolism, such as formate or H$_2$S, react with Fe$^{3+}$ chemically (Atlas and Bartha 1993).

The consumption of oxygen in the hypolimnion during stratification creates progressively more reduced conditions in the bottom waters (Wetzel 2001). The consumption of oxygen is greater near the sediments and at the metalimnetic plate creating an area of higher oxygen concentrations and less reduced conditions in the middle depths of the hypolimnion in Lake Lanier. Oxidation of reduced metals occurs in this region as they diffuse upward and are oxidized by oxygen, nitrate, and other electron acceptors. The progression of electron acceptors changes as these acceptors are consumed and conditions become progressively more reduced (Table 1.1). For example, MnO$_2$ sedimenting into
water containing ferrous ions is reduced and the ferrous iron is simultaneously oxidized to ferric hydroxide (Hutchinson 1957).

Newly formed oxidized iron, in particular, is poorly crystalline and has active surfaces for anion complexation; thus, it effectively binds soluble phosphate and other anions, preventing their circulation to surface waters at mixis (Stumm and Morgan 1996; Sposito 1994). Caraco and Valiela (1983), in a study of suspended particulates, found that iron oxides form at oxic/anoxic interfaces and rapidly remove phosphate from solution before it reaches the biota. Particulate iron and phosphorus peaks occurred at the oxycline at most samplings, indicating phosphate was scavenged by iron oxides. They also found that the peak in downward particulate phosphorus flux was associated with a peak in iron flux. They conclude that chemical scavenging by iron oxides is significant in controlling the supply of phosphate to the photic zone (Caraco and Valiela 1983). More recently, Roden et al. (2002) have proposed the coupling of bacterially mediated iron reduction and oxidation may create a primary pathway of carbon mineralization in low sulfate freshwater environments. The coupling of iron reduction and oxidation may thus produce an effective mechanism for inhibiting phosphate release to the photic zone due to chemical scavenging by newly formed iron oxides.

Release of Phosphorus

Phosphate can bind to oxidized metals in two different ways. Phosphate may be bound to mineral surfaces through surface sorption or may be more strongly bound into ferric phosphate mineral compounds. Phosphate bound by surface sorption is generally thought to be more available to the biota than that more strongly bound into ferric phosphate mineral compounds (Stumm and Morgan 1996). Orthophosphate sorbed to oxidized metal surfaces may become available through weak dissociation, desorption, or through chelation of either the oxidized metal or orthophosphate (Reynolds and Davies
Oxidized metals are positively charged at pH values below the zero point of neutral charge and can also form chemical complexes with clay, organic colloids, and biologically important anions. Elevated pH (> 8) can cause suspended oxidized metals to lose their positive charge and thus any complexed anions (Wetzel 2001). This release of anions may be important in waters where algal photosynthesis elevates the local pH.

As discussed previously, Southeastern Piedmont lakes have iron-rich, low sulfate waters with low alkalinity (>20 carbonate alkalinity, unpublished data) and little buffering capacity. This water chemistry creates a system that is responsive to changes in pH. Algal photosynthesis during summer stratification can elevate local pH due to bicarbonate uptake:

\[
H_{2}CO_{3}^{\text{bio}} = H^\% HCO_{3}^\% \times \left[H_2CO_3\right]_{\text{bio}} \quad (1)
\]

The biological uptake of carbonate results in a concomitant increase in water pH in poorly buffered systems. Thus, the algae modify pH as they photosynthesize and create conditions that can release DIP. Alkaline desorption can be expected to follow a diel cycle depending on the dominance of respiration or photosynthesis, and therefore pH, at a given time in the daily cycle, and may be particularly important in shallow sediments that cycle iron and phosphate on a diel cycle (Carlton and Wetzel 1988).

**Organic Carbon, Sediment, and Oxidized Iron: Effects on the Phosphorus Cycle**

Organic carbon and nutrients are delivered from the watershed and produced or regenerated internally in the waterbody. Much of the P transported to waterbodies is associated with particulates and sinks to the sediments where it is consumed and chemically transformed (Reynolds and Davies...
Sediment release of soluble inorganic phosphorus occurs when oxidized metals are used as electron acceptors for carbon mineralization by FeRB. Soluble P released from the reduction of metals in the sediments can be inhibited by resorption to newly formed iron oxides above the sediment water interface where the redox conditions are less reduced.

**Watershed Loading and Ecosystem Development**

The life cycle of a natural lake ecosystem is thought to progress from an oligotrophic to eutrophic state over long periods of time (hundreds to thousands of years) (Margalef 1968; Lampert and Sommer 1997). Lakes formed by impounding rivers or streams have characteristics of both natural lakes and flowing waters (Kennedy and Walker 1990). The life cycle of these man-made lakes or impoundments is thought to generally follow a trajectory similar to natural lakes. However, the higher loading rates of sediment, nutrients, and organic matter frequently shorten the time needed for impoundments to progress from oligotrophic to eutrophic (Thornton et al. 1990). Natural lake ecosystems and their surrounding watershed tend to develop simultaneously, e.g., following glacial or oceanic retreat, whereas impoundments generally are constructed in areas where the surrounding watershed has already developed in the ecosystem sense (alia Odum 1969). Hence, the loading of organic matter into impoundments occurs at much greater rates on a shorter time scale than those of natural lake systems.

Organic matter loading and consumption is important to phosphorus cycling. Consumption of organic matter by metal reducing bacteria in the sediments and hypolimnetic waters leads to reduction of iron and hence release of phosphate from oxidized iron-phosphate complexes. In more productive systems, organic matter that settles to the sediments during stratification tends to have been previously processed such that the more recalcitrant, less easily consumed forms of organic matter are commonly found in sediments of more developed systems (Kufel and Kulinowska 1997).
Porter et al. (1996) suggest a seasonal microbial loop in warm monomictic lakes with a bacterial abundance peak during summer stratification. The peak concentration of chlorophyll and peak abundance of bacteria follow the metalimnetic plate during summer stratification (Porter et al. 1996). The thermal and chemical gradients that develop during stratification create an environment where particulate settling velocities change. In strongly stratified systems, seiches can develop at this interface fueled by thermal differences (Kennedy and Walker 1990). The change in settling velocities combined with the internal mixing create an area where easily consumable organic matter can be rapidly processed (Levine et al. 1986). Hence the depth at which organic matter is most intensely cycled changes seasonally with stratification, and is most pronounced at the metalimnion during the period of stratification.

Lake systems with high algal and bacterial biomass, that become strongly stratified will have less easily consumable organic matter delivered to the sediments, due to increased particle processing. These productive systems are also likely to have earlier hypolimnetic hypoxia and anoxia during stratification, and are likely to have reducing conditions in the hypolimnion, where oxidized metals are reduced and phosphate is released into the hypolimnion as well as in the sediments. Hence, the sediments of these more productive systems will have lower concentrations of easily consumed organic matter. This lack of easily consumable organic matter may not prevent metal reduction and phosphate release, however. Cole and Pace (2003) found that the recalcitrant carbon that reaches the sediments can be consumed and respired. Thus, given the longer period of stratification and hypolimnetic anoxia even this more recalcitrant carbon will be consumed potentially releasing phosphate to the surface waters.
SUMMARY

Multiple parameters effect the cycling of phosphorus in circumneutral, low-sulfate, freshwater environments. The phosphorus cycle is controlled by the iron cycle in Piedmont impoundments. The cycling of iron is controlled by the loading of iron to the waterbody through sediment transport, and the reduction and oxidation of iron in the sediments and hypolimnion. The reduction of iron in the sediments (and to some extent its re-oxidation) is fueled by easily consumable organic carbon. These multiple parameters should be managed collectively, rather than independently, to ensure the best attainable water quality, and thus, watershed and reservoir management practices should focus on maintaining a balance of the biogeochemical processes in the waterbody.

This dissertation will seek to demonstrate the need to consider multiple water quality parameters by investigating the interactions of phosphorus, iron and organic carbon in the surface waters and sediments of impoundments in the Georgia Piedmont. We propose that the phosphorus cycle in lakes and impoundments of the Georgia Piedmont differs from the traditional phosphorus cycling paradigm in that iron plays a more significant role in the cycling of phosphorus than in the traditional phosphorus cycle (Figure 1.3). In the traditional phosphorus cycle shown on the left side of Figure 1.3, DIP enters the lake and leads to increased algal growth, which increases organic carbon, which leads to increased reduction of oxidized iron in the sediments, which leads to increased release of phosphate which is then circulated to the surface waters at mixis. In the phosphorus cycle that we propose for impoundments in the Georgia Piedmont, shown on the right side of Figure 1.3, DIP enters the lake and may be bound to oxidized iron, or may lead to increased algal growth, which can induce photosynthetically elevated pH in the surface waters, which can lead to increased phosphorus availability and increased algal growth, which increases organic carbon, which leads to increased reduction of oxidized iron and release of
phosphorus; phosphorus is readily resorbed to newly oxidized iron in the less reduced hypolimnetic waters and thus, is not released to the surface waters at mixis. Chapter 2 describes the role of iron-rich soil in sequestering phosphate in surface waters of the Georgia Piedmont (Figure 1.4). Chapter 3 explores the role of iron reduction in lake sediments and soil of the Georgia Piedmont, and the potential release of phosphate to the surface waters (Figure 1.4) following that reduction. Chapter 4 identifies the role of oxidized iron in the sorption and desorption of phosphate as mechanisms for sequestration and release in the oxic water column of Lake Lanier, a Georgia Piedmont impoundment (Figure 1.4). Chapter 5 summarizes the main points of the dissertation and discusses implications for management of surface waters.
LITERATURE CITED


Table 1.1. The primary redox reactions of organic matter degradation in sequence from the oxic to anoxic reactions with the appropriate stoichiometric ratios. Organic Matter (OM) = \((\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)\) assuming the Redfield ratio (From Cai et al., submitted).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{OM} + 138 \text{O}_2)</td>
<td>(106 \text{CO}_2 + 16 \text{HNO}_3 + \text{H}_3\text{PO}_4)</td>
</tr>
<tr>
<td>(\text{OM} + 0.8 \times 106 \text{NO}_3^- + 0.8 \times 106 \text{H}^+)</td>
<td>(106 \text{CO}_2 + 0.4 \times 106 \text{N}_2 + 16 \text{NH}_3 + \text{H}_3\text{PO}_4)</td>
</tr>
<tr>
<td>(\text{OM} + 2 \times 106 \text{MnO}_2 + 4 \times 106 \text{H}^+)</td>
<td>(106 \text{CO}_2 + 2 \times 106 \text{Mn}^{2+} + 16 \text{NH}_3 + \text{H}_3\text{PO}_4)</td>
</tr>
<tr>
<td>(\text{OM} + 4 \times 106 \text{FeOOH} + 8 \times 106 \text{H}^+)</td>
<td>(106 \text{CO}_2 + 4 \times 106 \text{Fe}^{2+} + 16 \text{NH}_3 + \text{H}_3\text{PO}_4)</td>
</tr>
<tr>
<td>(\text{OM} + 106/2\text{SO}_4^{2-})</td>
<td>(106 \text{CO}_2 + 106/2 \text{H}_2\text{S} + 16 \text{NH}_3 + \text{H}_3\text{PO}_4)</td>
</tr>
<tr>
<td>(\text{OM})</td>
<td>(106/2 \text{CO}_2 + 106/2 \text{CH}_4 + 16 \text{NH}_3 + \text{H}_3\text{PO}_4)</td>
</tr>
</tbody>
</table>
Figure 1.1. Location of Lake Sidney Lanier and Lake Oglethorpe in the Georgia Piedmont. The Piedmont region is located above the red line on the map of Georgia.
Figure 1.2. Suspended solids concentration regressed with total iron (TFe) and total phosphorus (TP) from tributaries to Lake Lanier.
Figure 1.3. Comparison of the traditional lake phosphorus cycle (left), and the improved lake phosphorus cycle (right) for Georgia Piedmont impoundments.
Figure 1.4. The improved phosphorus cycling figure highlighting the portions of the cycle discussed in each chapter of this dissertation.
CHAPTER 2

EVIDENCE FOR THE SEQUESTRATION OF PHOSPHATE BY SEDIMENT IN A SMALL SOUTHEASTERN PIEDMONT IMPOUNDMENT


25
Abstract. A small (2000 m³) impoundment in the Southeastern Piedmont was fertilized on three occasions during the summer of 2000. System response to nutrient addition was measured using the Environmental Process Control Laboratory, an integrated suite of water quality monitoring equipment that continuously collects sub-hourly data. Measurements of ammonium (NH₄), orthophosphate (PO₄) and turbidity (TUR) are reported here. The impoundment was fertilized with 8L of 11-37-0 (N-P-K) liquid fertilizer that was directly broadcast in the first two fertilizations. These first fertilizations showed a typical fertilization response with elevated levels of ammonium and orthophosphate in pond waters immediately after application. The third fertilization used a slurry mixture composed of liquid fertilizer (8 L), soil from the Bt horizon (55 kg), and pond water. The results of this third fertilization were no detectable increase in orthophosphate, and a reduced increase in ammonium. This study demonstrates the effectiveness of iron-rich sediments as a mechanism for removing phosphate from the bioavailable fraction in the water column of Piedmont impoundments, and supports the hypothesis that suspended iron-rich clay from Southeastern Piedmont soils sequesters nutrients in aquatic systems. We further tested the bioavailability of phosphate associated with sediment in a laboratory uptake study. Radiolabeled phosphate (³²P) was added to cultures of natural algal and bacterial assemblages either directly or as a sediment phosphate slurry. Radiolabeled phosphate was primarily retained in the phyto plankton fraction (0.45F m filter) in the no sediment treatment. Phosphate remained in the inorganic fraction in the sediment treatment, with no increase in organic phosphate over the incubation period.

Key Words: phosphorus, iron, transported sediment, iron-phosphate cycling, nutrient cycling, nutrient bioavailability, lake nutrients.
INTRODUCTION

The complex interactions of iron and phosphorus play a primary role in the cycling of phosphorus in surface waters (Hutchinson 1957, Wetzel 2001). The soils of the Georgia Piedmont are rich in oxidized iron primarily as iron hydroxides (USDA 1968). Iron hydroxides form a ligand exchange with phosphate ions (Stumm and Morgan 1996), removing phosphate from the dissolved, easily consumable fraction (Reynolds and Davies 2000). Illuminating the biogeochemistry of phosphorus in surface waters rich in iron hydroxides will provide information useful in setting local water quality criteria and standards, and will help identify regional differences in nutrient cycling that should be considered in larger scale (e.g., national) pollution management strategies.

The paradigm for phosphorus cycling was developed based on data from lakes in northern temperate regions that tend to be glacial in origin (Hutchinson 1957, Rodhe 1969, Carlson 1977). This paradigm states that phosphorus is either bound to mineral surfaces and settles to the bottom as inorganic particulates or is removed from the epilimnion by biological consumption, passed through the food chain, and recycled or settled to the bottom as detritus. Settled phosphorus is trapped in benthic sediments until it is released by chemical reduction or microbial action. Organic matter decomposition and the reduction of metal oxide-phosphorus complexes in the anoxic hypolimnion and sediments of stratified lakes result in a steady increase in hypolimnetic dissolved inorganic phosphorus (DIP) which is circulated in the water column at mixis (Einsele 1942, Hutchinson 1957, Wetzel 2001).

In contrast, Georgia Piedmont lakes are primarily man-made impoundments that were created after the surrounding ecosystem developed and typically receive greater loads of nutrients and organic carbon than naturally occurring lake systems. The climate in the southeastern US provides for a longer
growing season and warmer annual average temperatures than those found in north temperate regions. This difference in climate affects the strength and length of summer stratification, and creates the conditions for monomictic rather than dimictic lakes in the Georgia Piedmont. Soils in the Georgia Piedmont have a high iron content (~ 12 % iron [West, pers. comm.] vs. 3.8 %, global mean [Sumner 2000]) and thus iron is typically transported via runoff to aquatic systems in this region. Oxidized iron in the water column can bind phosphate via surface sorption and ligand exchange. Phosphate released to sediment porewaters may bind to oxidized iron in the water column above and precipitate back to the sediments, creating a layer of oxidized iron compounds at the oxic/anoxic interface (often the sediment surface). We hypothesize that this binding in Georgia Piedmont impoundments effectively removes inorganic phosphorus from the biologically available fraction and prevents the diffusion of phosphate to the hypolimnion and eventually to the surface waters at mixis typically found in the more traditional lake phosphorus cycle.

Many reservoirs in the Southeastern Piedmont conform to the traditional lake phosphorus cycle paradigm to the extent that P is bound by the iron-rich clay soils. The load of phosphate to Georgia Piedmont impoundments is often not reflected in the algal or chlorophyll a response (Hatcher 1994). Much of the phosphorus (P) entering these impoundments is neither accessed biologically nor is it transported downstream; most of the P entering these impoundments is thought to be sequestered in the sediments (Mayhew and Mayhew 1992; Burkholder 1993; Hatcher 1994). The release of associated inorganic phosphate as iron is reduced in the sediments is rarely seen as increased DIP concentrations in the anoxic hypolimnion or in releases of DIP to the surface water at mixis (Reckhow 1988; Mayhew and Mayhew 1992).
We postulate that the continuous supply of oxidized iron from sediment transported in runoff reduces the bioavailability of phosphate in Southeastern Piedmont impoundments and may supply enough oxidized iron to effectively inhibit phosphate release to the surface waters at mixis. We conducted a series of fertilization experiments in a small aquaculture pond to test the hypothesis that oxidized iron in Bt horizon soil from the Georgia Piedmont reduces the availability of phosphate and removes it from the fraction measured as orthophosphate. We tested the bioavailability of phosphate associated with sediment in phosphate uptake experiments with $^{32}$P to see if inorganic phosphate associated with sediment is rapidly incorporated into organic phosphate. The work presented here investigates the role of iron-rich sediment in removing phosphate from the biologically available fraction in Georgia Piedmont impoundments.

**METHODS**

This experiment examined the effects of fertilization with $\text{PO}_4^{3-}$ and $\text{NH}_4^+$ on nutrient availability in a small manmade pond in the Southeastern Piedmont. In the first two fertilizations liquid ammonium polyphosphate fertilizer was broadcast to the pond surface and fertilization effects were measured using continuous monitoring equipment at two points within the pond. In the third fertilization liquid ammonium polyphosphate fertilizer was mixed with 55 kg of Bt horizon soil and allowed to stand for 24 hours. The soil-fertilizer mixture was mixed with pond water to form a slurry before being broadcast to the pond surface; again, the results were monitored using continuous real-time monitoring equipment.

The fish pond fertilizer used in these experiments is described (by the manufacturer) as liquid ammonium polyphosphate fertilizer ($\text{NH}_4\text{P}_2\text{O}_5$) 11-37-0 N, P, K and requires hydrolysis to release phosphorus as orthophosphate. In the applications for which this fertilizer was designed, namely
fertilizing fish ponds, complete hydrolysis is accomplished by dilution in a short period of time (minutes to hours).

*Site Description*

The study site is located at Whitehall Forest near the University of Georgia campus (Figure 2.1). The site contains a small pond, which is used to culture fish for teaching and experimental purposes and has been limed and fertilized regularly. The volume of the pond is approximately 2000 m$^3$, the surface area is approximately 0.7 ha, and the maximum depth near the dam is less than 2 m. There is one influent tributary, which drains a small watershed of approximately 13 ha (watershed area to pond volume ratio = 65). The drainage area includes forest, deer holding pens, buildings, and parking areas. There is one outflow, which is regulated by a stand pipe near the dam. Low-flow conditions persisted throughout the study period due to drought.

*Environmental Process Control Laboratory (EPCL)*

We deployed an Environmental Process Control Laboratory (EPCL) from Capital Controls (Minworth Systems Limited) for surface water quality analysis in this study (http://www.modeling.uga.edu/epcl/public_html/). The EPCL is comprised of two mobile trailers that house components necessary to automatically analyze the water quality characteristics of a sample pumped from a given field location, and to communicate the resulting observations to a remote (host) location via modem. Each trailer receives samples pumped continuously from three locations. Sample switching devices are available within each trailer that can present each sensor with a sample from each of three streams, yielding a water quality measurement in each of the three sample lines once every 45 minutes. Each sample stream is provided with in-line membrane filtration units that allow the delivery of a solids-free filtrate separated from the main sample line for subsequent presentation to a sensor.
Filtrates from the three sample lines can be routed in sequence past a total organic carbon (TOC) analyzer and an ammonium-N sensor in one trailer, and through an orthophosphate-P monitor and a monitor for measuring nitrite-N and total oxidized nitrogen (NOx) concentrations in the other (Table 2.1). The EPCL was designed for deployment in a variety of contexts, but was used here in the analysis of surface water quality (Zeng and Beck 2001; Liu and Beck 2000).

Continuous Monitoring

Ammonium (NH$_4^+$) and soluble reactive phosphorus (PO$_4^{3-}$) were measured every 15 minutes using the EPCL. Water was pumped from two locations within the pond. Intake 1 was attached to a platform at the upstream end of the pond at a depth of 0.5 m. Intake 2 was stationed by the dam, also at a depth of 0.5 m. Orthophosphate was determined by filtering the influent stream through a 0.45 um filter and then monitoring the soluble phosphorus concentration using the automated ascorbic acid method (APHA 1999). Turbidity (TUR) was measured every 15 minutes using a Hydrolab Datasonde 4 equipped with a turbidity sensor. Ammonium concentration was monitored using a Minworth Systems Limited ion-specific electrode (APHA 1999).

The raw time series of PO$_4$-P (µg/L) and TUR (FTU) from June 15th, 2000, through October 16th, 2000, were measured at 15-minute sampling intervals (11,904 observations). However, for signal processing purposes, the original time series were decimated every 16 samples; thus the decimated raw data set only contains 744 observations. The extraction of trend and periodic components, interpolation of missed data, discrimination against possible outliers, and the smoothing of the decimated raw time series are accomplished through applications of Dynamic Harmonic Regression (DHR) models (Young 1998; Beck and Lin 2003) to the time series of interest (i.e., PO$_4$-P and TUR).
Description of Fertilizations

A total of three fertilization experiments were performed (Table 2.2). The first included a lime application followed by fertilizer application. Ca(OH)$_2$ was applied on July 2, 2000, by broadcasting 45 kg over the pond from a Jon boat over a period of 1-2 hours. Liming was followed three days later by the broadcast of 8 L of 11-37-0 liquid ammonium polyphosphate fertilizer to an approximate phosphorus concentration of 230 mg P/L. The second fertilization did not include lime application; 8 L of the same fertilizer was broadcast from the Jon boat on July 28, 2000.

On September 27, a few days prior to the third fertilizer treatment on October 1, a duckweed removal operation was performed. The pond had become 80-90% covered with duckweed (Lemna sp.), which could have confounded the interpretation of experimental results (see also Lin 2003). The duckweed was removed mechanically by seining and raking from a kayak.

The third fertilization used 8 L of 11-37-0 fertilizer mixed with 55 kg of the Bt horizon from a site mapped as Pacolet (fine, kaolinitic, thermic Typic Kanhapludults) (USDA 1968). The soil was air-dried, crushed, screened, weighed and mixed by hand with the fertilizer 24 hours before application. The ratio of PO$_4$ to soil was approximately 33.4 g-PO$_4$/kg-soil. On October 1, the soil-fertilizer mixture was mixed with water from the pond to form a slurry that was broadcast to the pond both from shore and from a Jon boat.

$^{32}P$ Uptake Experiments

We conducted laboratory investigations to determine if sediment bound phosphorus would be available for uptake by natural cultures of lake phytoplankton. Phytoplankton cultures were grown from phytoplankton samples collected in whole water samples from Lake Lanier. Four sterile flasks were filled with 500 mL of the collected phytoplankton in a sterile environment. These natural cultures
were placed in a growth room at 21°C with 24 hour illumination. Cultures were checked visually each day for growth. On the fifth day, the cultures were subsampled from the original flasks into nutrient enriched sterile filtered lake water media (50 mL of culture added to 300 mL N and P enriched filtered lake water). Enriched cultures were allowed to grow for ten days to increase phytoplankton density. Subsamples of enriched cultures were transferred to unenriched sterile filtered lake water (100 mL culture added to 200 mL sterile filtered lake water) and allowed to grow for an additional five days to induce nutrient limitation. The enriched and then starved cultures were used in uptake experiments with and without sediments.

We measured the uptake of orthophosphate in the absence of sediment by adding 10 FL of radiolabeled orthophosphate (³²P) to each of two flasks containing 300 mL of cultured phytoplankton and subsampling each at 2, 10, and 30 minute intervals. Each subsampling involved collecting whole water samples that were immediately mixed with scintillation fluid for measurement of ³²P in the whole water. Subsamples for measuring the filtered fractions were sequentially filtered through 0.45 FL, and then 0.2 FL filters. Filters and filtrates were added to scintillation fluid for analysis. All results are reported as radioactivity per mL for ease of comparison.

Phosphate uptake in the presence of iron-rich sediment was measured by first mixing ³²P-labeled orthophosphate with soil in a slurry. The slurry was prepared by adding three grams of sterile, 250 FL sieved, Bt horizon soil to thirty milliliters of 0.45 FL filtered, sterilized surface water from Lake Lanier (initial weight, 33.00 g) and stirred vigorously. Suspended soil and water were decanted off to create a suspended soil slurry. The larger, heavier soil particles were discarded leaving a soil slurry with a final weight of 28.65 g. Forty FL of radiolabeled orthophosphate was added to this slurry and stirred for twenty-four hours. Thirteen milliliters of the soil-³²P slurry were added to each of two flasks containing
300 mL of cultured phytoplankton for the sediment treatment. Each sediment treatment flask was subsampled at 2, 10, 30, and 60 minutes to follow the uptake of phosphate. This treatment followed phosphorus uptake for a longer time period to allow more time for uptake of bound P.

Whole water samples and sequentially filtered fractions (0.45, and 0.22 μm pore filters and filtrates) were collected at each time step and analyzed for radioactivity. Samples collected from the sediment treatment were split; half the sample was immediately processed and filtered (undigested whole water, 0.45 μm filter and filtrate, and 0.2 μm filter and filtrate); the remainder was digested with warm H₂O₂ to remove organic matter and release organic phosphate. Digested samples were further divided and half the sample was filtered through a 0.8 μm filter to remove larger particles released from the filters during digestion prior to analysis for radioactivity. All samples were counted on a Beckman 2000 scintillation counter to measure radioactive phosphorus.

RESULTS

Data for NH₄⁺, PO₄³⁻, and turbidity as monitored by the EPCL are presented in Figure 2.2 a-c. Figure 2.3 a-c show the interpolated time series analyses of the PO₄³⁻, NH₄⁺, and turbidity data, respectively, of all three fertilizations. Plots are overlain so that fertilization effects can be more easily compared; fertilization occurred on day five. Turbidity data was not available for the first fertilization, so the interpolated data for that time period are omitted.

The first fertilization resulted in a large peak in phosphate and ammonium concentrations, with no increase in turbidity, and produced a long tail of declining concentration as the phosphate was either consumed, adsorbed, or lost to sedimentation. Phosphate and ammonium showed a rapid increase at the time of fertilization. The phosphate concentration decreased at an exponential rate for a prolonged
period (approximately three weeks). Ammonium concentrations decayed more rapidly (approximately one day). Turbidity (a measure of both suspended inorganic and organic matter in the water column) did not respond immediately, but slowly rose over a two-week period, presumably due to increased phytoplankton in the water column as reflected in chlorophyll $a$ measurements not reported here (see Lin 2003).

The second fertilization produced a large peak in phosphate concentration and a spike in ammonium concentration double the increase seen in the first fertilization (Figure 2.3 a and b). The decline in phosphate concentration from the water column was more rapid following this fertilization. The rapid decrease in phosphate may be attributed to increased biological uptake. Duckweed ($Lemna$ sp.) began developing as mats at the edges of the pond just prior to this fertilization with a significant increase in the amount of pond surface covered by duckweed noted five days after this fertilization. The rapid decline in phosphate and ammonium may therefore be due to duckweed consumption (see also Lin 2003). The increased phosphate concentration shown beginning twelve days after the second fertilization corresponds to the increased turbidity and sediment disturbance created by the duckweed removal procedures.

The third fertilization with sediment showed no increase in phosphate concentration, a small increase in the ammonium concentration, and a substantial increase in turbidity due to the soil addition (Figures 2.2 and 2.3). The response to this fertilization showed substantially less measurable phosphate than in the previous fertilizations, and a large increase in turbidity from 10 to 32 formazine turbidity units (FTU), not seen in the previous treatments with fertilizer only. Turbidity returned to pretreatment levels over a five-day period as the added soil settled out of the water column into the sediments.
The interpolated data shown in Figure 2.3 more clearly emphasizes the dramatic difference in responses of the system to fertilizations with and without sediment. The smoothed curves reduce the noise in the signal by identifying and reducing outliers to more clearly illustrate the experimental results (Young 1998). The lack of phosphate or ammonium response are clearly demonstrated in Figure 2.3, indicating the efficient scavenging of these ions by sediment.

\( ^{32}P \) Uptake

The uptake of radiolabeled P in the treatment with no added sediment followed a predictable pattern with most of the phosphate passing through a 0.45 \( \mu \)m filter at the initial sampling, with progressively more phosphate retained on the 0.45 \( \mu \)m filter, and thus consumed by the phytoplankton, throughout the experiment (Table 2.3). No significant uptake was identified in the 0.2 \( \mu \)m filter or filtrate fractions during the no sediment treatment experiment. Biological uptake of radiolabeled P in the sediment treatment was not evident (Table 2.3); the majority of radiolabeled P was retained on the 0.45 \( \mu \)m filter which filters out the majority of the sediment sorbed \( ^{32}P \). The samples digested to release organic P, showed no increase in radioactivity over time as would be expected if radiolabeled P was consumed by the phytoplankton (retained on a 0.45 \( \mu \)m filter) or bacteria (retained on a 0.2 \( \mu \)m filter). There was no increase in any organic fraction (0.2 or 0.45 \( \mu \)m) over time, and no indication of biological uptake in the sediment treatment.

DISCUSSION

The responses monitored indicate that phosphate mixed with Piedmont subsoil remained bound to the soil; there was no increase in water column phosphate concentrations in the fertilization with sediment treatment. It is clear that a substantial reduction in measurable nutrients occurred due to the
addition of suspended solids at the time of fertilization. The lack of phosphate response, and the muted increase in ammonium indicates that sediment binds both ions, although ammonium appears to be bound less extensively.

Ammonium removal by sediments is attributed to cation exchange onto clay minerals. Kaolinite clay minerals are known to preferentially bind nitrogen-rich components, particularly amine groups (Aufdenkampe et al. 2001). The dominant forms of clay in the Bt horizon soils of the Georgia Piedmont are kaolinites (USDA 1968). Thus, the muted signature of ammonium in the fertilization with sediment treatment is most likely due to sorption on clay surfaces. The capacity of the soil to bind Po₄³⁻ appears to be high, as evidenced by the lack of a phosphate signal from the EPCL analyses during the third fertilization. Laboratory experiments have estimated the sorption capacity of similar clay soils to be 7.7 µg-P/g-soil (Mayhew and Mayhew 1992) over a two-minute period and 806 µg-P/g-soil over 24 hours (Parker, see Chapter Four this volume). The high sorption capacity of the soil for phosphate indicates that this may be the primary mechanism for inorganic phosphate removal in Piedmont tributaries and impoundments.

The results of these experiments indicate iron-rich clay soils in the Southeastern Piedmont sequester phosphate and ammonium. Evidence from studies of agricultural runoff indicates that the mechanical working of soil particles during transport can decrease the size and increase the availability of reactive surfaces of these soil particles (McDowell et al. 2002), potentially increasing their capacity for adsorbing phosphate and other anions during transport and in receiving waterbodies. Hatcher (1994) estimated that 80-90% of the P load to Lake Lanier, a large impoundment in the Piedmont of Georgia, does not leave the lake and is probably sequestered by sediments. Explanations for P retention include a lack of organic matter to power microbial reduction of Fe; reducing conditions that are not sufficient
to lower the redox potential to the level at which Fe$^{2+}$ appears (Hutchinson 1957); oxidation of Fe$^{2+}$ to Fe$^{3+}$ by bacteria under acidic conditions (Tate et al. 1995); and oxidation of Fe$^{2+}$ to Fe$^{3+}$ by inorganic processes (Hutchinson 1957; Stumm and Morgan, 1996). The data presented here indicate that an abundant supply of oxidized iron delivered via tributaries may also explain P retention in Georgia Piedmont impoundments.

The traditional lake phosphorus cycling paradigm fails in lake systems with an abundant supply of oxidized iron, such as those in the Georgia Piedmont. In these systems, oxidized iron introduced from tributaries reduces the bioavailability of phosphate in the surface waters and prevents the algal response to the phosphorus load from being realized. The global extent of iron rich soils is significant. In these regions, phosphorus may follow a very different cycle in the natural environment than the phosphorus cycle typically described in textbooks. This study provides evidence of the sequestering of phosphate on iron-rich sediments, and illustrates the need to consider watershed interactions in the water quality management of lakes and streams.

The $^{32}$P experiments further support the importance of transported sediment to the bioavailability of phosphorus in the surface waters of the Georgia Piedmont. The lack of biological uptake of radiolabeled phosphate associated with Bt horizon soil indicates that transported sediment can play an important role in removing phosphorus from the biologically available fraction. Our study shows that oxidized iron in transported sediment can reduce the bioavailability of DIP in Georgia Piedmont impoundments, and may be a significant control on P cycling. Thus, transported sediment plays a more significant role in the phosphorus cycle in impoundments of the Georgia Piedmont than in the north temperate systems where the traditional phosphorus cycling paradigm was developed.
MANAGEMENT IMPLICATIONS

Water quality concerns of the public, and federal water quality policies are forcing resource managers to more closely consider management of nutrients and sediments from natural, point, and non-point sources (USEPA 1998a, www.epa.gov/ost/standard/nutrient.html; USEPA 1998b, www.cleanwater.gov; 40 CFR 9, 122, 123, 124, and 130; www.epa.gov/owow/tmdl). Federal litigation is driving the development of total maximum daily load (TMDL) values for pollutants of concern in impaired waterbodies in Georgia (Fowler et al. 2002). Most waterbodies in Georgia that require TMDL development list sediment and bacteria as primary pollutants. The TMDL values being developed for sediment impairment focus on reducing in-waterbody turbidity. The most practical method for reducing turbidity in most cases is to reduce external sediment loading.

The results of this study indicate that iron-rich soil is important to the cycling of phosphate in these systems. Decreasing external sediment loads in these waterbodies then, may improve water quality with respect to one parameter (turbidity), and decrease water quality with respect to others (nutrients, algal and bacterial growth, chlorophyll). The complication that water quality improvement in one respect will cause increased impairment with respect to other water quality parameters emphasizes the need for water quality regulations and management practices that encourage whole ecosystem investigations (watershed and waterbody) on the interactions of multiple stressors, rather than seeking to control each parameter independently.
LITERATURE CITED


1942. The Exchange of Dissolved Substances between Mud and Water in Lakes.


Table 2.1. Parameters monitored and method of analysis used by the EPCL.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Method</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissolved Ammonia and Ammonium</td>
<td>Ammonia selective electrode method</td>
<td>APHA 1999</td>
</tr>
<tr>
<td>Dissolved Reactive Phosphate</td>
<td>Ascorbic acid method</td>
<td>Murphy and Riley 1962; APHA 1999</td>
</tr>
<tr>
<td>Nitrate-Nitrite (Total Oxidizable Nitrogen)</td>
<td>Modified cadmium reduction method</td>
<td>APHA 1999</td>
</tr>
</tbody>
</table>

Table 2.2. Schedule of treatments to Whitehall Pond.

| Date               | Treatment                                                      | Distribution Method                  |
|--------------------|                                                               |                                       |
| July 2, 2000       | Liming–45 kg Ca(OH)$_2$                                        | Broadcast from Jon boat               |
| July 5, 2000       | Fertilization–8 liters of 11-37-0 ammonium polyphosphate fertilizer | Broadcast from Jon boat               |
| July 28, 2000      | Fertilization–8 liters of 11-37-0 ammonium polyphosphate fertilizer | Broadcast from Jon boat               |
| September 27, 2000 | Duckweed removal                                               | Mechanical                            |
| October 1, 2000    | Fertilization–8 L of 11-37-0 ammonium polyphosphate fertilizer sorbed to 55 kg Bt horizon soil and mixed into a slurry with pond water | Broadcast from shoreline and from Jon boat |
Table 2.3. Radiolabeled phosphate uptake over time presented as percent in each fraction. Treatments are no sediment, sediment, and sediment with organic matter digestion (Sediment with Digestion). Data have been normalized by sample volume. Note the increase in the 0.45 Fm filter fraction (italicized) over time and the decrease in the successive fractions, indicating phytoplankton uptake of radiolabeled phosphorus in the no sediment treatment.

<table>
<thead>
<tr>
<th>Time (minutes)</th>
<th>No Sediment</th>
<th>Sediment</th>
<th>Sediment with Digestion</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 10 30</td>
<td>2 10 30 60</td>
<td>2 10 30 60</td>
</tr>
<tr>
<td>0.45 Fm filter</td>
<td>19.9 53.8 68.8</td>
<td>81.8 73.5 51.1 87.0</td>
<td>76.6 62.0 77.2 77.5</td>
</tr>
<tr>
<td>0.45 Fm filtrate</td>
<td>57.5 30.1 17.4</td>
<td>10.9 12.8 24.6 7.4</td>
<td>10.7 19.7 9.4 10.3</td>
</tr>
<tr>
<td>0.2 Fm filter</td>
<td>2.9 0.9 4.6</td>
<td>3.8 9.8 18.4 3.4</td>
<td>10.1 15.7 11.3 8.0</td>
</tr>
<tr>
<td>0.2 Fm filtrate</td>
<td>19.7 15.2 9.2</td>
<td>3.5 3.9 6.0 2.2</td>
<td>2.6 2.6 2.0 4.1</td>
</tr>
</tbody>
</table>
Figure 2.1. Location of Whitehall Pond in the Piedmont of Georgia.
Figure 2.2 a. Phosphate for the three fertilizations, arrows indicate timing of liming and fertilizer broadcast application.
Figure 2.2 b. Ammonium for the three fertilizations, arrows indicate timing of liming and fertilizer broadcast application.
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CHAPTER 3

IRON REDUCTION AND PHOSPHORUS RELEASE FROM LAKE SEDIMENTS AND Bt HORIZON SOIL: INCUBATION STUDIES TO EXPLORE PHOSPHORUS CYCLING

1Parker, Amanda K. and M. B. Beck. To be submitted to Limnology and Oceanography.
Abstract. Sediment from two Georgia Piedmont impoundments and soil from the Georgia Piedmont Bt horizon were incubated with sucrose, an easily consumable organic carbon substrate, in an anaerobic environment to observe iron reduction and phosphorus release. Incubation yielded 97% soluble iron in Bt horizon soil porewater, 96% soluble iron in Lake Lanier sediment porewater, and 93% of soluble iron in Lake Oglethorpe sediment porewater. Phosphorus release followed a similar trend with 83% of total P in Bt horizon porewaters, 77% of total P in Lake Lanier sediment porewater, and 61% of total P in Lake Oglethorpe sediment porewater in the soluble fraction (0.2 μm filtered) at the end of incubation. Analyses of organic acids indicates that added sucrose was actively consumed during the incubation, and converted primarily to acetate, pyruvate, and propionate. Organic acids produced during sucrose consumption indicate that carbon mineralization in this experiment was dominated by non-methanogenic anaerobic metabolism, and the high percentage of soluble Fe in the porewaters further supports iron reduction as the primary pathway of carbon mineralization in anaerobic sediments and soil tested. Sediment and soil characterizations show that the sediments and soil have high relative surface areas (~35 m²/g), and small particle sizes (>65 % of particles <0.05 mm). Iron reduction and phosphorus release observed in soil from Bt horizon collected in the Piedmont region of Georgia indicates that phosphorus transported to Piedmont impoundments may be made biologically available by microbially mediated iron reduction in sediments. We discuss the implications of this work for lake and watershed management in the Georgia Piedmont.

Key Words: Iron reduction, sediments, iron, phosphate, anaerobic metabolism, phosphate availability.
INTRODUCTION

The scientific basis for the conventional paradigm of phosphorus (P) cycling in lakes was developed with data primarily from north-temperate systems (Hutchinson 1957, Rodhe 1969, Carlson 1977). This paradigm involves the sinking of inorganic particulates and organic material from the surface (epilimnnetic) waters to the hypolimnetic waters of lakes during summer stratification. The depletion of oxygen and anoxic respiration in the hypolimnion creates reducing conditions in the buffered waters of north-temperate lakes. As iron-phosphorus compounds are reduced and organic matter is decomposed in the anoxic hypolimnion, there is a steady increase in DIP (dissolved inorganic phosphorus) which is circulated to the lake at fall mixis (Hutchinson 1957; Wetzel 2001). This phosphorus cycling paradigm does not adequately address the role of abundant oxidized iron in surface water and sediments that is found in Southeastern Piedmont impoundments (Parker and Rasmussen 2001; Mayhew et al. 2001).

The chemistry of the conventional phosphorus cycling paradigm is true for lakes and impoundments in the Georgia Piedmont to some extent. Inorganic and organic P are delivered to the waterbody; particulates sink to the hypolimnetic waters and sediments of lakes during summer stratification; the depletion of oxygen in the sediments and hypolimnetic waters leads to anoxic respiration; and oxidized metals are reduced as they are used as electron acceptors when carbon is consumed by metal reducing bacteria. The phosphorus cycle in Georgia Piedmont impoundments is similar to the conventional phosphorus cycle up to this point. Elevated phosphorus concentrations are rarely seen at mixis in Georgia Piedmont impoundments, however. The lack of increased phophorus at mixis is most likely due to the large amounts of oxidized iron that are supplied to these waterbodies via sediment loading, and the formation of new iron oxides that resorb P as reduced iron is mixed with oxygenated waters.
Oxidized iron in the soil and sediments of Georgia Piedmont impoundments has a high capacity for adsorbing phosphate (Parker and Beck, see Chapter 4 this volume), and thus we hypothesize that the lack of P release at mixis is due to the abundant supply of oxidized iron delivered from tributaries and shoreline erosion (Parker and Rasmussen 2001). In work discussed elsewhere (Parker and Beck, see Chapter 4 this volume), we demonstrate that iron oxides are being newly formed in surface waters of the Georgia Piedmont. Newly formed iron oxides are typically poorly crystalline, and thus have larger surface areas and greater sorption capacity for free anions than older more crystalline forms of oxidized iron. Poorly crystalline iron oxides also serve as electron acceptors for microbial organic matter mineralization in anoxic sediments in a metabolic pathway that can outcompete methanogenic food chains for sediment organic matter (Lovely and Phillips 1986).

The life cycle of a natural lake ecosystem is thought to progress from an oligotrophic to eutrophic state over long periods of time (hundreds to thousands of years) (Margalef 1968; Lampert and Sommer 1997). Lakes formed by impounding rivers or streams have characteristics of both natural lakes and flowing waters. The life cycle of these man-made lakes or impoundments is thought to generally follow a trajectory similar to natural lakes. However, the higher loading rates of sediment, nutrients, and organic matter frequently shorten the time needed for impoundments to progress from oligotrophic to eutrophic (Kennedy and Walker 1990). Natural lake ecosystems and their surrounding watershed tend to develop simultaneously, e.g., following glacial or oceanic retreat, whereas impoundments generally are constructed in areas where the surrounding watershed has already developed in the ecosystem sense (alia Odum 1969). Hence, the loading of organic matter into impoundments occurs at much greater rates on a shorter time scale than those of natural lake systems (Kennedy and Walker 1990).
Organic matter loading and consumption is important to phosphorus cycling. Consumption of organic matter by metal reducing bacteria in the sediments and hypolimnetic waters leads to reduction of iron and release of phosphate from oxidized iron-phosphate complexes. Accordingly, microbial activity in the sediments plays an important role in carbon degradation and nutrient regeneration and cycling. Sediments with large amounts of consumable organic carbon and an abundant supply of oxidants will support metal reducing bacteria and may release substantial amounts of sorbed or complexed anions, such as phosphate to the overlying water column. The amount of complexed anions released from oxidized metal complexes in the sediments is largely dependent upon the supply of oxidized metals and easily consumable organic carbon. In ecosystems where nutrient and organic matter cycling are tightly coupled (Odum 1969, Wetzel 2001), organic matter that reaches the sediments tends to be the more recalcitrant, less easily consumed forms of organic matter, e.g., humic substances, because the easily consumable forms utilized in the upper water column prior to reaching the sediments.

We conducted sediment incubation studies to compare iron reduction and phosphate release in sediments from two Georgia Piedmont impoundments and local Bt horizon soil. The reduction of easily consumable carbon substrate by metal reducing bacteria under anaerobic conditions follows metabolic pathways that result in the production of specific organic acids. We conducted organic acid analyses to help identify these metabolic pathways, and to determine if different pathways were utilized in the different sediments and Bt horizon soil. We are particularly interested in defining the conditions that would lead to sizeable reduction and dissolution of oxidized metals in the sediments and hypolimnia and the concomitant release of sorbed and bound phosphate. Hence, the work presented here explores the conditions that could lead to P release from the sediments of Georgia Piedmont impoundments and thus
lead to water quality degradation. We discuss management actions that need to be considered to prevent water quality degradation that might occur as a result of organic carbon consumption and metal reduction in anaerobic sediments and hypolimnetic waters.

METHODS

Study Site

Lake Oglethorpe is a small (30 ha; $z_{\text{max}} = 8.7$ m), warm monomictic, man-made impoundment in the Piedmont region of Georgia (Oglethorpe County, GA). Lake Oglethorpe was impounded in 1971 to create a privately owned waterbody for aesthetics and fishing in a residential community. The watershed of Lake Oglethorpe is largely rural, with chicken layer-egg production and cattle pasture as prominent agriculture covering approximately 33% of the 890 ha watershed. Most (67%) of the watershed is forested with mixed deciduous forest, and low intensity residential (density = one house per 8 ha) (Rashke 1993). The high percentage of forest cover in the watershed and the proximity of agricultural activity to Lake Oglethorpe assure a substantial supply of organic carbon, nutrients, and sediments to the impoundment. Winter mixis occurs from November through February, with development of thermal stratification in spring (March-April). The hypolimnion of Lake Oglethorpe typically becomes fully anoxic by late May and remains so until the onset of mixis in late October when the thermocline degrades (Porter et al. 1996).

Lake Lanier, located to the north of Atlanta and lying between the development corridors of I-75 and I-85, is arguably the single-most important impoundment in Georgia and the subject of intense public and political scrutiny. Created in 1958 on the Upper Chattahoochee River the lake occupies 15,580 ha. Its watershed is some 269,360 ha in extent, encompassing the foothills of the Appalachian
Mountains to the north, and covering a variety of land uses, including significant poultry and hog production, silviculture, and rapidly increasing suburbanization. Land cover in Lanier’s watershed in 1989 was categorized as: forest 77%, pasture 9%, open water 6%, suburban 3%, crops 4%, others 1%. By 1997 the suburban category had increased to 10%, at the expense of pasture and crops, which had fallen to 5% and 1%, respectively. Lanier itself is a multi-purpose impoundment, providing hydro-electric power generation, flood protection, drinking water supply, navigation, and recreational resources (Beck et al. 2002). The onset of mixis in Lake Lanier begins in late fall (October) and typically is fully mixed by late December-early January. Stratification typically begins in April, with the hypolimnion becoming fully anoxic in most embayments by late fall near the end stratification period (Hatcher 1994).

**Sample Collection**

Surficial sediments were collected in October and November 2002 from Lake Lanier and Lake Oglethorpe. The thermocline had begun to degrade, but neither system had reached complete mixis on the dates the sediments were collected. Lake Lanier samples were collected at the Flowery Branch embayment at a depth of approximately 28 m. Lake Oglethorpe samples were collected from the dam pool at a depth of approximately 8.5 m. Surface water temperatures at the sampling sites were 15°C and 9.8°C, respectively, at the time of sample collection. Triplicate Ekman dredge samples were collected at both sites and placed in plastic bags with minimal air exposure. Air was expelled from sample bags, and the bags were doubled to reduce oxygen contamination. An Eckman dredge was used for sediment sampling rather than a sediment corer due to the difficulties of retrieving sediment from Lake Lanier with a corer. Lake Lanier was created by flooding a valley, the trees and buildings in the valley were left standing at the time of flooding, hence the lake bottom is uneven and covered with
large debris. These conditions make sampling at depth in Lake Lanier difficult, and we found it impossible to retrieve intact cores from this site using a sediment corer. All sediment samples for incubation were thus collected using an Ekman dredge to reduce bias from different collection techniques. Soil was collected from an exposed Bt horizon at the University of Georgia’s Whitehall Forest from a site mapped as Pacolet (fine, kaolinitic, thermic Typic Kanhapludults) (USDA 1968) the common series for Bt horizon soil in the Georgia Piedmont.

**Incubation Studies**

Airtight one liter chambers for incubation studies were constructed of plexiglass; central PVC stems were used to support stirring paddles, sampling tubes and prefiltration devices, and N$_2$ tubes (Figure 3.1). O-ring seals lubricated with silicon vacuum grease provide an airtight seal on chamber lids and PVC stems that allows for movement of the stems to stir the sediment. This design enabled non-invasive sampling of porewaters and regular stirring of the sediments to reduce sediment porewater heterogeneity during incubation. Chambers were incubated at 12.5°C in a Precision 818 low temperature incubator.

Sediments from Lake Lanier and Lake Oglethorpe, and soil from the Bt horizon in Whitehall Forest were incubated with sucrose as the source of easily consumable organic carbon to determine differences in sediment characteristics with respect to oxidized iron reduction and phosphate release under anaerobic conditions. Wet sediment (280-315 g) from Lake Lanier, and Lake Oglethorpe, and Bt horizon soil wet with Lake Lanier hypolimnetic water were added to each of three incubation chambers, respectively, in an oxygen-free environment (N$_2$ filled Coy chamber, 5 % H$_2$). Filtered (0.45 Fm) hypolimnetic water from Lake Lanier was added to each chamber for a final volume of approximately 600 mL in each chamber. Five grams of sucrose (24.7 mM C) were added to each of
the nine incubation chambers to provide an easily consumable organic carbon substrate. Chamber headspace was filled with N\textsubscript{2} gas and a low constant flow of N\textsubscript{2} gas. Positive, steady flow was maintained by an Aalborg AFC 2600-PRO mass flow controller set at 32 standard cubic cm per minute (sccm) into the manifold that distributed N\textsubscript{2} gas to each of the chambers. The exhaust port of each chamber was checked daily to confirm positive pressure was maintained in each chamber.

Positive pressure of N\textsubscript{2} in each chamber headspace was used to maintain anaerobic conditions in each chamber during the twelve week incubation. Sediments were briefly stirred each day to reduce heterogeneity of biological activity, and to assure free exchange between the porewater and the overlying water.

Porewaters were sampled at the end of the incubation period to measure iron reduction and phosphate release from the sediments and soil. pH measurements were taken twice during incubation via the sampling tubes and an airtight O-ring sealed chamber designed for this purpose. Porewaters were sampled just above the sediment-water interface in the chambers through an airstone which was used as a prefiltration device to remove large particles. Unfiltered and filtered samples were collected for elemental analyses. Soluble iron and phosphorus were defined analytically by filtration. Filtered samples were pushed through a 0.22 µm Millipore cellulose nitrate syringe filter. Unfiltered samples represent the porewater total element concentrations; samples filtered through a 0.22 µm filter comprised the dissolved or soluble fraction. The samples were analyzed in a twenty-element sweep using an inductively-coupled argon plasma (ICAP) Thermo Jarrell-Ash 965 elemental analyzer.

Undiluted sediment porewaters were also analyzed using ICAP analysis. Sediments were centrifuged to extract porewaters and were pre-filtered through 0.8 µm syringe filters to remove large particles for total porewater concentrations and 0.22 µm filtered to separate the dissolved fraction prior to analysis.
Percentage of released phosphorus, iron, and manganese were calculated by difference between the unfiltered and filtered samples. Student t-tests were performed to identify significant differences between sample group means.

Undiluted sediment porewaters and porewaters from the sediment and soil incubations were analyzed for organic acids using ion exclusion HPLC with conductivity detection on a Dionex DX-500 ion chromatography system (Kotska et al. 2002) to determine organic acids produced as sucrose was consumed during incubation. Total organic carbon (TOC) in the sediments and soil was measured before and after incubation utilizing a Shimadzu TOC analyzer (USDA 1996). Sediments and soil were air-dried, pulverized and sieved through a 250 μm sieve prior to TOC analysis. Water content percentages were estimated by weight. Overlying waters were decanted off chamber sediments and the remaining wet sediment and soil was placed in pre-weighed beakers and air-dried to a constant weight. Percent water content was calculated by difference.

**Sediment Characteristics**

Dithionite-citrate extractable Fe and ammonium oxalate extractable Fe (USDA 1996) were determined for Bt horizon soil and Lake Lanier and Lake Oglethorpe sediment samples using an inductively-coupled argon plasma (ICAP) Thermo Jarrell-Ash 965 elemental analyzer to determine total Fe and oxidized iron percentages by weight. Iron extractions were performed on soil and sediment samples prior to and following incubation with sucrose. Samples were air-dried, pulverized and dry sieved through 2 mm and 250 μm sieves sequentially. Relative surface area of the soil and sediments were analyzed using a Gemini III 2375 (Micromeretics) Surface Area Analyzer to measure the multipoint BET surface area (Brunnauer, et al. 1938). Particle size determinations were also
conducted on the soil and sediments using the pipette and sieving method (USDA 1996). Water content was determined by difference of weight between wet and oven-dried sediments and soil.

RESULTS

The 88-97% of total iron in the porewaters was present as soluble iron, as was 55-88% of total porewater phosphorus (Table 3.1). A greater percentage of phosphorus was soluble in Bt horizon soil and Lake Lanier sediment incubations than in the porewaters from incubated Lake Oglethorpe sediments. Greater than 90% of the manganese was soluble in porewaters from all chambers, indicating that iron reduction had proceeded. Percentage of soluble porewater iron and phosphorus were different between sediment types.

Organic acid analyses identified the primary metabolic products as acetate, propionate, and pyruvate; formate, lactate, fumarate, and glycolate were also identified in the analyses, but at much lower concentrations. Acetate was found in the highest concentration as expected as a product of sucrose consumption by both fermentation and glycolytic pathways. Propionate is the second most abundant compound found in the organic acid analysis (Figure 3.2 a). Pyruvate is also found in millimolar concentrations. The other compounds identified in this analysis were found in much lower concentrations e.g., <50 FM (Figure 3.2 b). Most of these compounds are common products of carbon metabolism and are frequently found in sediment porewaters as longer chain carbon compounds are oxidized.

Organic acids in measurable concentrations in undiluted sediment collection porewaters in Lake Lanier include micromolar concentrations of pyruvic, glycolic, formic, and acetic acid (Figure 3.3). Lactic acid is present at about an order-of-magnitude higher concentration. Organic acids present in
Lake Oglethorpe samples include citric, glycolic, formic, acetic and malic acids. Lactic acid is also present at a higher concentration in these samples.

Concentrations of primary and secondary carbon metabolism products in incubations of Lake Lanier and Lake Oglethorpe sediments are similar, while concentrations of these products in incubations with Bt horizon soil are lower than those of either of the lake sediments. Lactate was found in Lake Oglethorpe and Lake Lanier samples as a metabolic product of sucrose consumption; lactate was not found in the organic analysis of incubated Bt horizon soil samples. The similarity among the types and concentrations of organic acids indicates that the active bacteria were similar in sediment from both Lake Lanier and Lake Oglethorpe. The percentage of TOC in the sediments of both Lake Oglethorpe and Lake Lanier was slightly elevated following incubation; there was no measurable TOC in the Bt horizon soil prior to or following incubation (Table 3.2). Water content by weight of incubated sediments was similar in Lake Lanier (81.8 %) and Lake Oglethorpe (81.2 %), but was much lower in the Bt horizon soil incubations (42 %).

The percentage of oxalate extractable iron (Fe$_o$) in Lake Lanier (2.11 % Fe$_o$ unincubated, 2.16 % Fe$_o$ incubated) and Lake Oglethorpe (2.94 % Fe$_o$ unincubated, 2.73% Fe$_o$ incubated) samples was not affected by the anaerobic incubation with sucrose (Table 3.2), however the percentage of oxalate extractable iron present in incubated Bt horizon soil (0.19 % Fe$_o$ unincubated, 1.18 % Fe$_o$ incubated) was greatly increased (Table 3.2). Lake Oglethorpe sediments had higher concentrations of iron in both Fe$_o$ and dithionite-citrate extractable iron (Fe$_d$) extractions than Lake Lanier sediments or Bt horizon soil (Table 3.2). The higher Fe$_o$/Fe$_d$ ratios found in the Lake Oglethorpe (0.87) and Lake Lanier (0.80) sediments indicate a greater proportion of active iron in sediment samples than in Bt horizon soil (0.50). The high Fe$_o$/Fe$_d$ ratios in the sediments are also indicative of ferrihydrite in the samples.
Surface area analysis indicates that all three of the samples, Lanier (34.4 m$^2$/g) and Oglethorpe (35.0 m$^2$/g) sediments and Bt horizon soil (36.2 m$^2$/g) have similar surface areas (Table 3.2). Surface areas in this range indicate that all three samples would be considered to be clay loam, or clay based on surface area alone, that is, all three soils have surface areas sufficient for appreciable surface sorption. Particle size determination also indicates an abundance of small particles (silt and clay sized) in all samples (Table 3.2). Bt horizon soil has the highest percentage of particles in the clay fraction (56.3 % clay), Lake Lanier sediment has the highest percentage of particles in the silt fraction (46.3 % silt), and the sand, silt and clay fractions were evenly distributed in the Lake Oglethorpe samples (33.7 % sand, 30.4 % silt, and 35.9 % clay). These distributions can be used to identify texture classes based on the % clay and % sand (Elghamry and Elashkar 1962) in the sample. Lake Oglethorpe and Lake Lanier samples would be identified as clay loam in texture; Bt horizon soil would be identified as clay in texture using this texture triangle.

DISCUSSION

The Bt horizon soil and Lake Lanier sediments yield the greatest percentage of iron and phosphorus in solubilized form (Table 3.1). A smaller percentage of the total P was dissolved in Lake Oglethorpe sediments. Oxalate and citrate dithionite extractable iron were found in higher concentrations in Lake Oglethorpe than in Lake Lanier or Bt horizon soil. It may be that reducible iron is more rapidly utilized in the anoxic hypolimnion and sediments of Lake Oglethorpe, leaving less available for solubilization during incubation than the Fe and complexed PO$_4$ in Lake Lanier sediments (Aller 1998, Crockford and Willett 2000).
Acetate was the organic acid found in the highest concentration in all samples after incubation with sucrose. This high concentration of acetate (~ 25 - 40 mM) is expected given the high concentration of sucrose added to the chambers. Acetate is the product of both fermentation and organic carbon mineralization through glycolysis, and as such is a common product of anaerobic carbon mineralization. Pyruvate and propionic acid are also common products of anaerobic consumption of easily consumable carbon compounds. The organic compounds found in lower concentrations are also typically found in sediment porewaters, and are commonly known to be the products of anaerobic carbon mineralization. The presence of these organic acids in the porewaters of the incubated sediments indicate that a diverse and active community of bacteria are present in the sediments of Lake Lanier and Lake Oglethorpe. Further, the presence of similar concentrations of the primary and secondary organic acids indicate that the active bacteria in these sediments are not unique to each system. The similarity among the types and concentrations of organic acids indicates that the active bacteria were similar in sediment from both Lake Lanier and Lake Oglethorpe (Figure 3.2). These similarities in organic acids suggest that the differences in iron reduction and phosphate solubilization might be attributed to differences in the sediment characteristics between sites, rather than differences in the bacteria that mediate the iron reduction reactions.

Approximately 24 mM of easily consumable organic carbon was added to each chamber resulting in an approximate 1:1 ratio (1) release of soluble Fe for each mM of C added to both Lanier (23 mM Fe released) and Oglethorpe (23 mM Fe released) sediments. The Fe release from the Bt horizon soil had a slightly different molar ratio of C:Fe released at a 1:1.3 ratio (0.77). The molar ratios of P released per C added were 1:133,1:141, and 1:109 in Lake Lanier sediments, Lake Oglethorpe sediments, and the Bt horizon soil, respectively. These release ratios are slightly higher than the
Redfield ratios of cellular content C:P 106:1. Consumption of easily consumable carbon then, releases approximately one mole of Fe and slightly less than ten millimoles (0.0075-0.0091 M) of P for each mole of C consumed.

Lake Oglethorpe has a larger watershed area to lake volume ratio than Lake Lanier (12.9 for Lake Oglethorpe versus 1.06 for Lake Lanier, based on the new conservation volume [Kundell et al. 1998]). The larger relative watershed coupled with shallower maximum depth, and the strength and extent of stratification and hypolimnetic anoxia in Lake Oglethorpe (Porter et al. 1996) could provide conditions for greater processing and cycling of inorganic and organic particles (Crockford and Willett 2000). The strong thermocline and chemocline established early in the summer season in Lake Oglethorpe create a metalimnetic plate that effectively separates surface and bottom waters (Porter et al. 1996). Wind mixing of surface waters allows for extensive processing of surficial inorganic and organic particles, thus the particles reaching the sediment in Lake Oglethorpe are likely processed in the surficial waters.

Lake Lanier sediments have fewer clay sized particles (29.1 % clay) than sediments from Lake Oglethorpe (30.4 % clay) and Bt horizon soil (56.3 % clay). Lake Oglethorpe sediments also have a higher percentage of active iron (3.14 %) than Lake Lanier sediments (2.70 %) and Bt horizon soil (2.24 %). Less P was released from Lake Oglethorpe sediments than from Lake Lanier sediments during anaerobic incubation. The release of less phosphate from sediments with higher iron concentrations can be explained in two ways. First, the lower phosphate release and higher extractable iron may be the result of the greater concentration of sulfur in the hypolimnetic waters of Lake Oglethorpe during summer stratification and hypolimnetic anoxia, as evidenced by green sulfur bacteria that exist in the anoxic hypolimnetic waters of Lake Oglethorpe during summer stratification that is not
found in Lake Lanier (Parker 1995). Sulfur can sequester iron by forming FeS in the presence of $H_2S$, and thus the phosphate bound in iron complexes may be released in the anoxic hypolimnetic waters before these complexes reach the sediments. Second, the more stable metalimnetic plate and the longer period of stratification in Lake Oglethorpe (Figure 3.4) allows for additional biological processing of particles due to the high biological activity at the metalimnetic plate and the extent of anoxia. Hence, oxidized iron may be reduced in the water column releasing phosphate prior to reaching the sediments. The enhanced biological activity surrounding the oxic/anoxic interface and the metalimnetic plate may increase biological processing of inorganic particles. This biological processing may consume or transform much of the accessible phosphorus prior to it reaching the sediments, leaving less phosphorus available for release from the sediments.

The shorter period of stratification, and the relatively weaker metalimnetic plate in most of Lake Lanier allow for more rapid settling, and thus less biological processing of organic and inorganic particles in the water column. The iron reduction and phosphorus release observed in soil from the Bt horizon collected in the Piedmont region of Georgia demonstrate that phosphorus bound to Bt horizon soil and transported to Piedmont impoundments may be made biologically available through iron reduction in the sediments. The high binding capacity of Bt horizon soil (see Parker and Beck Chapter 4, this volume) and the high iron content of Lake Lanier sediments indicate that much of the phosphorus in these sediments may be available for release as oxidized iron is reduced during carbon consumption by metal-reducing bacteria.
LITERATURE CITED


Table 3.1. Soluble Fe, P, and Mn from porewaters of sediment and soil anaerobic incubations as a percentage of total porewater concentrations. Student t statistics are reported for differences between sediment soil types with respect to these elements. Significantly different sample population means are indicated by italics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Fe</th>
<th>t statistic</th>
<th>P</th>
<th>t statistic</th>
<th>Mn</th>
<th>t statistic</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bt Soil</td>
<td>99.2</td>
<td>Bt vs. Lanier</td>
<td>87.9</td>
<td>Bt vs. Lanier</td>
<td>99.1</td>
<td>Bt vs. Lanier</td>
</tr>
<tr>
<td>Bt Soil</td>
<td>95.7</td>
<td>0.298</td>
<td>77.9</td>
<td>0.814</td>
<td>95.8</td>
<td>0.287</td>
</tr>
<tr>
<td>Lanier</td>
<td>97.1</td>
<td>Lanier vs. Ogleth.</td>
<td>82.4</td>
<td>Lanier vs. Ogleth.</td>
<td>97.6</td>
<td>Lanier vs. Ogleth</td>
</tr>
<tr>
<td>Lanier</td>
<td>95.9</td>
<td>0.029</td>
<td>71.9</td>
<td>0.067</td>
<td>95.8</td>
<td>0.071</td>
</tr>
<tr>
<td>Oglethorpe</td>
<td>94.0</td>
<td>Oglethorpe vs. Bt</td>
<td>71.3</td>
<td>Oglethorpe vs. Bt</td>
<td>92.9</td>
<td>Oglethorpe vs. Bt</td>
</tr>
<tr>
<td>Oglethorpe</td>
<td>93.8</td>
<td>0.316</td>
<td>57.9</td>
<td>0.144</td>
<td>94.6</td>
<td>0.411</td>
</tr>
<tr>
<td>Oglethorpe</td>
<td>90.8</td>
<td></td>
<td>55.3</td>
<td></td>
<td>94.6</td>
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</tr>
</tbody>
</table>
Table 3.2. Sediment characteristics for Lake Lanier sediment (LL), Lake Oglethorpe sediment (LO), and Bt horizon soil (Bt). Particle size distributions as determined by the pipette and sieving method (USDA 1996) presented as percentages. Iron extractions using both oxalate and citrate-dithionite before and after anaerobic incubation with sucrose, and oxalate extracted iron ($Fe_{o}$) to sodium dithionite-citrate extracted iron ($Fe_{d}$) which quantifies the proportion of more and less active fractions, respectively. Total organic carbon (TOC), BET multipoint surface area, and water content by weight are also presented.

<table>
<thead>
<tr>
<th>Particle Size Distribution</th>
<th>% Sand</th>
<th>% Silt</th>
<th>% Clay</th>
</tr>
</thead>
<tbody>
<tr>
<td>VC (2.0-1.0)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C (1.0-0.5)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>M (0.5-0.25)</td>
<td>0.2</td>
<td>0.2</td>
<td>0.1</td>
</tr>
<tr>
<td>F (0.25-0.10)</td>
<td>11.7</td>
<td>12.4</td>
<td>24.6</td>
</tr>
<tr>
<td>VF (0.10-0.05)</td>
<td></td>
<td>8.2</td>
<td>22.2</td>
</tr>
<tr>
<td>Total (2.0-0.05)</td>
<td></td>
<td></td>
<td>46.3</td>
</tr>
<tr>
<td>Total (0.05-0.002)</td>
<td></td>
<td></td>
<td>29.1</td>
</tr>
<tr>
<td>Total (&lt;0.002)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LL</td>
<td>0.1</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>LO</td>
<td>0.2</td>
<td>0.6</td>
<td>0.6</td>
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<tr>
<td>Bt</td>
<td>0.1</td>
<td>0.1</td>
<td>0.1</td>
</tr>
<tr>
<td>% Fe</td>
<td></td>
<td></td>
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<tr>
<td>Oxalate before incub.</td>
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<tr>
<td>Oxalate after incub.</td>
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<tr>
<td>Dithionite-Citrate before incub.</td>
<td>0.78</td>
<td>0.80</td>
<td>3.15</td>
</tr>
<tr>
<td>after incub.</td>
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<tr>
<td>% Fe$<em>{o}$/Fe$</em>{d}$</td>
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<td>TOC</td>
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<td>BET</td>
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<td>Water</td>
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<tr>
<td>Multi SA m$^{2}$/g</td>
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<td>Content %</td>
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<tr>
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<td>2.11</td>
<td>2.16</td>
<td>2.70</td>
</tr>
<tr>
<td>LO</td>
<td>2.94</td>
<td>2.73</td>
<td>3.14</td>
</tr>
<tr>
<td>Bt</td>
<td>0.19</td>
<td>1.11</td>
<td>2.24</td>
</tr>
</tbody>
</table>
Figure 3.1. Sediment incubation chamber with PVC pipe stems supporting stir paddle, prefiltration device (airstone), and tubing for sampling and N₂ flow. A pinchcock clamp seals the sampling and N₂ tubing when not in use. O-rings seal the top of the chamber and the stem.
Figures 3.2. Primary (a) and secondary (b) metabolic products from Lake Lanier (LL), Lake Oglethorpe (LO) and Bt soil (Bt soil) produced during incubation with sucrose. Note the different scales for primary and secondary metabolic products.
Figure 3.3. Organic acids analysis of undiluted porewater samples from Lake Lanier (LL) and Lake Oglethorpe (LO) sediment. Note the abundance of lactic acid in samples from both systems.
Figure 3.4. The shallowest depth of anoxia and the shallowest depth of the thermocline for three annual cycles of both Lake Lanier and Lake Oglethorpe. The enlarged data points indicate start and end of hypolimnetic anoxia. Anoxic depth is represented by 9 for Lake Lanier, and 6 for Lake Oglethorpe. Thermocline depth is indicated by • for Lake Lanier and x for Lake Oglethorpe.
CHAPTER 4

THE ROLE OF IRON-RICH SEDIMENT IN THE PHOSPHORUS CYCLE OF
LAKE LANIER, GEORGIA

\^Parker, Amanda K. and M. Bruce Beck To be submitted to *Limnology and Oceanography*.\n
77
Abstract. Phosphorus cycling in lake systems can be significantly affected by the iron cycle. Iron oxides bind inorganic phosphorus via ligand exchange. Bt horizon soil in the Georgia Piedmont is high in oxidized metals, especially iron and manganese. Impoundments in the Georgia Piedmont receive sediment laden with phosphorus and iron from tributary flow. We present here studies that explore the role of iron-rich sediment in the biogeochemical cycling of phosphorus in Lake Lanier, a Georgia Piedmont impoundment. X ray diffraction analysis of Lake Lanier surface water demonstrates that newly formed iron oxides are present in surface water samples. Experiments to investigate the capacity of iron oxyhydroxide, Piedmont soil from the Bt horizon, and Lake Lanier sediments to adsorb phosphate were conducted in a series of treatments. Lake Lanier sediments had the greatest capacity to sorb phosphate in all treatments, and sorbed all the phosphate in solution in most experiments. Alkaline desorption experiments were conducted with Bt horizon soil. Desorption of phosphate occurred at pH values greater than 8. The higher the pH the greater the desorption of phosphate from the soil. Iron-rich sediment plays a more significant role in the phosphorus cycle in impoundments of the Georgia Piedmont than in the north temperate systems where the traditional phosphorus cycling paradigm was developed. The photosynthetic elevation of the local pH may increase local phosphate availability by releasing phosphate from oxidized metal complexes, and thus may be a mechanism for niche construction by phytoplankton in poorly buffered surface waters.

Key Words: Phosphorus cycling, alkaline desorption, photosynthetic pH elevation, sorption capacity, iron oxidation, iron reduction.
INTRODUCTION

Phosphorus cycling in lake systems can be significantly affected by the iron cycle. Iron oxides bind inorganic phosphorus via ligand exchange. These ferric-phosphorus complexes can be transformed by reduction, and by desorption at elevated pH; both transformations release sorbed phosphate (Hutchinson 1957, Wetzel 2001). Newly formed iron oxides tend to be amorphous with greater surface area than the more crystalline forms they become as they age (Stumm and Morgan 1996, Sumner 2000). Amorphous iron oxides sorb phosphate more strongly than more crystalline forms under both aerobic and anaerobic conditions (Crockford and Willett 2000). Sorption capacity can also be increased during transport. Evidence from studies of agricultural runoff indicate that the mechanical working of soil particles during transport can decrease the size and increase the availability of reactive surfaces of these particles (McDowell et al. 2002), and thus may enhance their sorptive capacity.

Soil in the Georgia Piedmont is high in oxidized metals, especially iron (USDA 1968). Oxidized metals are positively charged and thus can form chemical complexes with clay, organic colloids, and biologically important anions. Oxidized metals and some clays that are mobilized by rain events bind phosphate and other anions during transport and in receiving waterbodies. These oxidized metal complexes can remain suspended in surface waters as colloidal particles for prolonged periods of time (Hutchinson 1957, Wetzel 2001). Further, Selig et al. (2002) found that iron- and aluminum-bound phosphate in the water column of a German lake remained stable from March to November, while dissolved organic phosphorus increased and particulate phosphorus and dissolved inorganic phosphorus decreased.
Impoundments in the Georgia Piedmont receive sediment laden with phosphorus and iron from tributary flow (Figure 4.1). Much of the phosphorus associated with sediment that enters lakes and reservoirs is complexed to oxidized metals and settles or precipitates out of solution into the sediments (Hayes and Rigler 1958, Tarapchak and Nalewajko 1986, Caraco and Valiela 1983, Wetzel 2001) depending on tributary flow and water chemistry characteristics. Suspended sediment concentrations are quickly attenuated in most lakes as sediments are deposited, though may persist for relatively longer periods of time when the particles are small enough to have a slower settling rate (Kennedy and Walker 1990, Wetzel 2001). We present here studies that explore the role of transported sediment in the biogeochemical cycling of phosphorus in Lake Lanier, an impoundment in the Georgia Piedmont that is characterized by poorly buffered, iron-rich, circumneutral waters typical of those found in the southern Piedmont. We conducted x ray diffraction analyses of surface water solids, Bt horizon soil, and deposited Lake Lanier sediments to determine if newly formed iron oxides were present in these samples. We tested the sorption capacity of Bt horizon soil, Lake Lanier sediments, and FeOOH for soluble reactive phosphorus (SRP). We tested the availability of sediment bound phosphorus in experiments of two different scales. In the larger scale, we tested the availability of sediment bound phosphorus to a pond system using continuously monitoring equipment in an experiment described in detail elsewhere (Mayhew et al. 2001; Parker et al., Chapter 2 this volume). The small scale benchtop experiment involved adding radiolabelled phosphorus to natural lake water cultures with and without added sediment to trace the uptake of phosphorus by bacteria and phytoplankton. We conducted laboratory tests to determine if soluble reactive phosphorus is released from sediment at elevated pH in a process called alkaline desorption. We propose a potential pathway for algal access to P via this mechanism. The data presented here describe the role of iron-rich sediments in the phosphorus cycle.
of Piedmont impoundments. We contrast this role of iron-rich sediments in impoundments of the southeastern Piedmont with the role of sediments and iron in the traditional lake phosphorus cycle.

METHODS

**X ray Diffraction**

Sediment from Flowery Branch Bay of Lake Lanier, soil from an exposed Bt horizon at Whitehall Forest, and 10 liters of surface water collected at Flowery Branch Bay were dried in a 70°C drying oven. X-ray diffraction analysis was conducted on powder mounted soil and sediment samples. X-ray diffraction spectra were collected with CuKα radiation using an X-ray diffractometer (Phillips Analytical Inc., Natick, MA) equipped with a focusing monochromator and operated at 35 KV and 20 mA. Samples were scanned from diffraction angles of 3 to 60° 2θ at a rate of 2° 2θ/min.

**Sorption Experiments**

A series of experiments to explore the capacity of iron oxyhydroxide (FeOOH), Bt horizon soil, and Lake Lanier sediments to sorb phosphate were conducted. Soil and sediments were air dried, pulverized and sieved through 2 mm and 250 µm sieves. Three grams of catalyst grade FeOOH, Bt horizon soil, or Lake Lanier sediments were added to 50 mL centrifuge tubes. Thirty mL of deionized water and stock phosphate solution (KH₂PO₄ + deionized H₂O) was added to create final phosphorus concentrations of 0, 100, 500, 1000, 1500 mg P per tube. The tubes were shaken for 24 or 48 hours, vacuum filtered through a 0.45 µm filter or centrifuged for 15 minutes at 3800 rpm, and the filtrate or supernatant was stored at 4°C until analyzed (within 24 hours of filtration or centrifugation). Solutions were analyzed for soluble reactive phosphorus using Murphy-Riley analysis with a Shimadzu UV mini spectrophotometer following APHA (1999) methods.
Sorption/Desorption Experiments

Four grams of Bt horizon soil was placed in each of 18 50 mL centrifuge tubes. Stock phosphate solution and deionized H₂O were added for a final solution concentration of 50 F̜ g P/mL. The centrifuge tubes were shaken for 24 hours, and centrifuged to separate the sediment from the supernatant. The concentration of soluble reactive phosphorus in the supernatant was determined as described above. The amount of soluble reactive phosphorus sorbed to the soil was calculated by difference. Temporal desorption at multiple pH values was tested by adding HCl and/or NaOH to deionized water to make solutions of pH 7, 8, 9, 10. Thirty ml of water at each pH was added to three centrifuge tubes, with deionized water added to the rest (pH 5.9) as a control. The soil and specific pH solution were shaken for 24 hours. pH was measured in each tube. Tubes were centrifuged and the soluble reactive phosphorus concentration of the supernatant was measured. Desorption was calculated by difference. An equilibrium desorption experiment was also conducted. Fifty grams of Bt horizon soil (250 F̜ m sieved) were added to each of two beakers. Five hundred mL of potassium phosphate solution (25 F̜ g/mL) were added to each beaker. The beakers were stirred for 24 hours and pH was measured to be 4.775. Sodium hydroxide solution (10 M) was added while stirring until the pH stabilized at 7.0, 8.0, 8.5, 9.0, 10.0, and 11.0. Subsamples were taken for soluble reactive phosphorus analysis at the initial pH and at each stable pH.
RESULTS

X-ray Diffraction

X-ray diffraction analysis of Lake Lanier surface water demonstrates that iron oxides are present. The peaks in the x-ray diffraction spectra for Lake Lanier surface water were not similar to those in the Bt horizon soil, or Lake Lanier sediments. The mica, kaolin, and quartz peaks found in the Bt horizon soil and Lake Lanier sediments are not present in the x-ray diffraction spectra from Lake Lanier surface waters. All three samples do show a lepidicrocite peak, indicating the presence of newly formed iron oxides in all samples (Figure 4.2). The x-ray diffraction spectra show the presence of gibbsite, mica, kaolinite and quartz in the Lake Lanier sediments and Bt soil. The broader peaks indicate less crystalline forms of these minerals than those with sharper more defined peaks (Figure 4.2). The x-ray diffraction spectrum of Lake Lanier surface water is substantially different from the spectra from Lake Lanier sediment and Bt soil. The x-ray diffraction spectra show that Lake Lanier sediment is similar in mineral forms and content to Bt soil (Figure 4.2.)

Sorption Experiments

Experiments to investigate the capacity of iron oxyhydroxide, Piedmont soil from the Bt horizon, and Lake Lanier sediments to adsorb phosphate were conducted in a series of treatments. Lake Lanier sediments had the greatest capacity to sorb phosphate in all treatments, and sorbed all the phosphate in solution in most experiments (Table 4.1). Bt horizon soil sorbed more phosphorus than iron oxyhydroxide (FeOOH). The amount of phosphate sorbed by Bt horizon soil and iron oxyhydroxide was greater in the 48 hour experiments than in the treatment shaken for 24 hours (Table 4.1). There was sorption to sediment or soil in all treatments, with the majority of the phosphate bound to the soil or sediment rather than in solution at the end of all experiments.
Sorption/Desorption Experiments

Alkaline desorption experiments were conducted with Bt horizon soil. Average initial sorption in these experiments was 806 \( \text{Fg P/g soil} \) (out of a possible 1000 \( \text{Fg P/g soil} \)). Temporal desorption of phosphate occurred at pH values greater than 8, although the pH had returned to 5.9 at the end of the temporal desorption experiment. The higher the initial pH the greater the desorption of phosphate from Bt horizon soil (Figure 4.3). Desorption of phosphate also occurred in the equilibrium pH experiment with increasing amounts of phosphate desorbed as the stable pH was increased. The concentration of phosphate in solution was higher than the initial solution (144 \( \text{Fg/mL} \)) concentration only at pH values greater than 8.5, that is, at pH 9.0 (152 \( \text{Fg/mL} \)), 10.0 (159 \( \text{Fg/mL} \)), and 11.0 (177 \( \text{Fg/mL} \)).

DISCUSSION

Caraco and Valiela (1983) found that iron oxides effectively scavenge phosphorus at oxic/anoxic interfaces, before phosphorus can be circulated to surface water biota. Their work demonstrated that iron oxides concentrate at the oxycline and this concentration of iron oxides corresponded to minimal dissolved phosphorus concentrations. More recently, Roden et al. (2002), have proposed that microbially mediated iron reduction and oxidation form a coupled system. Iron reducing bacteria in the anoxic sediments and bottom waters supply iron oxidizing bacteria at the oxic/anoxic water column interface with ferrous iron in an efficient transfer of electron donors and acceptors for carbon mineralization. They suggest that iron reducing bacteria could become the primary form of organic matter mineralization in the sediments of circumneutral, low-sulfate freshwater environments such as Lake Lanier. The coupling of iron reducing and iron oxidizing bacteria at the anoxic/oxic interface in the water column (during stratification) or sediments (during mixis) could create an efficient mechanism for
carbon mineralization and phosphorus scavenging that will prolong the period of time that phosphorus is
sequestered in the sediments, and inhibit internal loading of phosphorus from iron-rich sediments. The
presence of newly formed iron oxides in Lake Lanier surface water as determined here in x ray
diffraction studies, and the release of soluble iron and phosphorus from Lake Lanier sediments (see
Chapter 3) indicate that Lake Lanier could support such a coupled system.

The sorption capacity experiments show that the iron-rich Bt horizon soil has the capacity to bind
large amounts of phosphorus. Lake Lanier sediments sorbed all P in solution in all treatments, and the
sorption capacity of Bt horizon soil was >90%. This high degree of sorption indicates that the
maximum sorption capacity of Bt soil and Lake Lanier sediments is likely much greater than 500 \( \text{F g P/g}
\) soil or sediment, as is further evidenced by the high sorption of P (806 \( \text{F g P/ g soil} \)) in the desorption
experiments, and by the regression relationship of 2 \( \text{F g P/ mg SSC} \) from log transformed data collected
from Lake Lanier tributaries (Figure 4.1). Hatcher (1994) estimated that 80-90% of the P load to
Lake Lanier does not leave the lake and is probably sequestered by sediments. The oxidized iron
transported with sediments has the capacity to bind phosphate.

Lake Lanier sediment has a greater capacity for sorbing phosphate than either FeOOH or Bt
horizon soil. This may be due to the larger percentage of clay sized particles in Lake Lanier sediments,
as compared to the Bt horizon soil (see Parker and Beck, Chapter 3 this volume). Lake Lanier
sediments used in these experiments are primarily composed of silt and clay sized particles. The larger
quantity of smaller particles provides for greater reactive surface area for sorption of anions and cations
in solution, and consequently there is a greater capacity for phosphate sorption than for larger-sized
particles in the Bt horizon Piedmont soil and catalyst grade FeOOH. In addition, as the concentration
of phosphate in solution increases, more phosphate is bound to Bt horizon soil and FeOOH. This effect
may be due to the difference in ionic strength. Solutions with a greater ionic strength can effectively increase the area of sorption by increasing the area of the diffuse charge around the oxidized iron molecule which results in more phosphate binding in the diffuse layer as ionic strength increases.

An experimental test of the effect of Bt horizon soil on the availability of phosphate in a small impoundment is described in results reported previously (Mayhew et al. 2001; Parker et al., Chapter 2 this volume). A small pond was fertilized on multiple occasions with different fertilizer treatments. Twice the pond was fertilized with ammonium polyphosphate pond fertilizer (11-27-0 N-P-K) alone, and the third time the fertilizer was sorbed to Bt horizon soil prior to distribution in the impoundment. The Bt horizon soil plus fertilizer treatment resulted in no significant increase of soluble reactive phosphorus to the water column. The work described here provides information about sorption of phosphate to Bt horizon soil, emphasizing the role of transported sediment in the formation of particulate inorganic phosphate (PIP), and provides evidence that oxidized iron in transported sediment reduces the bioavailability of DIP in Georgia Piedmont impoundments. Thus, transported sediment plays a more significant role in the phosphorus cycle in impoundments of the Georgia Piedmont than in the north temperate systems due to the greater sediment loading of impoundments as opposed to natural lakes (Kennedy and Walker 1990), the high iron content and proportion of reactive iron in transported sediments (Parker and Beck, Chapter 3 this volume), and the lack of buffering capacity and low sulfate availability that is more typical in the naturally formed north temperate lakes where the traditional phosphorus cycling paradigm was developed.

Desorption of phosphate from Bt soil at elevated pH provides evidence that increased pH can increase availability of phosphate in surface waters. In the poorly buffered waters of the Georgia Piedmont, algal photosynthesis can cause pH elevation. The elevated pH can, in turn, result in release
of sorbed phosphate from transported Bt soil (Figure 4.3). Results from the chemical equilibrium model Visual MINTEQ (Figure 4.4) indicate that alkaline desorption of phosphate from oxidized iron occurs at pH values greater than 8. The data presented here indicate that high pH can also result in the release of sorbed phosphate from Georgia Piedmont Bt soil. pH values as high as 11 have been measured in impoundments in the Piedmont region of Georgia (Painter, unpublished data from Jackson Lake Clean Lakes Study 1990). The results of the desorption experiments indicate that alkaline desorption can play a significant role in the cycling of phosphorus in surface waters. These experiments provide data to indicate that alkaline desorption (Parker and Rasmussen 2001) may increase local phosphate availability in the surface waters of Piedmont impoundments.

Organic carbon is delivered from the watershed and produced internally in the waterbody as carbon is fixed during phytoplankton production (Wetzel 2001). Sediment release of soluble inorganic phosphorus occurs when oxidized metals are used as electron acceptors for carbon mineralization by sediment bacteria. Soluble P released from the reduction of metals in the sediments can be inhibited by resorption to newly formed iron oxides above the sediment water interface where the redox potential is higher, this oxidation reaction can occur in the absence of oxygen when more energetically favorable ions are reduced in the oxidation of iron (Table 4.2), or may be mediated by iron oxidizing bacteria at the oxic/anoxic interface (Roden et al. 2002). Newly formed iron oxides are less crystalline and typically have a greater surface area for sorption than older more crystalline forms, and therefore more strongly sorb phosphate and more effectively remove phosphorus from the biota (Sposito 1980). The presence of amorphous iron oxides in surface water and sediments indicate that new iron oxides are being formed, and may sorb phosphate during transport and in the water body prior to settling into the
sediments, and may prevent release of phosphorus into the water column when the oxic/anoxic interface is at or near the sediment surface.

Concentration of biological and chemical components occurs at the metalimnion during summer stratification. The thermal density gradient set up at the metalimnetic plate enhances the chemical gradient and reduces settling velocities of biota and particulates at this interface (Kufel and Kalinowska 1997). Below the metalimnetic plate, the water is cooler, and becomes more oxygen depleted as oxygen is consumed, but not resupplied through mixing or photosynthetic activity. Over the course of stratification, the density gradient at the metalimnetic plate becomes more pronounced effectively eliminating light below the metalimnion and thus inhibiting most photosynthetic activity in the hypolimnetic waters. The condition of concentrating biota and chemical components at the metalimnetic plate makes this region very active in the cycling and recycling of nutrients, and in the consumption and production of oxygen (Porter 1996, Wetzel 2001). The removal of oxygen from the hypolimnetic waters is greater just below the metalimnetic plate than it is at depth, due to respiration of the concentrated biota. The retardation of sinking particulates in the cooler, denser waters of the hypolimnion, enhances this effect as the consumption of oxygen continues as scenscing algae and bacteria slowly sink into the hypolimnion in the absence of photosynthetic oxygen evolution. The concentration of algae and bacteria in the metalimnion also result in rapid cycling of organic constituents, hence organic phosphate is rapidly cycled here and oxygen consumption and carbon oxidation are also increased in this area of the water column as compared to that in the epilimnion and the deeper hypolimnion.

The rapid recycling of nutrients, and the ‘concentration’ of phytoplankton in the epilimnetic and metalimnetic waters creates conditions whereby the pH can become locally elevated due to the removal
of bicarbonate from the poorly buffered waters of Piedmont reservoirs. The conditions that retain nutrient laden sediment particles and ‘concentrate’ the phytoplankton help form the environment for alkaline desorption of phosphate from oxidized metals transported with sediment into the reservoir. Elevation of pH values to those greater than 8.5 will cause the release of phosphate from ligand exchanges formed with oxidized metals, thus potentially increasing local availability of phosphate. pH values greater than 8.5 have been measured in specific embayments in Lake Lanier and other Georgia Piedmont reservoirs (Jackson Lake).

Data from the tributaries indicate that 2Fg of P are delivered to Lake Lanier with every mg of suspended sediment concentration (SSC). The biological response that would be expected from this phosphorus load is never realized within Lake Lanier. The lack of response to the phosphorus load may be attributed to the reduced biological availability of phosphorus bound to oxidized metals. X ray diffraction analyses indicates that iron oxides are being newly formed in surface waters. Newly formed iron oxides sorb phosphate more strongly than older more crystalline forms. The formation of new iron oxides in surface water indicates that dissolved phosphate is likely to be quickly scavenged by oxidized iron and removed from biological availability. The photosynthetic elevation of the local pH may increase local phosphate availability by releasing phosphate from oxidized metal complexes, and thus may be a mechanism for niche construction by phytoplankton in poorly buffered surface waters. These characteristics of Georgia Piedmont impoundments lead to a biogeochemical cycling of phosphorus that is not often seen in systems that are less iron-rich, better buffered, and less strongly stratified. We therefore propose a different phosphorus cycle for these systems that illustrates the differences among Georgia Piedmont systems and those with the more traditional phosphorus cycle (Figure 4.5). In the traditional phosphorus cycle shown on the left, DIP enters the lake and leads to increased algal growth,
which increases organic carbon, which leads to increased reduction of oxidized iron in the sediments, which leads to increased release of phosphate which is then circulated to the surface waters at mixis. In the phosphorus cycle that we propose for impoundments in the Georgia Piedmont, shown on the right, DIP enters the lake and may be bound to oxidized iron, or may lead to increased algal growth, which can induce photosynthetically elevated pH in the poorly buffered surface waters, which can lead to increased phosphorus availability and increased algal growth, which increases organic carbon, which leads to increased reduction of oxidized iron and release of phosphorus; phosphorus is readily resorbed to newly oxidized iron in the less reduced hypolimnetic waters and thus, is not released to the surface waters at mixis.

ACKNOWLEDGMENTS

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LITERATURE CITED


Sumner, M. 2000.


USDA. 1968. Soil Survey: Clarke and Oconee Counties, Georgia. United States Department of Agriculture, Soil Conservation Service in cooperation with University of Georgia College of Agriculture Agricultural Experiment Stations. Washington, DC.

Table 4.1. Sorption capacity of Lake Lanier sediment, Bt horizon soil, and catalyst grade FeOOH for phosphate.

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<th>24 Hour</th>
<th>48 Hour</th>
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<tr>
<td>Sediment</td>
<td>500 (100%)</td>
<td>500 (100%)</td>
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<tr>
<td>Bt Soil</td>
<td>472 (94.4%)</td>
<td>488 (97.6%)</td>
</tr>
<tr>
<td>FeOOH</td>
<td>406 (81.2%)</td>
<td>377 (75.4%)</td>
</tr>
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</table>
Table 4.2. The primary redox reactions of organic matter degradation in sequence from the oxic to anoxic reactions with the appropriate stoichiometric ratios. Organic Matter (OM) = \((\text{CH}_2\text{O})_{106}(\text{NH}_3)_{16}(\text{H}_3\text{PO}_4)\) assuming the Redfield ratio (From Cai et al., submitted).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Products</th>
</tr>
</thead>
<tbody>
<tr>
<td>OM + 138 O(_2)</td>
<td>106 CO(_2) + 16 HNO(_3) + H(_3)PO(_4)</td>
</tr>
<tr>
<td>OM + 0.8 x 106 NO(_3^-) + 0.8 x 106 H(^+)</td>
<td>106 CO(_2) + 0.4 x 106 N(_2) + 16 NH(_3) + H(_3)PO(_4)</td>
</tr>
<tr>
<td>OM + 2 x 106 MnO(_2) + 4 x 106 H(^+)</td>
<td>106 CO(_2) + 2 x 106 Mn(^{2+}) + 16 NH(_3) + H(_3)PO(_4)</td>
</tr>
<tr>
<td>OM + 4 x 106 FeOOH + 8 x 106 H(^+)</td>
<td>106 CO(_2) + 4 x 106 Fe(^{2+}) + 16 NH(_3) + H(_3)PO(_4)</td>
</tr>
<tr>
<td>OM + 106/2SO(_4^{2-}) 106 H(^+)</td>
<td>106 CO(_2) + 106/2 H(_2)S + 16 NH(_3) + H(_3)PO(_4)</td>
</tr>
<tr>
<td>OM</td>
<td>106/2 CO(_2) + 106/2 CH(_4) + 16 NH(_3) + H(_3)PO(_4)</td>
</tr>
</tbody>
</table>
Figure 4.1. Suspended solids regressed with total iron (TFe) and total phosphorus (TP) for tributaries of Lake Lanier.

TFe = 0.164 SSC^{0.6963}

TP = 0.0082 SSC^{0.6896}
Figure 4.2. X-ray diffraction spectra for Bt soil, Lake Lanier sediment, and Lake Lanier surface water solids with offset for better viewing.
Figure 4.3. Desorption of P at alkaline pH. Phosphate begins desorption at pH values above 8.5.
Figure 4.4. VMINTEQ output, P adsorbed to Fe: pH sweep. Note that the inflection point for desorption (50% P adsorbed) begins at pH 8.5.
Figure 4.5. A simplified phosphorus cycle for lakes without (above) and with (below) coupled iron oxidation and reduction.
CHAPTER 5

CONCLUSIONS

The soils of the Georgia Piedmont are rich in oxidized iron which is transported in runoff to receiving waterbodies. Sorption characteristics of oxidized iron in these transported soils help to inhibit internal biological production in receiving waterbodies by removing inorganic phosphorus from biological access (see Chapter 2 and Chapter 4, this volume). The transformation of oxidized iron in anoxic sediments and in high pH surface waters can release bound phosphorus and make it available for biological uptake (see Chapter 3, this volume). The release of phosphate from oxidized metals via reduction in the anoxic sediments is rarely realized in Georgia Piedmont impoundments, most probably due to resorption of phosphate to newly oxidized iron (see Chapter 4, this volume) when soluble iron from sediment porewaters is re-oxidized in the less reduced hypolimnetic waters, or when phosphate is sorbed to oxidized iron supplied in runoff from tributaries.

Iron-rich transported soil plays a role in the cycling of phosphorus in specific ways during summer stratification. Surface waters, the epilimnion, receive transported sediment where it can remove phosphate from biotic access by sorption to oxidized metals (see Chapter 2 and Chapter 4). Oxidized iron-phosphate complexes settle and precipitate out of the surface waters (transport P within the water column). Oxidized iron and sorbed phosphate can remain suspended in surface waters for long periods of time if the complexes are colloidal sized particles. Selig et al. (2002) found that phosphorus bound to oxidized metals remained fairly constant throughout the year. In surface waters where phytoplankton can concentrate during summer stratification, photosynthesis can effectively remove bicarbonate from
the water. Bicarbonate removal can elevate the pH in waters with little buffering capacity (see Chapter 4, this volume). The highly weathered soils of the Georgia Piedmont are low in sulfate and high in iron and manganese. This parent geology creates poorly buffered, circumneutral, low sulfate water chemistry conditions in impoundments in this region. Concentrations of photosynthetically active phytoplankton can locally elevate the pH in poorly buffered waters. Positively charged oxidized iron loses its charge at elevated pH and releases complexed anions. This mechanism could result in the increased availability of phosphate for biotic consumption and may constitute niche construction by phytoplankton.

The role of transported sediment in the epilimnion then is: to remove phosphate from biological access; to transport oxidized iron and phosphate to the bottom waters and sediments as settling particulates; to release sorbed anions in certain water chemistry conditions (elevated pH), which may also increase biological access to those released anions.

The middle depths of the water column, the metalimnion, receive sediment transported through settling, surface mixing processes, or by flow in former river channels. In the metalimnion, sediment can be transformed by reduction in the oxygen poor waters just below the metalimnetic plate, and by oxidation when circulated to oxygenated surface waters. This region is the area where the oxycline forms. The oxycline develops in conjunction with the thermocline, creating strongly stratified conditions with denser cooler waters below the metalimnetic plate, and warmer, fully oxygenated, less dense waters at the surface. The density gradient provides for development of a region of changing settling velocities and internal mixing that concentrates settling biota, and organic and inorganic particulates. This concentration of biota and particulates creates an area of active consumption of organic carbon and nutrients, and of chemical transformations. The oxycline is a place of rapid oxidation of reduced
metals, and the subsequent resorption of anions, including phosphate (Caraco and Valeila 1983). The concentration of bacteria and phytoplankton make the metalimnion an active region of phosphorus cycling, photosynthesis, and respiration. This area of active biological and chemical change is the first area that should be investigated for locating the coupled oxidation and reduction system that has been suggested for FeRB and FeOB by Roden et al. (2002).

The bottom waters, or hypolimnion, has cooler, denser waters during summer stratification. The concentration of biota and particulates in the metalimnion, effectively extinguishes light penetration in the hypolimnion so that very little photosynthetic oxygen production occurs. Respiration by biota consumes oxygen, as do chemical reactions in the increasingly reduced conditions of the hypolimnion during summer stratification.

Oxygen is consumed most rapidly just beneath the metalimnion, and just above the sediment surface in the hypolimnion of Lake Lanier, leading to a ‘bulge’ of oxygenated water in the middle depths of the hypolimnion before the hypolimnion becomes fully anoxic. This oxygen gradient creates a gradient of reduced conditions such that the hypolimnetic waters are most oxygen deficient at or near the sediment surface, and immediately below the metalimnetic plate. The higher concentration of oxygen in the middle depths of the hypolimnion create conditions for rapid redox cycling of iron at these depths in the hypolimnion. The re-oxidation of reduced metal species also provides for resorption of anion, especially phosphate, in these depths.

Sediments of Georgia Piedmont impoundments are typically anoxic millimeters to centimeters below the surface. Consumption of organic matter by metal reducing bacteria in the sediments and hypolimnetic waters leads to reduction of iron and hence release of phosphate from oxidized iron-phosphate complexes. Accordingly, microbial activity in the sediments plays an important role in
carbon degradation and nutrient regeneration and cycling. Sediments with large amounts of consumable organic carbon and an abundant supply of oxidants will support metal reducing bacteria and may release substantial amounts of sorbed or complexed anions, such as phosphate, at mixis. The amount of complexed anions released from oxidized metal complexes in the sediments is largely dependent upon the supply of oxidized metals and easily consumable organic carbon. In more productive systems, organic matter that settles to the sediments during stratification tends to have been previously processed such that the more recalcitrant, less easily consumed forms of organic matter are more commonly found in sediments of more developed systems. Therefore, less easily consumable organic carbon is available for consumption in the surficial sediments of more productive systems and hence less iron reduction and phosphate release takes place.

Caraco and Valiela (1983) found that iron oxides effectively scavenge phosphorus at oxic/anoxic interfaces, before phosphorus can be circulated to surface water biota. Their work demonstrated that iron oxides concentrate at the oxycline and this concentration of iron oxides corresponded to minimal dissolved phosphorus concentrations. More recently, Roden et al. (2002), have proposed that microbially mediated iron reduction and oxidation form a coupled system. Iron reducing bacteria in the anoxic sediments and bottom waters supply iron oxidizing bacteria with ferrous iron in an efficient transfer of electron donors and acceptors for carbon mineralization. Roden and Gorby (2002) suggest that iron reducing bacteria could become the primary form of organic matter mineralization in the sediments of circumneutral, low-sulfate freshwater environments such as Lake Lanier. The coupling of iron reducing and iron oxidizing bacteria at the anoxic/oxic interface could create an efficient mechanism for carbon mineralization and phosphorus scavenging that will prolong the period of time that phosphorus is sequestered in the sediments, and inhibit internal loading of phosphorus from iron-rich
sediments. The presence of newly formed iron oxides in Lake Lanier surface water as determined here in X-ray diffraction studies, and the release of soluble iron and phosphorus from Lake Lanier sediments (see Parker and Beck, Chapter 3 this volume) indicate that Lake Lanier could support such a coupled system.

Roden et al. (2002) suggest a potential for coupling of FeRB and FeOB to supply electron shuttles for carbon mineralization with less energetic expense. Georgia Piedmont impoundments are an excellent place to look for the coupling of these bacteria. The thermal regime creates conditions that allow for depletion of oxygen in the sediments and bottom waters, followed by oxygenation at mixis. There is evidence of iron oxide formation at the sediment surface during mixis. The release of soluble Fe and P in the incubation studies presented here indicate abundant P is available for release from the sediments given the right conditions. If FeOB are present at the sediment-water interface, they could be utilizing the abundant Fe^{2+} present and thus enhance the oxidation of Fe^{2+} and the subsequent sorption of phosphate to the newly formed oxidized iron. This coupling of FeRB and FeOB could create an effective mechanism for P sequestration in Piedmont impoundments.

The primary factors that affect the sequestration of P in the sediments are supply the supply of oxidized iron, and the supply of easily consumable organic carbon to the sediments. As the impoundment ages and the internal supply of organic carbon increases, carbon mineralization in the sediments may exhaust the supply of oxidized iron and sulfate reduction and methanogenesis may become more competitive paths for carbon mineralization. Currently however, in the low sulfate and poorly buffered waters of Lake Lanier, iron reduction appears to be the primary metabolic mechanism of carbon mineralization.
Lake Oglethorpe has a greater watershed load to lake volume ratio than Lake Lanier (Parker and Beck Chapter 3, this volume). The load of organic carbon to Lake Oglethorpe is likely also greater on a lake volume basis, due to land application of livestock waste and the higher percentage of livestock in the watershed. Watershed loading coupled with shallower maximum depth, and the strength and extent of stratification and hypolimnetic anoxia in Lake Oglethorpe (Parker 1995) allow for greater processing and cycling of inorganic and organic particles (Crockford and Willett 2000). The strong thermocline and chemocline established early in the summer season in Lake Oglethorpe create a metalimnetic plate that effectively separates surface and bottom waters. Wind mixing of surface waters allows for extensive processing of surficial inorganic and organic particles, thus the particles reaching the sediment in Lake Oglethorpe are likely processed in the surficial waters.

The shorter period of strong stratification, and the relatively weaker metalimnetic plate in much of Lake Lanier allow for more rapid settling, and thus less processing of organic and inorganic particles in the surface waters. The iron reduction and phosphorus release observed in soil from the Bt horizon collected in the Piedmont region of Georgia demonstrates that phosphorus bound to Bt soil and transported to Piedmont impoundments may be made biologically available through iron reduction in the sediments (see Parker and Beck Chapter 3, this volume). The high binding capacity of Bt soil (see Parker and Beck Chapter 4, this volume) and the high iron content of Lake Lanier sediments indicates that much of the phosphorus in these sediments may be available for release as organic carbon is delivered to the sediments and oxidized iron is reduced during carbon consumption by metal-reducing bacteria (see Parker and Beck Chapter 3, this volume).
Sorption Capacity

Sorption capacity experiments (see Parker and Beck Chapter 4, this volume) show that the iron-rich Bt horizon soil has the capacity to bind large amounts of phosphorus. Lake Lanier sediments sorbed all P in solution in all treatments, and the sorption capacity of Bt horizon soil was >90%. This high degree of sorption indicates that the maximum sorption capacity of Bt soil and Lake Lanier sediments is likely much greater than 500 \( \text{Fg P/g soil or sediment} \), as is further evidenced by the high sorption of P (806 \( \text{Fg P/g soil} \)) in the desorption experiments, and by the regression relationship of 2 \( \text{Fg P/mg SSC} \) from log transformed data collected from Lake Lanier tributaries. Hatcher (1994) estimated that 80-90% of the P load to Lake Lanier does not leave the lake and is probably sequestered by sediments. The oxidized iron transported with sediments has the capacity to bind phosphate.

Lake Lanier sediment has a greater capacity for sorbing phosphate than either FeOOH or Bt horizon soil. This may be due to the size of the particles in Lake Lanier sediments, as compared to the Bt horizon soil and FeOOH. Lake Lanier sediments used in these experiments are primarily composed of silt and clay sized particles. The larger quantity of smaller particles provides for greater reactive surface area for sorption of anions and cations in solution, and consequently have a greater capacity for phosphate sorption than do the sized particles in the Bt horizon Piedmont soil and catalyst grade FeOOH. In addition, the greater the concentration of phosphate in solution, the greater the capacity for Bt horizon soil and FeOOH to bind the phosphate. This effect may be due to the difference in ionic strength. Solutions with a greater ionic strength can effectively increase the area of sorption by increasing the area of the diffuse charge around the oxidized iron molecule which results in more phosphate binding in the diffuse layer as ionic strength increases.
The $^{32}$P experiments discussed in Chapters 2 and 4 (this volume) further support the importance of transported sediment in the availability of phosphorus in the surface waters of the Georgia Piedmont. The lack of biological uptake of radiolabelled phosphate sorbed to Bt soil, indicates that transported sediment plays an important role in removing phosphorus from the biologically available fraction. The work described here provides information about sorption of phosphate to Bt horizon soil, emphasizing the role of transported sediment in the formation of particulate inorganic phosphate (PIP), and provides evidence that oxidized iron in transported sediment reduces the bioavailability of DIP in Georgia Piedmont impoundments. Thus, transported sediment plays a more significant role in the phosphorus cycle in impoundments of the Georgia Piedmont than in the north temperate systems where the traditional phosphorus cycling paradigm was developed.

**Alkaline Desorption**

Desorption of phosphate from Bt soil at elevated pH provides evidence that increased pH can increase availability of phosphate in surface waters. In the poorly buffered waters of the Georgia Piedmont, algal photosynthesis can cause pH elevation. The elevated pH can, in turn, result in release of sorbed phosphate from transported Bt soil. Results from the chemical equilibrium model Visual MINTEQ presented in Chapter 4 indicate that alkaline desorption of phosphate from oxidized iron occurs at pH values greater than 8. The data presented here indicate that high pH can also result in the release of sorbed phosphate from Georgia Piedmont Bt soil. pH values as high as 11 have been measured in impoundments in the Piedmont region of Georgia. The results of the desorption experiments indicate that alkaline desorption can play a significant role in the cycling of phosphorus in surface waters. These experiments provide support for the hypothesis that alkaline desorption (Parker
and Rasmussen 2001) may increase local phosphate availability in the surface waters of Piedmont impoundments.

The biological response that would be expected from the phosphorus load to Lake Lanier is never realized within the lake. The lack of response to the phosphorus load may be attributed to the reduced biological availability of phosphorus bound to oxidized metals. X-ray diffraction analyses indicates that iron oxides are being newly formed in surface waters. Newly formed iron oxides sorb phosphate more strongly than older more crystalline forms. The formation of new iron oxides in surface water indicate that dissolved phosphate is likely to be quickly scavenged by oxidized iron and removed from biological availability. The photosynthetic elevation of the local pH may increase local phosphate availability by releasing phosphate from oxidized metal complexes, and thus may be a mechanism for niche construction by phytoplankton in poorly buffered surface waters.

Organic carbon is delivered from the watershed and produced internally in the waterbody as carbon is fixed during phytoplankton production (Wetzel 2001). Sediment release of soluble inorganic phosphorus occurs when oxidized metals are used as electron acceptors for carbon mineralization by sediment bacteria. Soluble P released from the reduction of metals in the sediments can be inhibited by resorption to newly formed iron oxides above the sediment water interface where the redox conditions are less reduced, this oxidation reaction can occur in the absence of oxygen when more energetically favorable ions are reduced in the oxidation of iron, or may be mediated by iron oxidizing bacteria at the oxic/anoxic interface (Roden et al. 2002). Newly formed iron oxides more strongly sorb phosphate and so more effectively remove phosphorus from the biological availability. The presence of amorphous iron oxides in surface water indicate that new iron oxides are being formed, and may sorb phosphate during transport and in the water body prior to settling into the sediments.
Management Implications

Most waterbodies in Georgia that require TMDL development list sediment and bacteria as the primary pollutants. The TMDLs being developed for sediment impairment focus on reducing in waterbody turbidity. The most practical method for reducing turbidity in most cases is to reduce external sediment loading. The work presented here indicate that reductions in sediment loads to Piedmont impoundments may increase availability of phosphate in these systems and may lead to more rapid eutrophication and water quality degradation. Decreasing external sediment loads in these waterbodies then, may improve water quality with respect to one parameter (turbidity), and impair water quality with respect to others (nutrients, algal and bacterial growth, chlorophyll). The complication that water quality improvement in one respect will cause increased impairment with respect to other water quality parameters emphasizes the need for water quality regulations that encourage whole system investigations on the interactions of multiple stressors, rather than regulations that seek to control one parameter at a time.

Multiple parameters effect the cycling of phosphorus in circumneutral, low-sulfate, freshwater environments. The phosphorus cycle is controlled by the iron cycle in Piedmont impoundments. The cycling of iron is controlled by the loading of iron to the waterbody through sediment transport, and the reduction and oxidation of iron in the sediments and hypolimnion. The reduction of iron in the sediments (and to some extent its re-oxidation) is fueled by easily consumable organic carbon. These multiple parameters should be managed collectively, rather than independently, to ensure the best attainable water quality, and thus, watershed and reservoir management practices should focus on maintaining a balance of the biogeochemical processes in the waterbody.
Management practices that decrease the amount of oxidized iron relative to organic carbon in the water column and sediment porewaters should be investigated, as the supply of oxidized iron inhibits internal phosphorus regeneration from the anoxic sediments. The work presented here indicates that phosphorus can be regenerated from Lake Lanier sediments (Chapter 3), even though this release has yet to be seen in the surface waters at mixis. However, the loadings of iron-rich sediment and organic carbon to Lake Lanier embayments should be monitored to maintain a balance of oxidized metals and organic matter that will prevent substantial release of phosphorus from the sediments at mixis.

Conditions that might lead to more rapid development of Lake Lanier as a lake ecosystem, i.e., increases in organic carbon input through increased wastewater effluent, and or decreases in oxidized iron input by reduction in sediment loading could lead to increased iron reduction in the sediments and thus an increased release of phosphorus to the surface waters. The management of the Lake Lanier watershed should be carefully considered to balance the water quality needs of the impoundment with the potential effects of management actions on the cycling of phosphorus in this system. In Lake Lanier the reduction of sediment loading with its delivery of oxidized iron, could cause proportionally greater delivery of organic carbon to the sediments and thus result in an increase in iron reduction and phosphorus release from the sediments and bottom waters. It is imperative that the full impact of management actions be considered before they are implemented.

The traditional lake phosphorus cycling paradigm fails in lake systems with an abundant supply of oxidized iron. In these systems, oxidized iron prevents the release of solubilized phosphate to the surface waters at mixis. The global extent of iron rich soils is significant. In these regions, the cycling of phosphorus in the natural environment may follow a very different cycle than the cycle typically described by educators and researchers. The research presented in this dissertation provides evidence
of the sequestering of phosphate on iron-rich sediments as a mechanism for removal of measurable phosphate from the water column of iron-rich Piedmont impoundments. Water quality management of lakes and streams in regions with iron-rich soils, therefore, requires careful consideration of the consequences of reducing sediment in runoff.
LITERATURE CITED


----------- 1942. The Exchange of Dissolved Substances between Mud and Water in Lakes.


biogeochemistry, microbial diversity, and bioremediation, Coates, J.D., and C. Zhang eds., Kluwer.


USDA. 1968. Soil Survey: Clarke and Oconee Counties, Georgia. United States Department of Agriculture, Soil Conservation Service in cooperation with University of Georgia College of Agriculture Agricultural Experiment Stations. Washington, DC.


