

Mark River Research Statement

My research occurs at the intersection of hydrology and sediment biogeochemistry. I apply my background in engineering, along with the use of various high-tech tools and an interdisciplinary approach, to explore the biogeochemical cycles of iron, phosphorus, manganese, nitrogen, and carbon and their effects on aquatic ecology.

Portions of my research have thus far been published in *Water Research* and *Ambio*, with additional manuscripts currently under external review. I have also been invited to give talks at several different universities within my watershed of study. Specific research to date has focused on the particle size distribution of suspended sediment, the transport of phosphorus- and iron-containing nanoparticles, the use of in-situ turbidity sensors as a proxy for particulate phosphorus flux, and the biogeochemistry of wetland/reservoir sediment. Future research will focus on the bioavailability of particle-bound nutrients.

Hydrologic Transport of Nanoparticles

The hydrologic transport of naturally-occurring, iron and phosphorus-containing nanoparticles is generally ignored in traditional analyses of streams and groundwater, due to the operational distinction between “dissolved” and “particulate” fractions via filtration with a 0.45μ filter. This black box approach can limit our understanding of the sources and hydrologic pathways of nutrients. As seen in Figure 1, many particles are much smaller than this operational cutoff in the southern Piedmont (and beyond), and therefore are traditionally quantified in the “dissolved” fraction simply because they pass through a filter. My research shows that a single drop of baseflow can contain millions of nanoparticles smaller than the arbitrary dissolved/particulate cutoff of 0.45μ . This research has implications for sources of reactive phosphorus, selection of best management practices, and algal bioavailability.

Using transmission electron microscopy (TEM) with energy-dispersive X-ray spectroscopy (EDS) and electron diffraction (SAED), I analyze nanoposphorus on a particle-by-particle basis to understand the types of particles responsible for transport in baseflow and stormflow. After analyzing dozens of discrete particles in a certain hydrologic period of interest (for example peak stormflow), I then use this knowledge to scale up to analyses of bulk water samples; for example, via centrifugation to separate out discrete size classes of particles, and/or via X-ray diffraction to analyze for a particular mineralogy corresponding with a bulk measure such as turbidity. Exploring the fractions of particulate suspended sediment not visible to the naked eye can provide insights into stream chemistry and sediment biogeochemistry of receiving waters, not obtainable via traditional wet chemistry.

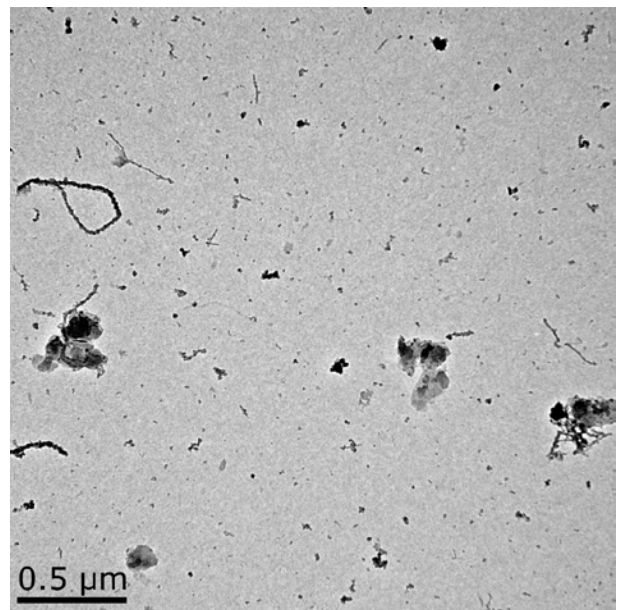


Figure 1: River and Richardson *in review*. TEM image of nanoparticles in baseflow.

Particle Size Distribution of Suspended Sediment in Stormwater

Sediment is often classified into sand, silt, and clay fractions. I use flow-imaging particle size analysis to instead classify suspended sediment into 100 different size bins, approaching a continuous particle size distribution. The behavior of individual particles can then be mechanistically modeled under conditions similar to those in a stormwater treatment wetland, allowing mechanistic insights which cannot otherwise be obtained with sand/silt/clay fractionation.

For example, my research shows that a more detailed treatment of particle size fractions better predicts the actual removal of particulate phosphorus (PP), compared to traditional first-order decay models which are commonly used. Figure 2 shows the results of a laboratory test comparing actual PP removal over time to a simple mechanistic model, classifying suspended sediment and its associated phosphorus (PP) into 100 different size fractions using the following equation based on Stokes' Law, where g = acceleration of gravity (cm/sec^2); d = particle diameter (cm); ρ_p = density of particle (g/cm^3); ρ_m = water density (g/cm^3); μ = water dynamic viscosity:

$$\text{PP}_{\text{removed}} = \sum_d \left(\frac{gd^2(\rho_p - \rho_m)}{18\mu} * \frac{t}{h} * n_d * 4\pi * \left(\frac{d}{2}\right)^2 \right)$$

Similarly, because particle size distribution is the dominant control on turbidity, turbidity can then be used as a proxy for the cumulative projected surface area of all stormflow particles:

$$\text{Turbidity} \sim \sum_d \left(4\pi \left(\frac{d}{2}\right)^2 \right) * n_d$$

This is potentially a useful tool to predict numerous elemental fluxes, as iron oxides are generally associated with the surfaces of individual particles, and are therefore predicted by total surface area. Other elements such as phosphorus and arsenic are preferentially adsorbed onto these iron oxide coatings, and are therefore also predicted by surface area. This means that turbidity, when paired with a nearby flow gauge, has strong potential to be used as a proxy for phosphorus fluxes in watersheds dominated by particulate phosphorus. Where particle size distributions are consistent across different storm events, turbidity can be a strong predictor of suspended sediment flux as well. In-situ turbidity sensors and in-situ fluorescent organic matter sensors, along with standard wet chemistry in the laboratory, are tools I use to explore the relationship between suspended sediment and elemental fluxes. My research shows that in the southern Piedmont, turbidity is a strong proxy for

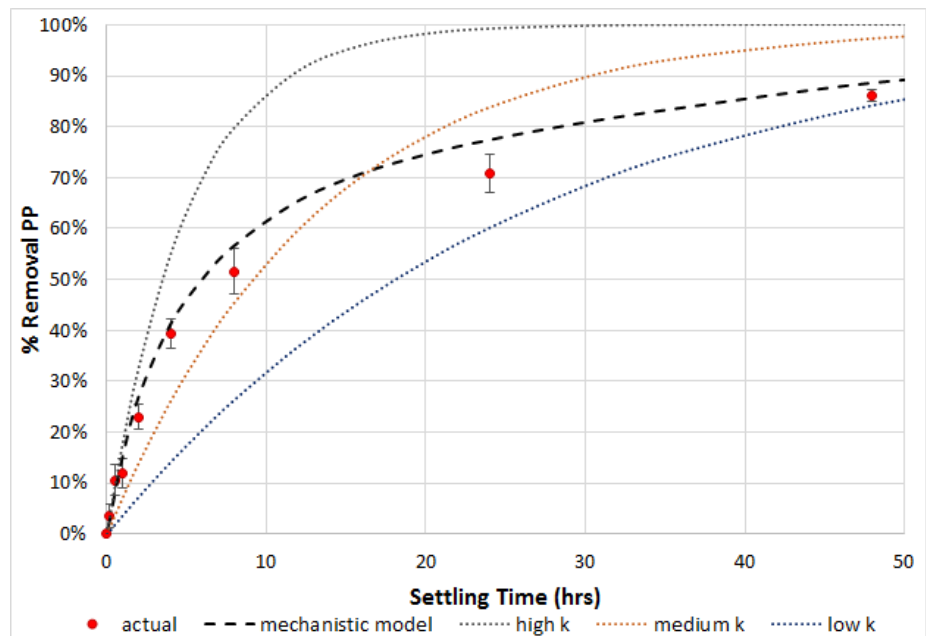


Figure 2: River and Richardson 2017. *Ambio*. Mechanistic model of particulate phosphorus removal, compared to traditional first-order exponential decay models.

phosphorus and suspended sediment transport, both for rural and urban streams. In-situ turbidity, measured at 15-minute intervals, tends to track the storm hydrograph, suggesting energy-limited sediment transport. Mineralogy of suspended sediment, measured via X-ray diffraction, can then be determined at different stages of the hydrograph and for different sediment loads.

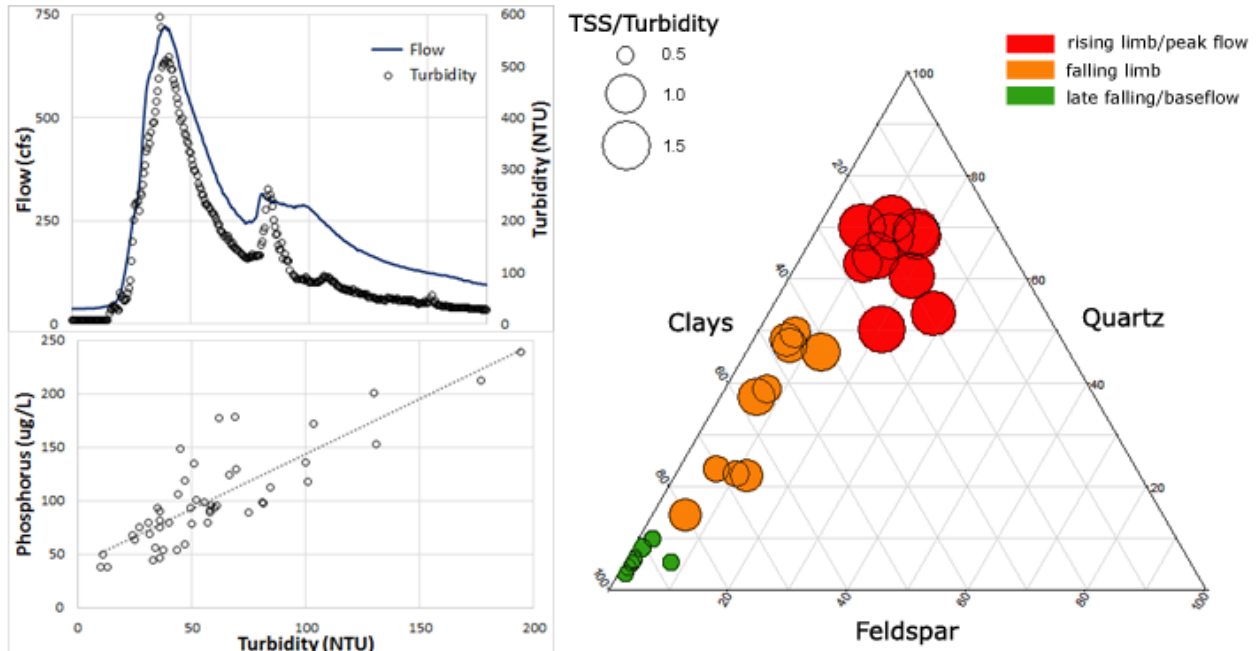


Figure 3: River and Richardson *in prep.* Typical turbidity/flow relationship during a storm; turbidity/phosphorus relationship for southern Piedmont streams; and mineralogy of Piedmont suspended sediment.

Biogeochemistry of Wetland and Reservoir Sediment

Reservoirs are increasingly utilized to supply drinking water for large cities; for example, in Raleigh, North Carolina, 500,000 residents get their drinking water from a single reservoir. However, eutrophication and the trend towards larger and more frequent blooms of toxic cyanobacteria can threaten these water resources. Constructed wetlands are often used to trap stormwater sediment before it reaches a reservoir. Nutrient release from sediment is often the least understood part of the biogeochemical cycle for numerous elements in wetlands and reservoirs. My research aims to better quantify this cycle for the two leading nutrients responsible for eutrophication: nitrogen and phosphorus. I also study the biogeochemical cycling of iron, carbon, sulfur, and manganese, as these are intricately related to the nitrogen and phosphorus cycles through organic matter decomposition, the availability of alternative electron acceptors, and the formation of minerals under reduced conditions in buried sediment.

Using basic laboratory wet chemistry along with tools such as inductively coupled plasma atomic emission spectroscopy (ICP-AES), scanning electron microscopy (SEM), FT-IR, and X-ray diffraction, I explore the dynamics in sediment and porewater, as seen in Figures 4 and 5. In the southern Piedmont, this has resulted in predictions of the phosphorus-binding capacity of reservoir sediment. High porewater values of manganese and iron indicate reduced conditions in Piedmont reservoir sediment, yet phosphorus concentrations in porewater are very low. Furthermore, there is very little gradient in phosphorus concentrations in the sediment itself ranging from recent deposits to deeper sediment which is decades old. Where there is a change in phosphorus in the sediment it generally corresponds with a change in aluminum. Thus, most particulate phosphorus delivered to Piedmont reservoirs with high aluminum

concentrations is ultimately buried on decadal timescales, in contrast to models which show high levels of phosphorus release from sediment once iron is reduced.

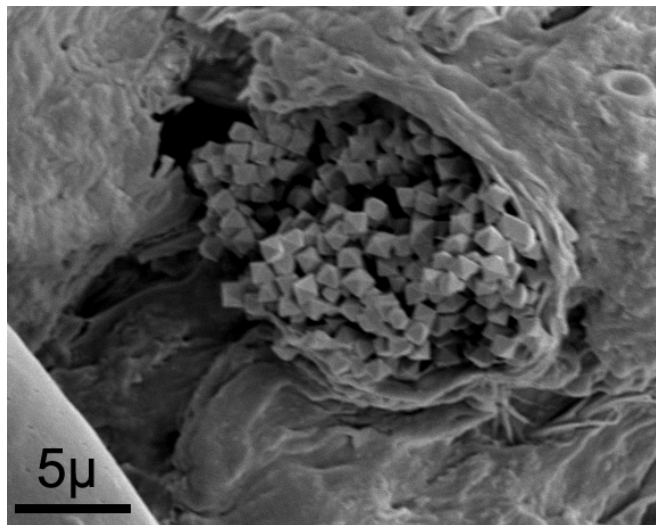


Figure 4: SEM image of pyrite (FeS_2) in sediment from a peatland, giving insight into coupled Fe, S, and P cycles.

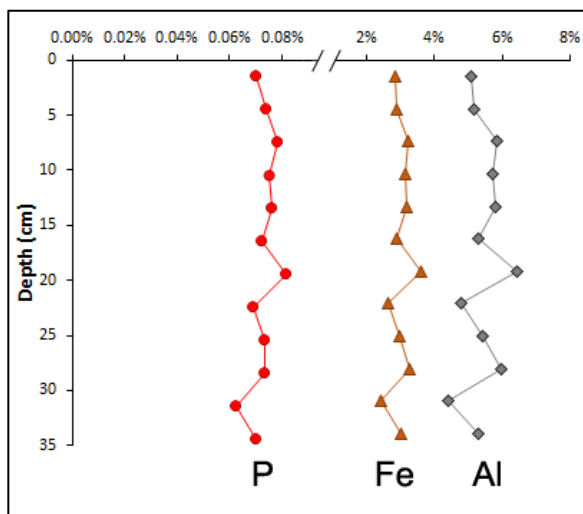


Figure 5: River and Richardson *in prep.* P, Fe, and Al in sediment from a drinking water reservoir.

Future Research: Bioavailability of Particle-bound Nutrients

A future direction of research will be to use green algae (*Selenastrum*) to better understand the bioavailable fraction of particle-bound nutrients in both suspended sediment and wetland/reservoir sediment, along with the kinetics of nutrient release. The bioavailability of different forms of N and P is lacking in the scientific literature. In fact, state/federal regulations for N and P in many watersheds are based on total elemental concentration/flux, even though much of the N and P transported via streams is not immediately available to biota, and upon reaching reservoirs is ultimately buried on a decadal timescale. Very little is known about the bioavailability of the nanoparticle fraction of particulate nutrients since this fraction is not currently differentiated from true solutes in operational definitions. It is likely that the nanoparticle fraction has different bioavailability than larger particles, and/or that amorphous nanoparticles have different bioavailability than N and P associated with crystalline aluminosilicates. This is a very exciting area of future research with implications for calculating elemental fluxes in freshwater, modeling aquatic ecosystem response to nutrient loading, and designing improved best management practices in urban and agricultural landscapes.

In summary, my current research expands the existing scientific knowledge of particle size distribution of suspended sediment, the hydrologic transport of nanoparticles, and the biogeochemistry of wetland/reservoir sediment. Applications of my research include more effective management of nutrients in agricultural and urban landscapes, and improved best management practices at the watershed scale. Future research will include studies of the bioavailability of particulate N and P. Many of the tools I utilize can leverage existing shared university resources such as electron microscopy, X-ray diffraction, FT-IR, and ICP-AES, thus keeping my overall future lab costs down. The technologies I use also lend themselves well to undergraduate student research; for example, I have worked with student interns on analyzing samples via SEM and in preparing samples for X-ray diffraction and FT-IR. Potential funding for my research includes partnerships with city and county soil/water management agencies, industry, private foundations, and state and federal grant programs.