# PHOSPHORUS BINDING BY IRON-RICH SOIL IN THE SOUTHEASTERN PIEDMONT: IMPLICATIONS FOR POINT AND NON-POINT SOURCES OF PHOSPHORUS

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Abstract: A small impoundment in the Southeastern Piedmont was fertilized on three occasions during the summer of 2000. Liquid fertilizer was directly broadcast over the pond in the first two treatments; in the third treatment the fertilizer was mixed with clay soil and water. The system response to nutrient addition was measured using the Environmental Process and Control Laboratory, which measures a variety of parameters. Only ammonium  $(NH_4)$ , orthophosphate  $(PO_4)$  and turbidity (TUR) are reported here. Response to the first two fertilizations was a similar, immediate elevation in levels of PO<sub>4</sub> and NH<sub>4</sub>. The third fertilization produced no detectable increase in PO4 and a minimal increase in NH4. These data support the hypotheses that 1) suspended iron-rich clay from piedmont soils sequesters PO4 and 2) clay soils sequester NH4 in aquatic systems. These mechanisms of nutrient segestration have important implications for bioavailability in piedmont systems: nonpoint, sediment-bound nutrients are less available than nutrients from point sources.

# INTRODUCTION

Phosphorus (P) availability is crucial in many freshwater systems, and is often considered the limiting nutrient. Indeed, P may be more universally important than just in freshwater. Hutchinson (1957) noted that "Of all the elements present in living organisms, phosphorus is likely to be the most important ecologically, because the ratio of phosphorus to other elements in organisms tends to be considerably greater than the ratio in the primary sources of the biological elements."

The form of P available to algae in freshwater is soluble phosphate ( $PO_4$ ), and, unlike nitrogen, is not generally reduced or transformed into other oxidation states by microbial or inorganic processes (Atlas and Bartha, 1993). What complicates the cycling of P through ecosystems is the multitude of ways it can be bound to organic molecules and to metals such as iron  $(Fe^{+3})$  and aluminum  $(Al^{+3})$ , and the effects that pH, Eh, light and microorganisms may have on its solubility.

The prevailing paradigm for productive north temperate and European lakes is that P is removed from the epilimnion during the growing season by algal growth, passed through the food chain, and settled to the bottom as detritus. The settled P is trapped in benthic sediments until it is released by microbial action. P may be bound more permanently by adsorption to iron oxyhydroxides at pH values less than 8. If the sediment becomes anoxic,

P may be released by reduction of ferric  $(Fe^{+3})$  to ferrous  $(Fe^{+2})$  iron. Ferrous iron is more soluble than ferric, and releases P into the hypolimnion, where it is mixed into the photic zone at overturn, resulting in availability of P for algal growth.

Many reservoirs in the Southeastern Piedmont conform to this paradigm to the extent that P is bound by the ironrich clay soils; however, there is often little release of P from the hypolimnion during mixis (Mayhew and Mayhew, 1992; Reckhow, 1988). Hatcher (1994) estimated that 80-90% of the P load to Lake Lanier 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 extreme enough to drop Eh to the level at which  $Fe^{+2}$  appears (Hutchinson, 1957); oxidation of  $Fe^{+2}$  to  $Fe^{+3}$  by bacteria under acidic conditions; and oxidation of  $Fe^{+2}$  to  $Fe^{+3}$  by inorganic processes (Hutchinson, 1957; Stumm and Morgan, 1996).

#### METHODS

This experiment examined the effects of fertilization with  $PO_4$  and  $NH_4$  on nutrient availability in a small pond in the Southeastern Piedmont. We report the results of

treatment of the pond with ammonium polyphosphate liquid fertilizer (11-37-0) and subsequent treatment with the same fertilizer mixed with Bt-horizon subsoil. The hypothesis is that the iron in the subsoil sequesters the  $PO_4$ , resulting in little or no increase in  $PO_4$  after fertilization. We also report the effects of suspended solids on NH<sub>4</sub> availability.

### Location

The study site is located at Whitehall Forest near the University of Georgia campus. The site contains a small farm pond, which is used for fish culture for teaching and experimental purposes and has been limed and fertilized regularly. The volume of the pond is approximately 2000 m<sup>3</sup>, 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. The drainage area includes forest, a deer experimental area, buildings, and parking areas of the experimental station. There is one outflow, which is regulated by a stand pipe near the dam. Low flow conditions pertained throughout the study period due to drought.

## Data Collection

Ammonium (NH4), soluble reactive phosphrous (PO4) and turbidity (TUR) were measured every 15 minutes using the Environmental Process Control Laboratories (EPCL), consisting of two mobile laboratories stationed next to the pond. Water was pumped from two location 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.

#### Laboratory Methods

Soluble Reactive Phosphate was determined by filtering the influent stream through a 0.45 um filter and then monitoring the soluble phosphorus concentration using the Murphy-Riley Method. Turbidity was determined using a nephelometric sensor. Ammonium concentration was monitored using an ion-specific electrode (Minworth Systems Limited, 1997).

# **Fertilization Regimes**

A total of three fertilization experiments were performed. The first included a ime application followed by fertilizer application. Lime was applied on July 2 by broadcasting 45 kg of Ca(OH)<sub>2</sub> 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 (approximately 1 kg of NH4 and 3 kg of PO4). The second fertilization did not include lime application; 8 L of the same fertilizer was broadcast from the Jon boat on July 28.

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, which would have seriously affected the experiment. The duckweed was removed by seining and by raking from a kayak.

The third fertilization used 8 L of 11-37-0 fertilizer mixed with 55 kg of Typic Ultisol, Pacolet Series Bt horizon soil (USDA, 1968) collected from a road cut in Whitehall Experimental Station. The soil was air-dried, crushed, screened, weighed and mixed by hand with the fertilizer 24 hours before application. The ratio of PO<sub>4</sub> to soil was approximately 50 g-PO4/kg-soil. On October 1, the soil-fertilizer mixture was mixed with water from the pond to form a slurry that was broadcast from shore and from a Jon boat.

RESULTS

Figure 1 shows PO4, NH4 and TUR from the pond for the period before and after the first fertilization. This first fertilization was performed in the absence of additional suspended solids. Note the rapid increase in PO4 and NH4 at the time of fertilization to approximately 1000 and 2000  $\mu$ g/L, respectively. Note also that the PO4 concentration decreased at a log-linear rate for a prolonged period (approximately three weeks). NH4 concentrations decayed more rapidly (approximately one day). TUR (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.

Figure 2 again shows PO4, NH4 and TUR concentrations resulting from fertilization, in this case from the third fertilization in which the fertilizer was added to the Bt subsoil to form a suspended slurry in the pond. Note the substantially reduced PO4 and NH4 responses (less than 100  $\mu$ g/L) and the large increase in turbidity from 10 to 32 FTU.. Turbidity then slowly returned to pretreatment levels over a five-day period. It is clear that a substantial reduction in nutrient availability occurred due to the addition of suspended solids at the time of fertilization.



Figure 1. Phosphorus (PO4), ammonium (NH4), and turbidity (TUR) concentrations after fertilization with ammonium polyphosphate (11-37-0) without sediment.



# DISCUSSION

The most clear-cut result is that PO4 mixed with Piedmont subsoil remained bound to the soil; there was no substantial increase in PO4 in the October fertilization. It also appears that NH4 was bound, although less extensively, by the soildue to anion exchange capacity (AEC) of the soil. The capacity of the clay to bind PO4 appears to be high, because much of the 40 mg-PO<sub>4</sub>/g-soil was sorbed. Laboratory experiments have estimated the sorptive capacity of similar clay soils to be 7.7  $\mu$ g-P/gsoil over a two-minute period and 23.4  $\mu$ g-P/g-soil over 24 hours (Mayhew and Mayhew, 1992). It also appears that NH4 was bound by clay minerals due to cation exchange.

## CONCLUSIONS

Whitehall Pond experiments indicate that the biological response to fertilization is substantially muted by the presence of suspended sediments. Iron-rich clay soils in the Southeastern Piedmont adsorb and sequester PO4 and NH4. PO4 removal by sediments is attributed to ligand bonding onto iron oxyhydroxide minerals. NH4 removal by sediments is attributed to cation exchange onto clay minerals.

Future investigations should focus on the influence of soil mineral composition (e.g., iron, manganese, and aluminum oxyhydroxides) and organic matter loading on the ability of sediments to sequester nutrients. Additional experiments in this pond, or in systems which have not been previously fertilized, will be needed to fully understand nutrient dynamics in Southeastern Piedmont impoundments.

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