

## ABSTRACT

Title of Thesis: RESERVOIR SCOUR AS A MAJOR SOURCE OF BIOAVAILABLE PHOSPHORUS TO A COASTAL PLAIN ESTUARY?

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Suspended sediment and particulate phosphorus (P) loads from the Susquehanna River, the largest tributary to the Chesapeake Bay, have been increasing due to the infilling of the Lower Susquehanna reservoirs and event-driven scour of sediment from behind the dams. A synthesis of sediment-water exchange data along the Bay salinity gradient confirmed that P likely remains associated with particles except under sulfate reducing conditions in the mid-Bay, where the formation of iron sulfides releases iron-bound phosphate to the water column. To estimate what fraction of scoured particulate P could become bioavailable through iron sulfide formation, P was extracted from reservoir sediment samples using a sulfide solution. Other extractions were used to quantify total P, inorganic P, and iron. Sulfide-extractable P ranged up to about 35% of total P. Findings showed that the reactivity of scoured particulate P would likely be limited and dependent on environmental conditions at the site of deposition.

RESERVOIR SCOUR AS A MAJOR SOURCE OF BIOAVAILABLE  
PHOSPHORUS TO A COASTAL PLAIN ESTUARY?

by

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# Chapter 1: Extraction of phosphorus from sediments using a sulfide solution

## **Introduction**

About 95% of the phosphorus (P) load in rivers is particulate, 60% of which is inorganic (Follmi, 1996). Phosphorus bound to iron oxides can be converted to bioavailable dissolved inorganic P when ferric iron is reduced in anoxic sediment layers, and can be released to the water column when bottom water oxygen is depleted (Mortimer, 1942). This mechanism of P mobilization is enhanced in marine systems because of high sulfate concentrations and sulfate reduction, due to the formation of solid iron sulfides. When Fe reduction is dominated by chemical reduction by sulfides, rather than microbial reduction to dissolved Fe(II), iron is buried in the sediment where it is not re-oxidized, allowing greater efflux of Fe-bound P (Caraco et al., 1989, 1990; Jordan et al., 2008; Krom & Berner, 1980; Lehtoranta et al., 2009; Roden & Edmonds, 1997).

Sequential extraction techniques often use either citrate-dithionite-bicarbonate (CDB) or ascorbate to quantify the reactive pool of Fe-bound P (Table 1). Dithionite is a strong reducing agent, which may dissolve the more crystalline phases of Fe oxyhydroxides (FeOOH) and overestimate the amount of Fe-bound P that is bioavailable (Anschutz et al., 1998; Jordan et al., 2008; Kostka & Luther III, 1994; Scicluna et al., 2015). On the other hand, the more moderate reducing agent ascorbate

only reduces amorphous and poorly crystalline FeOOH and may not adequately represent all of the potentially mobile P, since some crystalline Fe oxides can be reactive (Anschutz et al., 1998; Kostka & Luther III, 1994).

If sulfide is important to sediment P release, hydrogen sulfide may be a useful extractant. Krom and Berner (1981) bubbled H<sub>2</sub>S gas through coastal sediment/water mixtures and measured the resulting phosphate content in the water. Phosphorus extracted from oxic surface sediment by this method was comparable to the difference between inorganic P in the oxic and anoxic layers. Li et al (2016) performed P extractions using a range of sulfide concentrations, finding that P release increased with increasing concentrations of added sulfide. Our work using sulfide as an extractant has suggested that the colorimetric analysis of soluble reactive phosphorus (SRP) can be limited by the formation of black colloidal iron monosulfides (Vulgaropulos and Cornwell, unpublished).

The objective of this study was to develop a reliable method of colorimetrically analyzing phosphate extracted from sediment using a sulfide solution. This was done by drying the extract, allowing colloidal FeS to oxidize, and re-dissolving the residue with HCl, as outlined below.

### **Materials and Methods**

A 0.4 M stock sulfide solution was prepared by adding 25 g Na<sub>2</sub>S\*9H<sub>2</sub>O to a 250 ml volumetric flask with deionized water that had been purged of oxygen by bubbling with N<sub>2</sub> gas for 20 minutes. The addition of 13 ml 12N HCl lowered the pH

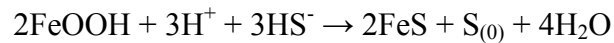
to 7, making the solution approximately equimolar with respect to  $\text{H}_2\text{S}$  and  $\text{HS}^-$ . Additional oxygen-free deionized water was added to bring the final volume to 250 ml.

The samples used in the sulfide extraction experiments were sediments collected in the three reservoirs of the Lower Susquehanna River in August 2015 and April 2016. A time course experiment was conducted to determine the ideal extraction time. Both wet and dry replicates were used to assess the effect of drying sediment. A mass of 0.10 g dry sediment (or the dry equivalent weight of wet sediment, based on calculations of percent water) was placed in 15 ml centrifuge tubes. To each tube 9.4 ml deoxygenated deionized water and 0.6 ml 0.4 M sulfide solution were added, for a final sulfide concentration of 24 mM. To minimize oxidation, the headspace of each tube was purged with  $\text{N}_2$  gas for 30 seconds. The tubes were shaken for different lengths of time, from one day to 10 days.

At the end of each extraction, the samples were centrifuged at 3000 rpm for 15 minutes. Because black colloidal  $\text{FeS}$  in the supernatant prevented direct P analysis by colorimetry, 4-5 ml of the extract was pipetted into vials and left open under a fume hood for 1-2 days to allow  $\text{H}_2\text{S}$  to diffuse into the air or oxidize in the water. The open vials were then placed in a drying oven for several days until all the water had evaporated. The residue was then re-dissolved with 4 ml 1 N  $\text{HCl}$  and analyzed colorimetrically (Parsons et al., 1984). Some replicates were filtered before analysis to determine if filtering could minimize the interference of any remaining oxidation products.

The resulting P concentrations were compared to calculations of the difference between HCl-extractable P in untreated and sulfide-treated sediment samples. After the supernatant was removed, the remaining sediment was washed with 10 ml 1 M MgCl<sub>2</sub> followed by 10 ml deionized water, and centrifuged and decanted after each treatment. The sediment was dried completely and P was extracted using 1 N HCl and analyzed colorimetrically (Aspila et al., 1976; Parsons et al., 1984). These values were subtracted from HCl-extractable P in untreated replicates to estimate the P fraction lost through the sulfide extraction. This calculation by difference is herein referred to as the “difference” method, as opposed to directly analyzing sulfide-extractable P by drying and re-dissolving the extract, which is referred to as the “direct” approach.

Iron oxyhydroxides are most efficiently converted to Fe sulfides through the following reaction:



Since the above reaction consumes protons, it should be accompanied by a rise in pH. To further assess the appropriate reaction time, an experiment was performed to continuously measure pH in sulfide solution added to sediment over about 36 hours. A volume of 10 ml of 24 mM H<sub>2</sub>S/HS<sup>-</sup> solution was added to three glass vials: one with 0.10 g dry sediment, one with 0.20 g dry sediment, and one control with no sediment. Stir bars were added to the vials and pH electrodes were placed in the top and sealed with parafilm. The samples were stirred while pH was logged every minute.

To minimize interferences for colorimetric analysis, other experiments were conducted in which the dried residue and the dried sulfide-treated sediment were ashed, and the results compared to analyses of un-ashed dried extract and sediment. For these experiments, extractions were performed in glass centrifuge tubes, and the supernatant was dried in glass vials. After the sulfide extraction, the glass tubes of dried sediment and supernatant were ashed in a muffle furnace at 550 C for two hours. Phosphorus was then extracted from the sediment using 1 N HCl and compared to 1 N HCl extractions on ashed, non-sulfide-treated sediment (total P; Aspila et al., 1976; Parsons et al., 1984) to calculate the P yield from the sulfide extraction. The ashed dried solution was re-dissolved with 1 N HCl as before.

Possible interferences in the re-dissolved sulfide extract (“direct” method) were evaluated by spiking the solution with a known amount of P and determining recovery. A standard  $\text{PO}_4^{3-}$  solution was added to 10 samples of un-ashed, re-dissolved extract at a concentration of either 3 or 4  $\mu\text{mol L}^{-1}$ . These spiked samples were analyzed colorimetrically and compared to unspiked samples to calculate percent recovery. Two replicates were analyzed for each sample.

## **Results**

The ideal extraction time was assessed using the time course extraction experiment and continuous pH logging. The time course extraction experiment yielded similar P concentrations after one day and 2 days (Fig. 1). Since the similarity between the one-day and 2-day extractions suggested the reaction had gone to completion, we waited until day 6 to analyze the next set of samples. After 6 and 10

days, the extracted P had decreased substantially, likely because slow diffusion of air into the centrifuge tubes allowed eventual reoxidation of reduced Fe. With the pH logging experiment, pH initially increased as expected and plateaued around 9.5 (in the vial with 0.20 g sediment) and 8.5 (in the vial with 0.10 g sediment) after about 16 hours (Fig. 2). Both of these experiments indicated that 24 hours was a sufficient extraction time for the system to reach equilibrium, with all reactive iron oxides converted to iron sulfides.

Phosphorus concentrations measured by drying and re-dissolving the sulfide extract (“direct” method) were compared to those calculated by difference compared to HCl-extractable P (“difference” method) to assess accuracy. Using un-ashed Conowingo Reservoir sediment, values calculated by difference were lower than those measured directly ( $p < 0.01$ ); percentage differences ranged from 48 to 56%. However, when the dried sulfide-treated sediment was ashed, the two methods yielded more similar P concentrations for the Conowingo replicates, which were 12% different on average (Fig. 3). Some of other reservoir samples still showed discrepancies between the two methods: samples LC-5-7, Aldred, and Clarke all had significant differences between the “direct” and “difference” methods ( $p < 0.05$ ) (Fig. 3). For the “direct” method, ashing the dried extract yielded similar P concentrations as un-ashed residue (Fig. 3); the ashed and un-ashed replicates were no more than 13% different. The coefficient of variation ranged from 2.1 to 15% for the directly measured samples (using un-ashed dried residue), and 1.8 to 49% for the samples measured by difference (using ashed sediment).

In general there was no significant difference in P extracted using wet sediment versus dry, although for one sample the wet and dry replicates were 23% different. Filtering the solution after drying and re-dissolving lowered the variability between replicates, likely by removing leftover elemental sulfur that may interfere with colorimetry. Phosphorus recoveries in the spiked re-dissolved extracts averaged 108% with a standard deviation of 10%.

### **Discussion**

The addition of a  $\text{H}_2\text{S}/\text{HS}^-$  solution to sediment results in P release from Fe oxides that are converted to Fe sulfides. This is supported by previous studies showing that the addition (or in-situ generation) of sulfide enhances P release from sediments (Chambers et al., 1995; Krom & Berner, 1981; Li et al., 2016; Roden & Edmonds, 1997).

Some discrepancies remain between directly measured sulfide-extractable P and difference-based estimates. It is possible that the sulfide solution reduces some crystalline Fe(III) oxides not extracted by HCl, although these would have lower  $\text{PO}_4^{3-}$  sorption capacity than amorphous Fe(III) oxides (Roden & Edmonds, 1997). The colloidal FeS in the supernatant may have some adsorbed  $\text{PO}_4^{3-}$ , but it is likely a negligible fraction of the total P content. Since variation is magnified for values obtained by difference, we concluded that the direct approach was suitable for quantifying sulfide-extractable P. The optimal procedure was determined to be a 24-

hour extraction on dry sediment samples, with the supernatant dried, re-dissolved with 1 N HCl, and filtered prior to colorimetric analysis.

Future work may further optimize this method by comparing results to other P extraction techniques, such as CDB and ascorbate. Sulfide-extracted P could also potentially be removed from solution by precipitating  $\text{Mg}(\text{OH})_2$  and dissolving the precipitate with HCl, as in the MAGIC technique (Huerta-Diaz et al., 2005; Karl & Tien, 1992). It would also be useful to apply the method to a wider variety of sediments from different systems.

This method has potentially important applications in systems where Fe-bound P is a dominant P pool and high sulfate reduction rates lead to enhanced  $\text{PO}_4^{3-}$  mobilization due to Fe sulfide formation. One such system is Chesapeake Bay, which is examined using this sulfide extraction method in the following chapter.



Table 1. Fe(III) oxide minerals that can be extracted by various reducing agents in order to quantify Fe-bound P.

Extractant	Fe(III) oxide minerals extracted		
	Amorphous FeOOH	Poorly crystalline FeOOH	Crystalline Fe oxides and oxyhydroxides
HCl	Yes	Yes	Partially
Citrate Dithionite Bicarbonate (CDB)	Yes	Yes	Yes
Ascorbate	Yes	Yes	No
Sulfide	Yes	Yes	Partially?

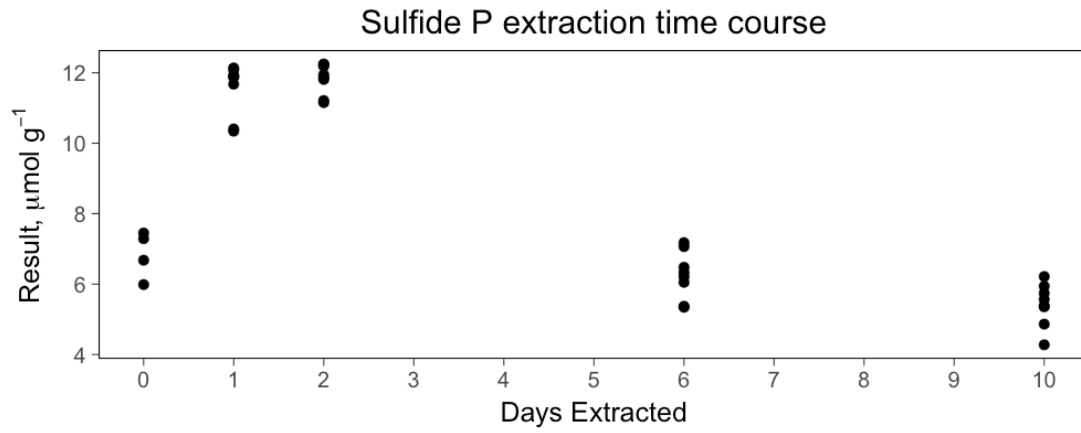


Figure 1. Phosphorus concentrations in sediment extracted using a 24 mM sulfide solution for varying lengths of time. All replicates are plotted for each time point.

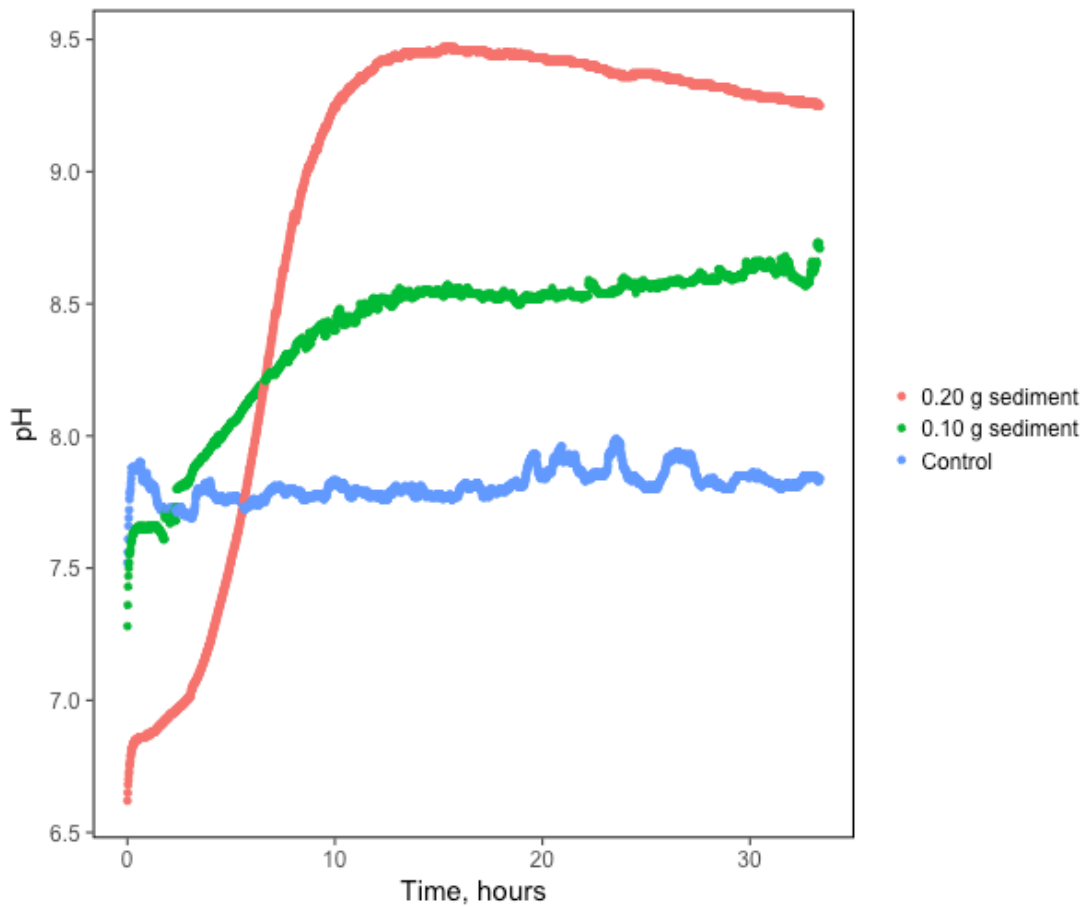


Figure 2. pH values of 10 ml of 24 mM sulfide solution added to different amounts of sediment (0.20 g, 0.10 g, and none) and stirred for multiple days. The control solution stayed close to neutral pH for the entire time, while the solutions mixed with sediment initially increased before plateauing at around 15 hours.

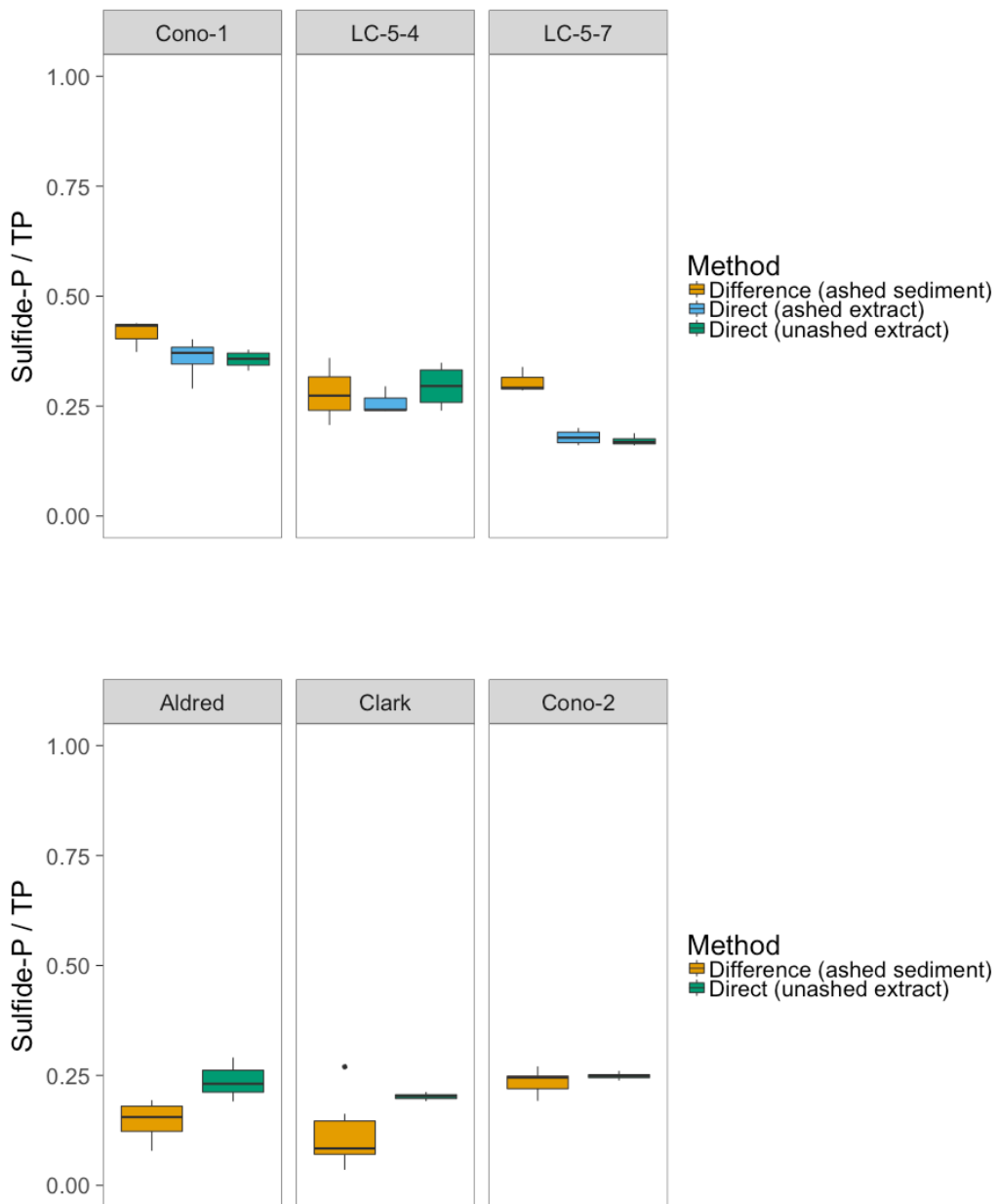


Figure 3. The proportion of total phosphorus (TP) extracted by sulfide using direct measurement (drying and redissolving the extract with HCl) and calculation by difference (HCl-extractable P in sulfide-treated vs. untreated sediment). With some of the replicates (top panel) the dried residue was ashed prior to dissolution in HCl. The samples used were homogenized surface sediment from the three Lower Susquehanna reservoirs – Aldred, Clarke, and Conowingo (Cono-1 and Cono-2) – as well as two discrete samples from a 3-meter-long Conowingo Reservoir core (LC-5-4 and LC-5-7). Four replicates were analyzed for each sample/method combination.

## Chapter 2: Potential bioavailability of scoured particulate P in the Chesapeake Bay

### Introduction

Eutrophication due to anthropogenic nutrient enrichment often is a major problem in estuarine and coastal systems. Large increases in phytoplankton production and biomass, as well as other effects such as anoxia and loss of benthic photosynthesis, occur with high inputs of nitrogen (N) and phosphorus (P) (Cloern, 2001; S. W. Nixon, 1995). While nitrogen can be removed as N<sub>2</sub> gas through denitrification, phosphorus gaseous losses are negligible so burial and transport out of the system are the main outputs (Boynton et al., 1995). Another key difference between N and P cycles is that most of the N load in rivers is transported in the dissolved form, whereas about 95% of the P load is in particulate form (Follmi, 1996). Not all of this particulate P will necessarily be released as dissolved, bioavailable phosphate. Primary production is usually limited by P in freshwater and N in coastal seawater (Howarth & Marino, 2006; S. Nixon et al., 1996; Schindler, 1974). Estuaries, where fresh and saline water mix, are often characterized by spatial and seasonal variation in N and P limitation. In the Chesapeake Bay, for example, phosphorus is typically limiting in the spring due to inflowing fresh water high in dissolved N, while N limitation dominates in summer when dissolved inorganic N is depleted and phosphate is released from anoxic sediments (Conley, 2000; Fisher et

al., 1992, 1999; Kemp et al., 2005). Thus, due to the dynamic nature of estuarine systems, both N and P must be considered in nutrient management strategies. While strategies often focus on N, P is not as well understood and is difficult to characterize.

Particulate inorganic P, which makes up nearly 60% of fluvial particulate P loads (Follmi, 1996), can be converted to bioavailable dissolved inorganic P through reducing processes enhanced by increased salinity (Caraco et al., 1990; Jordan et al., 2008). Phosphorus bound to iron oxyhydroxides (FeOOH), a significant fraction of the P load, can be released to solution when FeOOH is reduced in anoxic sediment layers (Fig. 4). Under aerobic freshwater conditions, reduced dissolved Fe(II) can diffuse upward to aerobic sediments and become re-oxidized to FeOOH, which has a high surface area and affinity for inorganic P. Phosphorus can also be immobilized under anaerobic freshwater conditions due to sorption to Fe(II) hydroxides and/or precipitation of ferrous-phosphate minerals such as vivianite (Roden & Edmonds, 1997). In contrast, in more sulfate-rich saltwater sediment, sulfides formed by sulfate reduction in anoxic sediment layers chemically reduce Fe(III) to iron sulfides; this immobilizes iron in the sediment and enhances the efflux of iron-bound phosphorus to the water column (Caraco et al., 1989, 1990; Jordan et al., 2008; Krom & Berner, 1980; Lehtoranta et al., 2009; Roden & Edmonds, 1997). Significant phosphate mobilization through this pathway requires high inputs of labile organic carbon, which decreases the redox potential and allows the dominance of sulfate reduction (Cornwell & Sampou, 1995; Lehtoranta et al., 2009). Even when the water column is re-oxidized, the burial of iron as iron sulfides minimizes resorption of phosphate to iron oxides (Lehtoranta et al., 2009; Roden & Edmonds, 1997).

Various extraction techniques have been used to differentiate pools of particulate P and assess the bioavailable fraction. Citrate-dithionite-bicarbonate (CDB) solutions are often used in sequential extractions to extract P bound to FeOOH (Ruttenberg, 1992). However, since this strong reducing agent dissolves crystalline iron oxides, it may overestimate the amount of Fe-bound P that is bioavailable (Anschutz et al., 1998; Jordan et al., 2008; Kostka & Luther III, 1994; Scicluna et al., 2015). Alternatively, more moderate reducing agents such as ascorbate can also be used to extract potentially mobile Fe-bound P (Anschutz et al., 1998; Kostka & Luther III, 1994; Scicluna et al., 2015). However, ascorbate only reduces amorphous FeOOH and may not include the potentially mobile P associated with crystalline Fe oxides (Anschutz et al., 1998; Kostka & Luther III, 1994). Because sequential extraction methods often have overlaps between the pools of P extracted in each step, the extraction categories are often operationally defined.

While nutrient loading contributes to eutrophication and harmful algal blooms in Chesapeake Bay, the role of suspended fluvial sediments has largely been relegated to concerns about light attenuation rather than particulate nutrient dynamics. The Susquehanna River is responsible for nearly half the freshwater input to the Bay as well as a large portion of the sediment and nutrient loads, although a significant portion of these loads are trapped in reservoirs behind three hydroelectric dams near the mouth of the river. The two upstream reservoirs have been in long-term equilibrium with respect to sediment storage since the mid-1900s, a few decades after their construction (Langland, 2009). Conowingo Reservoir, the farthest downstream, has reached about 92% of its storage capacity (Langland, 2015). Recent reports

suggest that outputs of sediment, phosphorus, and nitrogen from the reservoir have increased due to reservoir infilling and event-driven scour (Hirsch, 2012; Langland, 2015; Zhang et al., 2013, 2016). This increased flux of sediment and nutrients complicates the attainment of water quality goals established by the Total Maximum Daily Loads (TMDLs; Linker et al., 2016), which target watershed nitrogen, phosphorus, and sediment reductions from the Chesapeake Bay watershed. Although Conowingo Dam construction in 1928 resulted in a trapping efficiency of 70-75% of sediment inputs to the reservoir, current trapping efficiency has been reduced to 45-50% (Langland, 2015). Flow-normalized loads of suspended sediment and particulate nutrients have increased at Conowingo Dam since the 1990s, while inputs to the reservoir system have decreased (Zhang et al., 2013). This decrease in net deposition of sediment and nutrients has a greater effect on Chesapeake Bay P loading than N loading, since most P is particulate (Zhang et al., 2013, 2016). A large fraction of sediment transport across the dam occurs during high-flow events due to scouring of reservoir deposits (Langland, 2015). Although scoured sediment itself is not a significant threat in terms of long-term water clarity, nutrients associated with sediment are detrimental to water quality (Cercio & Noel, 2016).

The reactivity of particulate P transported from Conowingo Reservoir to the Chesapeake Bay during a scour event is strongly dependent on the salinity of the Bay areas where sediments are deposited. In subestuaries of the Chesapeake Bay, mobilization of Fe-bound P is enhanced with increasing salinity due to the conversion of Fe oxides to Fe sulfides (Hartzell et al., 2010, 2017; Jordan et al., 2008). In the Bay mainstem, soluble reactive P (SRP) efflux from sediment is most pronounced in the



mesohaline mid Bay relative to the upper and lower Bay (Cowan & Boynton, 1996). Iron sulfide formation and burial is highest in the mid Bay due to the greater availability of sulfate and organic matter and the fine-grained nature of the deposits (Cornwell & Sampou, 1995; Cowan & Boynton, 1996; Marvin-DiPasquale et al., 2003; Marvin-DiPasquale & Capone, 1998).

Although storm scour is likely to transport increased loads of particulate P from the Lower Susquehanna reservoir system to the Chesapeake Bay, it is unclear what fraction of this scoured P is likely to be reactive. The objective of this study is to assess the potential bioavailability of P in reservoir sediments based on both the chemical nature of the particulate P and the areas in which it is deposited. First, we examine benthic SRP flux along the Chesapeake Bay salinity gradient and the reservoir system in order to evaluate differences in P reactivity depending on environmental conditions at the site of deposition. Then, we characterize reservoir sediments using extractions of P and Fe, including P extraction through the addition of a sulfide solution as described in Chapter 1. Results are combined with recent studies of Bay sediment transport and deposition to estimate the water quality impact of a large storm event in terms of scoured P.

## **Materials and Methods**

### **Study Site**

The Chesapeake Bay is a 300 km long coastal plain estuary with an average depth of ~7 m, and depths exceeding 25 m in the central channel in the mid

(mesohaline) portion of the Bay. An average of  $2,300 \text{ m}^3 \text{ s}^{-1}$  of freshwater flows into the Bay from its  $167,000 \text{ km}^2$  watershed, with the Susquehanna River at the head of the Bay supplying over half of the flow (Schubel & Pritchard, 1986). The Susquehanna contributes 25% of the P loads and 27% of the suspended sediment loads to the Bay on an average annual basis (Linker et al., 2016). Water discharge from the Susquehanna River to the Chesapeake is controlled by the Conowingo Dam, 14 km upstream of the mouth of the river, which is the last of three dams forming the Lower Susquehanna Reservoir System (Fig. 5). Above Conowingo Reservoir is Lake Aldred (formed by Holtwood Dam) and Lake Clarke (formed by Safe Harbor Dam). The reservoirs total over 50 km in length and up to about 2 km in width. About half of the sediment load from the watershed is trapped in the reservoir system (Langland, 2015). Scour events periodically erode material from the reservoirs and transport it to the Bay; this typically occurs at streamflows above  $400,000 \text{ ft}^3/\text{s}$  ( $11,320 \text{ m}^3/\text{s}$ ), which has happened 11 times since 1972 (Langland, 2015).

### **Reservoir Sampling**

Three-meter-long cores were collected in August 2015 at five sites along the length of the Conowingo Reservoir (Table 2; Fig. 5). Cores were collected in 61 cm long thin walled Shelby tubes using a piston tub sampler (ASTM 1587) deployed from a barge. From the 5 Shelby tubes, eight 10-cm long sections were taken from each core, homogenized, and dried for solid phase analyses.

In addition, short cores were collected on five occasions during 2015 and 2016 at a total of 13 stations throughout the Conowingo Reservoir. Three short cores were also collected in April 2016 from each of the two upper reservoirs (Lake Clarke

and Lake Aldred) (Table 1). Intact surface sediment was collected using a box corer or pole corer, then subcored with 7-cm inner diameter acrylic cores, with ~15 cm of sediment and ~15 cm of overlying water. The cores were incubated for sediment-water exchange measurements, after which the top 1 cm of sediment was dried for solid phase analysis.

### **Sediment-Water Exchange Methods**

Short cores were transported to the Horn Point Laboratory, submerged in water from the reservoir, and bubbled overnight in the dark at field temperatures. Sediment-water SRP exchange was measured using intact 7 cm i.d. cores with a magnetic stirring mechanism (Owens and Cornwell 2016); samples were collected over 4 time points. Colorimetric analysis of SRP followed Parsons et al. (1984) and fluxes were estimated from regression of SRP concentrations over time.

### **Solid Phase Analyses**

Total and inorganic phosphorus were measured using a 1 N HCl extraction of ashed and unashed sediment, respectively (Aspila et al., 1976). Phosphorus concentrations in the extract were determined by the molybdate blue technique using a UV/VIS spectrophotometer for colorimetric analysis (Parsons et al., 1984). Organic P was estimated as the difference between total and inorganic P. Iron was determined by analysis of the unashed 1 N HCl extract using flame atomic absorption spectroscopy (Gibbs, 1979; Leventhal & Taylor, 1990).

Phosphorus was also extracted from sediment using a sulfide solution, after the technique described in Chapter 1. Briefly, a 24 mM H<sub>2</sub>S/HS<sup>-</sup> solution was added

to dry sediment samples in centrifuge tubes, which were then shaken for 24 hours. The resulting extract was dried and the residue was re-dissolved with 1 N HCl, then analyzed by colorimetry using the molybdate blue technique.

### **Benthic P Flux Data Synthesis**

Analysis of patterns of benthic P flux along the salinity gradient of the Chesapeake Bay utilized a sediment-water exchange database maintained at the Chesapeake Biological Laboratory (Boynton et al., 2017). Data were collected at 82 stations along the mainstem Bay from 1980 to 1998 using core flux incubations (Cowan & Boynton, 1996). For this study, we utilized summer (June-August) SRP fluxes from these stations, totaling 227 measurements. These data were augmented by sediment flux measurements made in summer 2014 and 2015 in the Susquehanna Flats area of the upper Bay (Gurbisz et al., 2017), and in the Conowingo Reservoir. The locations of all of the sediment-water flux sites are shown in Fig. 6.

In this study, we examined SRP flux rates in relation to latitude as well as various water quality parameters. To assess spatial variation, the stations were separated by latitude into four regions: the Conowingo Reservoir, the Upper Bay, the Mid Bay, and the Lower Bay. The boundaries between the three Bay regions were set at 39 N (near the Bay Bridge) and 38 N (at the mouth of the Potomac estuary). Two-sample t-tests were used to evaluate differences between SRP flux rates in each region. Relationships between SRP flux and different water quality parameters were tested using linear regression.

## **Results**

### **Benthic P Flux Along Salinity Gradient**

Observed summer SRP effluxes in the Bay mainstem were highest in the Mid Bay region, with a mean  $\pm$  1 standard deviation of  $29.1 \pm 25 \mu\text{mol m}^{-2} \text{h}^{-1}$  (Fig. 7). Fluxes of SRP in the Upper Bay had occasional high outliers, but overall were significantly lower than in the Mid Bay ( $p < 0.01$ ), averaging  $9.69 \pm 17 \mu\text{mol m}^{-2} \text{h}^{-1}$ . Data from the Lower Bay were limited, but SRP effluxes did not range as high as in the Mid Bay, the highest measurement being  $38.1 \mu\text{mol m}^{-2} \text{h}^{-1}$ . Fluxes of SRP were lowest in the Conowingo Reservoir, with a mean of  $-0.79 \pm 5 \mu\text{mol m}^{-2} \text{h}^{-1}$ . The upper two reservoirs were not sampled for sediment-water exchange during the summer, but April measurements yielded no detectable SRP efflux.

Significant ( $p < 0.01$ ) relationships were observed between SRP flux and bottom water salinity, station depth, and bottom water dissolved oxygen (Fig. 8). Given the vertical stratification in the bay, some of these relationships are likely driven by the low oxygen concentrations of deeper, more saline water masses (Kemp et al., 2005). Indeed, oxygen was the strongest predictor of SRP efflux.

### **Reservoir Sediment Characterization**

Inorganic P made up most of the particulate P in all of 5 3-meter-long vertical profiles in the Conowingo Reservoir, especially at the upper two stations (Fig. 9). Inorganic P in the long cores ranged from  $0.072$  to  $1.0 \text{ mg g}^{-1}$ , and total P ranged from  $0.13$  to  $1.4 \text{ mg g}^{-1}$ . Inorganic P varied with depth within each core and was generally higher at the stations closest to the dam (8, 9, and 13). Inorganic P and Fe were

positively correlated ( $p < 0.05$ ) in all of the profiles except station 5 (Fig. 10A). The overall higher P concentrations and more significant correlations with iron closer to the dam were likely related to finer grain size; average mud content increases towards the dam (Palinkas & Russ, 2016).

Sulfide-extractable P did not vary with depth as much as inorganic P. Sulfide-P in the long cores ranged from about 0.01 to 0.37 mg g<sup>-1</sup>, or 5 to 33% of total P (median 22%). As with inorganic P, sulfide-P concentrations were higher closer to the dam (stations 8, 9, and 13) compared to stations 2 and 5 (Fig. 9). Sulfide-P was not correlated with Fe in the long core profiles (Fig. 10B).

In surface sediment collected over multiple seasons in the three reservoirs, inorganic P again made up most of total P (Fig. 11). Inorganic P ranged from 0.22 to 0.90 mg g<sup>-1</sup> and total P ranged from 0.28 to 1.3 mg g<sup>-1</sup>. Inorganic P, organic P and Fe increased in concentration closer to each of the three dams. Sulfide-extractable P concentrations increased slightly as well (Fig. 12). In the surface sediment, sulfide-P ranged from 0.10 to 0.47 and made up 13 to 46% of total P (median 27%). Both inorganic P and sulfide-P in the surface sediment were correlated with Fe ( $p < 0.01$ ) (Fig. 13).

The seasonal variability of inorganic P was low at the lower end of the Conowingo Reservoir, and higher at the stations in the upper reservoir (Fig. 11C). Different stations showed different seasonal patterns, likely reflecting spatial heterogeneity of sediment erosion and deposition. Iron was seasonally variable throughout the reservoir, tending to be highest in late spring and summer (Fig. 11D). The variability of iron concentrations drove the inorganic P to Fe molar ratio to be

lowest during late spring and summer (May and July) and highest from fall through early spring (September, December, and April) (Fig. 14).

## **Discussion**

### **Benthic P Flux Along Salinity Gradient**

Summer SRP fluxes along the salinity gradient from the Lower Susquehanna reservoirs through the Chesapeake Bay mainstem were variable but generally highest in the Mid Bay, indicating that P efflux from scoured sediment would most likely occur if it were deposited in this mesohaline region. Previous studies of sediment-water exchange in the Bay have also reported that SRP fluxes are highest in the mid-Bay relative to the upper and lower Bay, and are enhanced by high temperatures and hypoxia (Boynton et al., 1991; Cowan & Boynton, 1996). Salinity transition zones in estuaries are likely to be areas with high levels of P mobilization because the availability of sulfate and organic matter allows enhanced sulfate reduction and iron sulfide formation (Capone & Kiene, 1988; Cornwell & Sampou, 1995; Kemp & Boynton, 1984). Sulfate reduction is not limited by sulfate concentrations at higher salinities, but sulfide re-oxidation by bioturbation in the Lower Bay has been shown to limit iron sulfide burial efficiency (Cornwell & Sampou, 1995). Algal production and net deposition of organic matter is highest in the mesohaline zone of the Chesapeake (Kemp and Boynton 1984, Cowan and Boynton 1996, O'Keefe 2007) while refractory terrestrial organic material, combined with low sulfate concentrations, limits sulfate reduction in the oligohaline zone (Marvin-DiPasquale et

al., 2003; Marvin-DiPasquale & Capone, 1998). In general it is observed that Fe-bound P decreases with increasing salinity (Hartzell et al., 2010, 2017; Jordan et al., 2008). The observed high P fluxes in the mid-Bay, and the positive correlation between salinity and P efflux, are consistent with particulate P conversion to bioavailable SRP in the mid-Bay due to iron sulfide formation. It is clear that this process is enhanced by hypoxia and anoxia, since SRP flux decreased with increasing bottom water dissolved oxygen, and the highest fluxes were found in deeper water where seasonal stratification and oxygen depletion is more likely (Kemp et al., 2005).

### **Reservoir Sediment Characterization**

Various extraction methods have been used to differentiate iron-associated P from other P forms, but it is difficult to determine what fraction of this iron is reducible and likely to release dissolved phosphate. In sequential extraction techniques such as SEDEX, a citrate-dithionite-bicarbonate solution is used to extract P bound to Fe oxyhydroxides (Ruttenberg, 1992). A problem with using this strong reducing agent is that it may extract P from the more crystalline forms of FeOOH that are not likely to be reduced. Therefore, P bioavailability may be poorly predicted or over-predicted by these methods (Jordan et al. 2008, Kostka and Luther III 1994, Scicluna et al. 2015). Alternatively, other studies have used the more moderate reducing agent ascorbate (Kostka and Luther III 1994, Scicluna et al 2015), but this reduces only amorphous FeOOH and may underestimate the amount of P that could be mobilized. Phosphorus release from iron oxides in the Chesapeake Bay is predominantly caused by iron sulfide formation (Jordan et al., 2008; Roden & Edmonds, 1997); therefore an extraction using a sulfide solution should more directly



represent the fraction of iron-bound P that is potentially bioavailable in the Bay. We found that up to ~35% of total HCl-extractable P could be extracted using a 24 mmol L<sup>-1</sup> sulfide solution, which is a significantly higher sulfide concentration than would be found in the mid-Bay (Roden & Tuttle, 1992). Li et al. (2016) also found that P could be released from sediment through the addition of a sulfide solution, with P concentrations in the overlying water increasing with increasing concentrations of added sulfide.

Total particulate P concentrations in the reservoir sediment ranged from about 0.13 to 1.4 mg g<sup>-1</sup>, and generally over two thirds of it was inorganic. These concentrations were similar to those found in tidal freshwater deposits in various Chesapeake Bay subestuaries (Hartzell et al., 2010, 2017; Jordan et al., 2008). Sulfide-extractable P generally made up ~10-30% of total P. The amount of inorganic P not extracted by the sulfide solution averaged about 0.4 mg g<sup>-1</sup>, which is similar to IP concentrations measured in sediment at 15 cm depth in the mid-Bay (Cornwell, unpublished data). This suggests that sulfide-extractable P is a realistic representation of the amount of P that is released from sediment under sulfidic conditions in the Bay.

The positive correlation between inorganic P and iron in Conowingo Reservoir sediments was likely a reflection of the iron-bound P fraction as well as grain size differences, since both iron and phosphorus are preferentially associated with smaller particles. Iron oxides are strongly associated with surfaces and increase with increasing relative surface area (Pacini & Gächter, 1999; Poulton, 2005). Concentrations of various fractions of particulate P have been shown to increase with decreasing grain size (Pacini & Gächter, 1999; Stone & English, 1993; Yao et al.,

2016). Small particles provide more surface area not only due to their size, but also due to the laminated structure of clay minerals, which provides many internal surfaces for interactions with iron oxides and phosphorus (Pacini & Gächter, 1999; Poulton, 2005). Sulfide-extractable P was also moderately well correlated with HCl-Fe in surface sediment from the three reservoirs. Interestingly, however, sulfide-P generally did not correlate with Fe in the deep cores from Conowingo Pond, and was more constant with depth than TP and IP. This likely points to the presence of less reactive forms of iron-associated P that cannot be released through iron sulfide formation.

The increase in inorganic P and sulfide-P with distance along each reservoir is also likely due to the prevalence of finer particles in the downstream areas of the reservoirs (Palinkas & Russ, 2016). In addition, the higher temporal variability of inorganic P at the upper end of the Conowingo Reservoir may be due to periodic erosion and deposition of sediment in these shallow environments.

### **Potential Impact of a Scour Event**

Storm events can be responsible for a large fraction of the total sediment input from the Susquehanna River to the Chesapeake Bay (Langland, 2015). As the reservoirs have reached capacity, sediment fluxes also include reservoir scour during high flows. A discharge of 400,000 ft<sup>3</sup>/s (11,320 m<sup>3</sup>/s), which has a recurrence interval of 4.8 years, is thought to be the threshold above which sediments can be scoured from behind the Conowingo Dam, although some scour may occur at lower flows as well (Langland, 2015; Linker et al., 2016). Tropical Storm Lee in September 2011 was responsible for the second highest discharge ever recorded at Conowingo,

peaking at  $\sim 22,000 \text{ m}^3/\text{s}$ . An estimated 6.7 million tons of sediment were transported across the Conowingo Dam during T.S. Lee (Palinkas et al., 2014), of which  $\sim 3.5$  million tons were scoured from the Lower Susquehanna reservoirs (Langland, 2015). The percent of the sediment load that is from scour increases with streamflow and also varies based on characteristics (timing, magnitude, duration) of different events (Cercio & Noel, 2016; Langland, 2015). For instance, a January 1996 flood event had a similar daily-mean streamflow as T.S. Lee, but over 80% of the sediment load was scoured material, likely because it was partly a snowmelt event that conveyed lower sediment loads from the watershed (Cercio & Noel, 2016).

Assuming a total particulate P concentration of  $1 \text{ mg g}^{-1}$  based on reservoir core data, and a scoured sediment load of 3.5 million tons, an event similar to T.S. Lee would deposit 3,500 tons of particulate P in the Bay. With sulfide-extractable P comprising up to about 35% of total P, this would mean up to 1,225 tons of scoured P could be converted to bioavailable SRP through Fe sulfide formation. This input of potentially bioavailable P from an extreme scour event is about a third of the average annual benthic P flux in the Mid Bay, which totals about 3,580 tons (Boynton et al., 1995). As previous studies and historical flux data have shown, P mobilization is more likely to occur in the Mid Bay than the Upper Bay due to enhanced sulfate reduction. After T.S. Lee, flood deposits of at least 1 cm thickness reached as far south as  $38.7^\circ \text{ N}$ , near station R-64, where the highest benthic SRP fluxes are generally found. However, most scoured sediment is deposited in the Upper Bay, where it is more likely to be buried in the solid phase. For significant P efflux from scoured and redeposited sediment to occur, the material must be deposited in the Mid

Bay, and also must be subject to hypoxic or anoxic conditions, which depends on the timing of the scour event.

### **Summary and Conclusions**

Findings from this study suggested that although event-driven reservoir scour is increasingly likely to cause greater P loading to Chesapeake Bay, not all of this scoured P is likely to be bioavailable. Future work may further constrain the water quality impact of particulate P transported from the reservoir system during a storm. The analysis of P pools in reservoir sediment could be combined with studies of sediment deposition from T.S. Lee for a more thorough spatial analysis of P loading and bioavailability. In addition, these extraction methods could be applied to suspended sediment or size-fractionated samples to control for grain size; this would be useful since finer particles tend to have higher P content and are also more likely to be scoured and transported to the Bay.

The P extracted from reservoir sediments using a sulfide solution is likely a conservative estimate of potentially mobile Fe-bound P, since most scoured sediment would be deposited in the Upper Bay where Fe sulfide formation is limited. Significant P efflux from scoured sediment would also require bottom water oxygen depletion, meaning only a late spring or summer event would be likely to result in P mobilization. Flux data analysis and sediment characterizations indicate that the majority of scoured particulate P transported to the Chesapeake Bay during a storm event is unlikely to be bioavailable.

Table 2. Locations and sampling dates for short cores collected for sediment-water exchange measurements, and long cores collected August 2015 in the Lower Susquehanna River reservoir system.

Site ID	Lat N	Long W	May 19 2015	July 22 2015	Sept 22 2015	Dec 3 2015	April 13 2016	April 27 2016	Long Cores
Conowingo Reservoir									
1	39.77340	76.26538	X						
2	39.77679	76.25802	X	X	X	X	X		X
3	39.76044	76.24958	X	X	X		X		
4	39.75986	76.24252	X						
5	39.74719	76.24574	X	X	X	X	X		X
6	39.72934	76.23305	X						
7	39.72224	76.23582	X	X	X		X		
8	39.69210	76.21880	X	X	X	X	X		X
9	39.69676	76.21145	X	X	X	X	X		X
10	39.66166	76.18556	X						
11	39.66305	76.18528	X	X	X	X	X		
12	39.66582	76.18250	X						
13	39.66916	76.18111	X	X	X	X	X		X
Lake Clarke									
LC1	39.92560	76.41412						X	
LC2	39.93180	76.43603						X	
LC3	39.96837	76.47240						X	
Lake Aldred									
LA4	39.84358	76.35012						X	
LA5	39.85738	76.35657						X	
LA6	39.87347	76.37805						X	

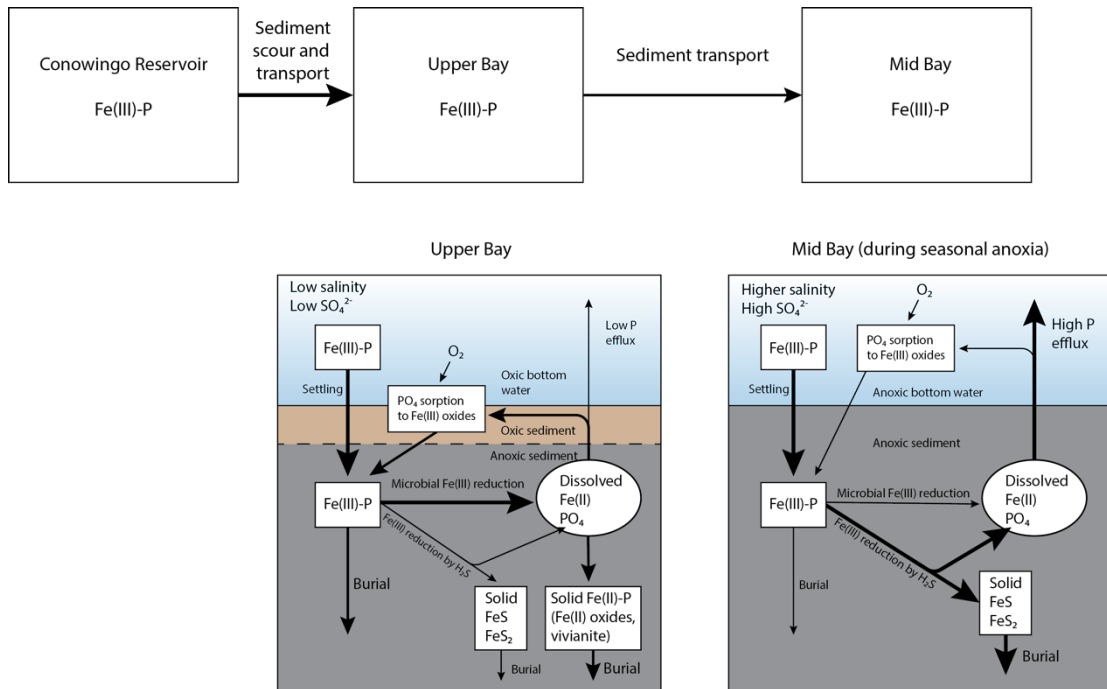


Figure 4. Sedimentary iron (Fe), phosphorus (P), and sulfur (S) cycling in the Upper vs. Mid Chesapeake Bay. In the Upper Bay and similar oligohaline systems, iron reduction is the dominant anaerobic metabolic pathway, and P efflux is limited due to sorption to Fe oxides and precipitation of Fe(II) minerals. In contrast, in higher salinity regions such as the Mid Bay where sulfate reduction dominates, Fe is reduced by sulfides to Fe sulfides, burying Fe and allowing greater P efflux.

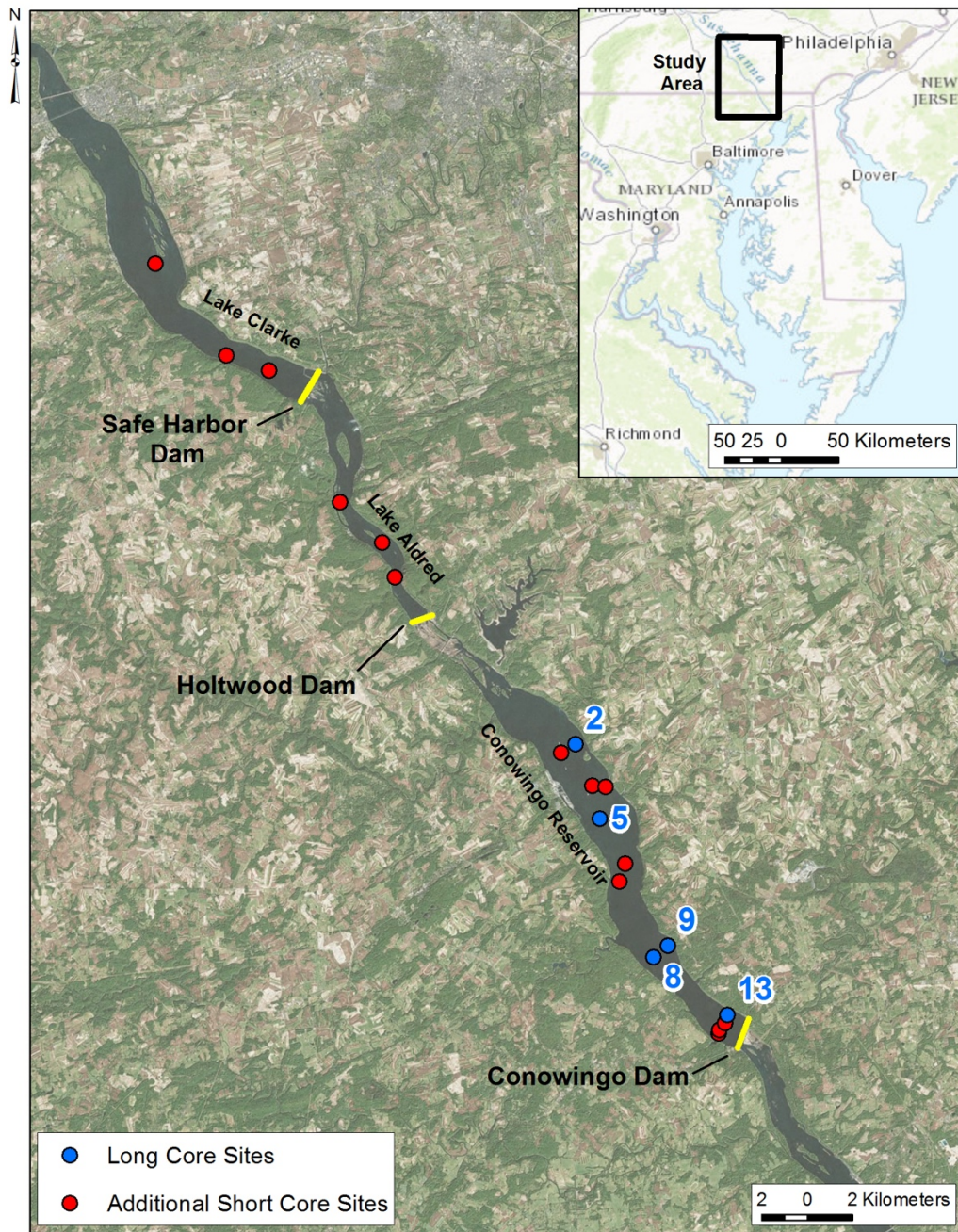


Figure 5. Sampling locations in Conowingo Reservoir, Lake Clarke, and Lake Aldred. Short cores were collected at all stations, and long cores were collected at stations marked in blue.

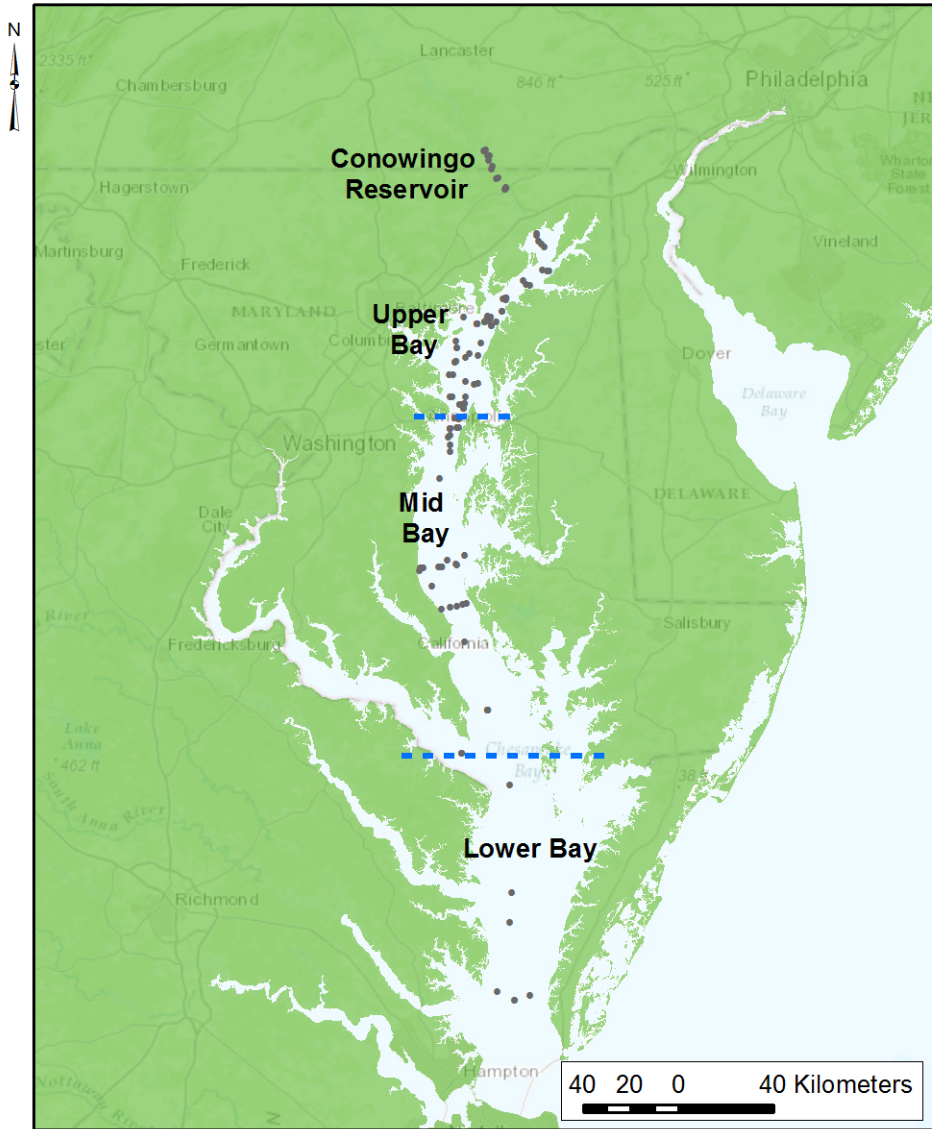


Figure 6. Site locations for sediment-water exchange measurements.



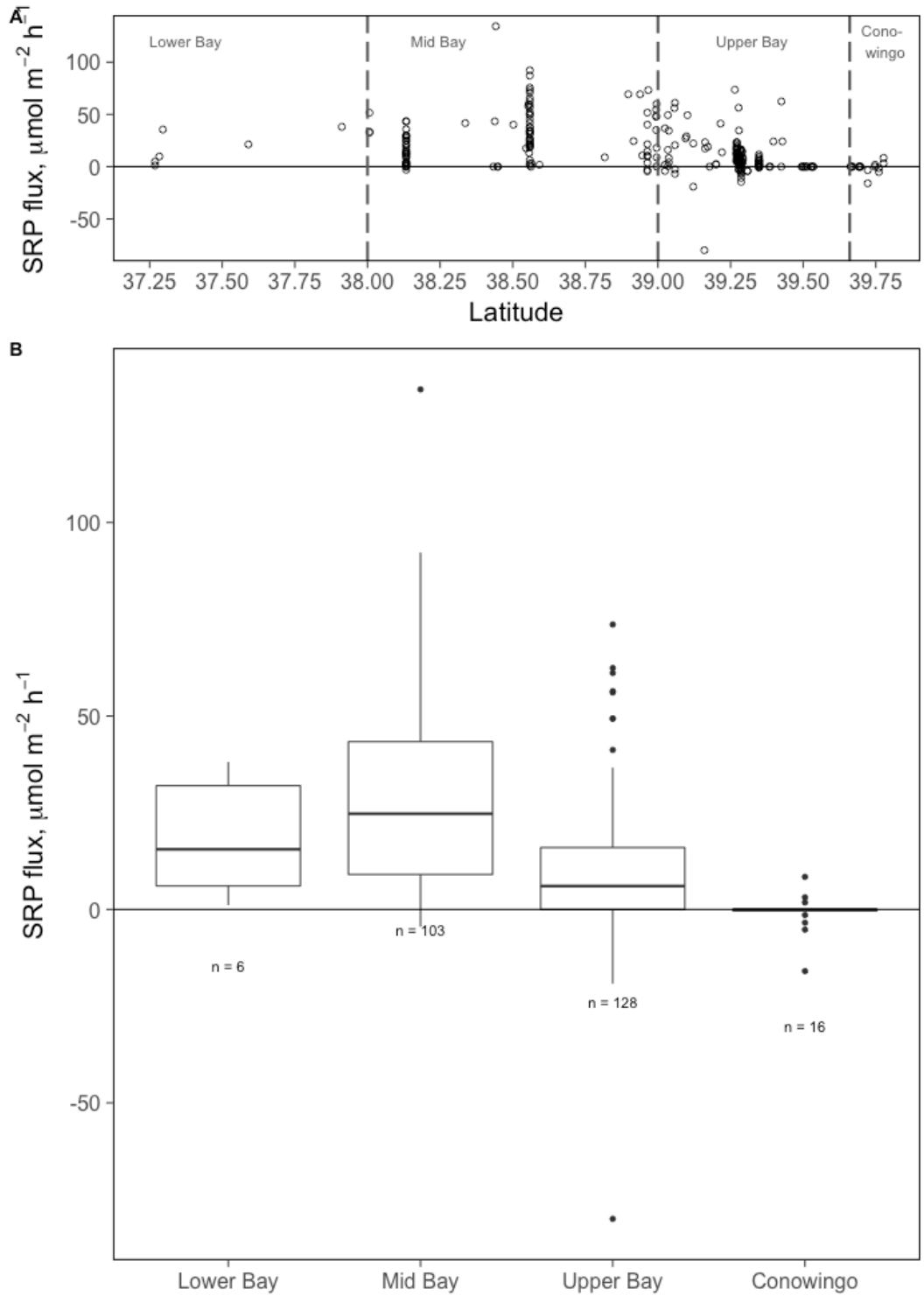


Figure 7. Summer SRP fluxes along the Chesapeake Bay salinity gradient and Conowingo Reservoir (A) and box plots of the same flux data for each region (B).

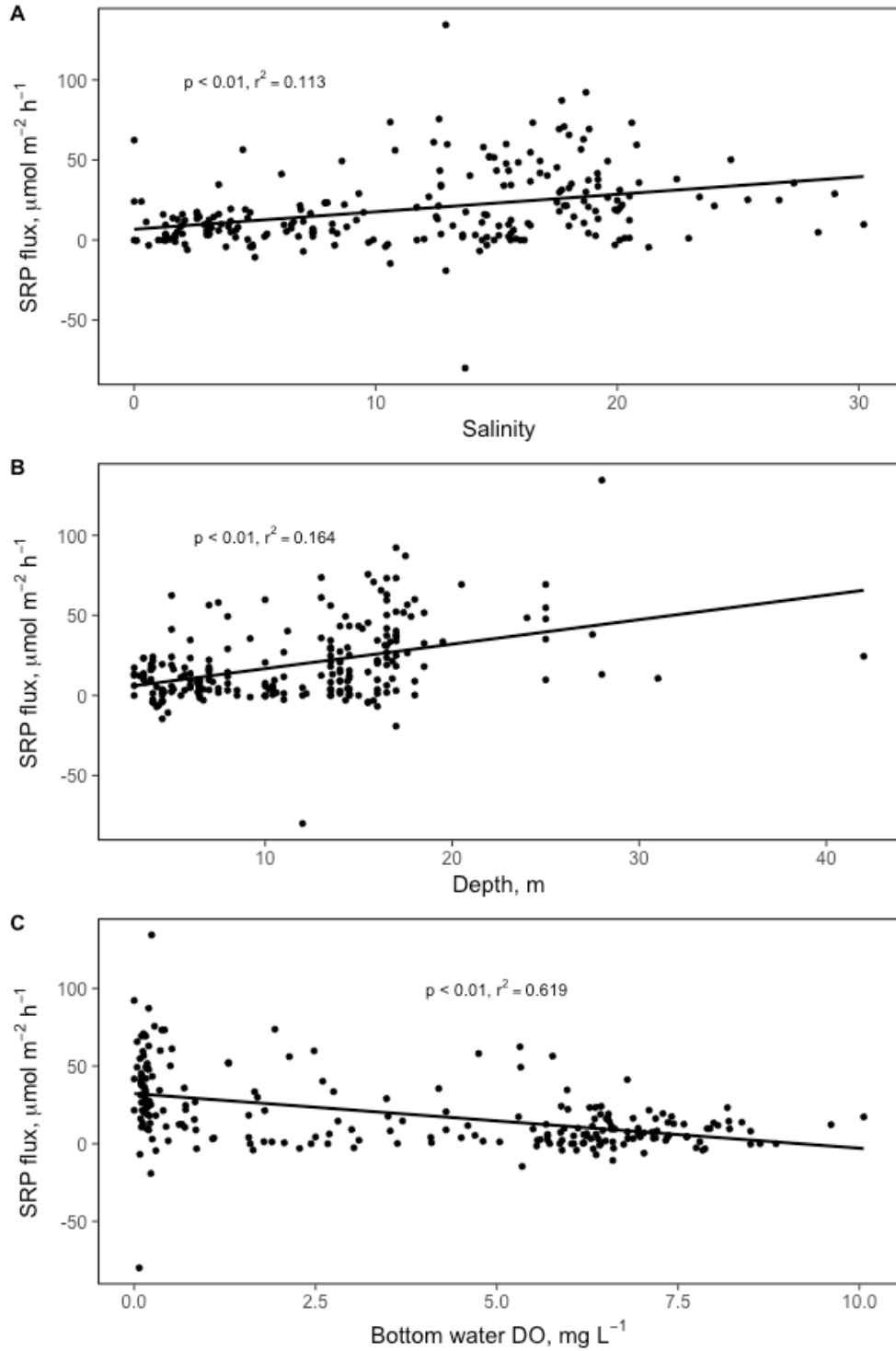


Figure 8. Relationships between summer SRP flux in the Bay mainstem and different water quality parameters: salinity, station depth, and bottom water dissolved oxygen (DO).

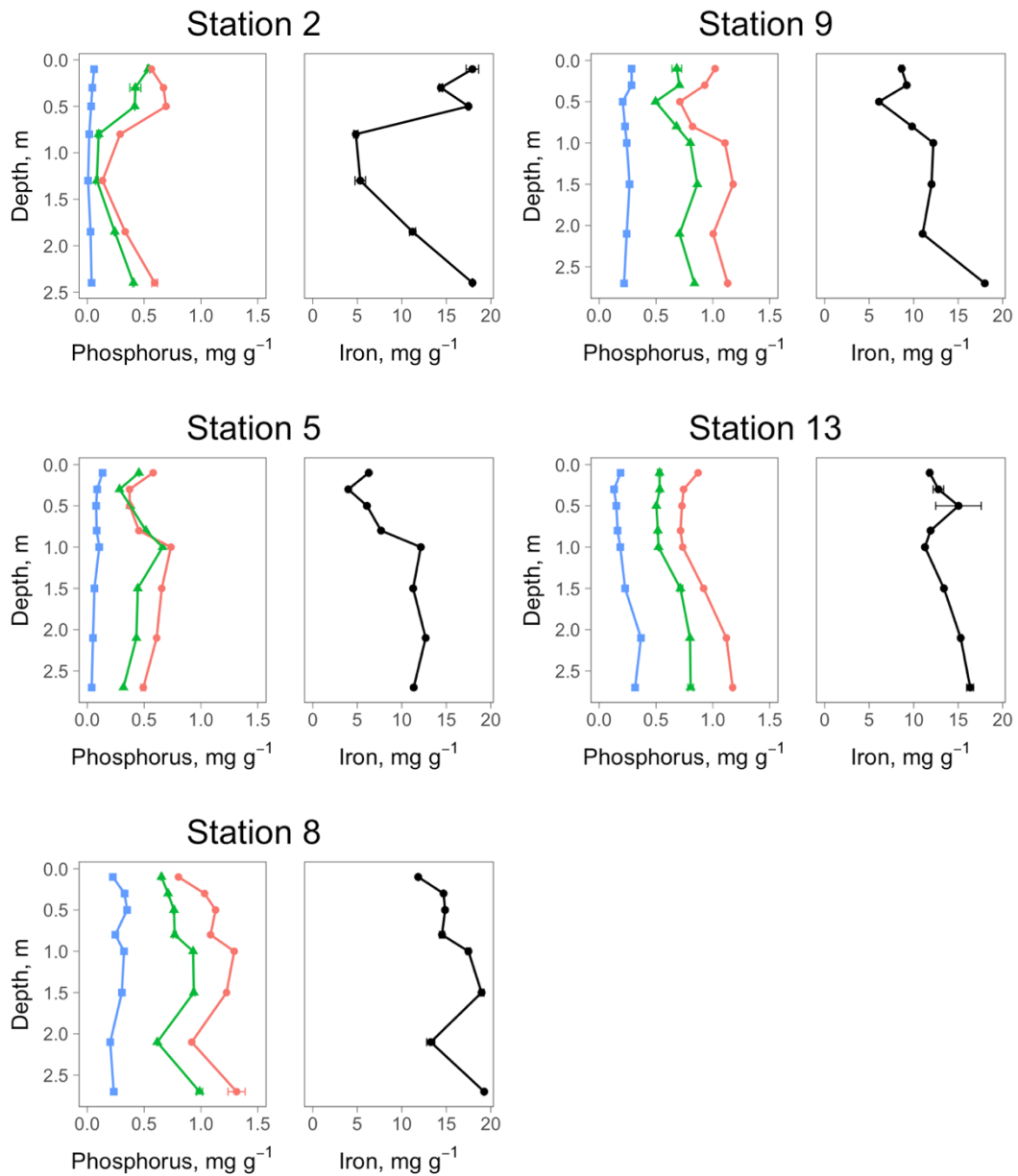


Figure 9. Concentration depth profiles of different phosphorus forms and iron in Conowingo Reservoir sediments. Red = total P, green = inorganic P, and blue = sulfide-extractable P. For samples with replicates, error bars denote the range of values measured. Sample locations are shown in Figure 5.

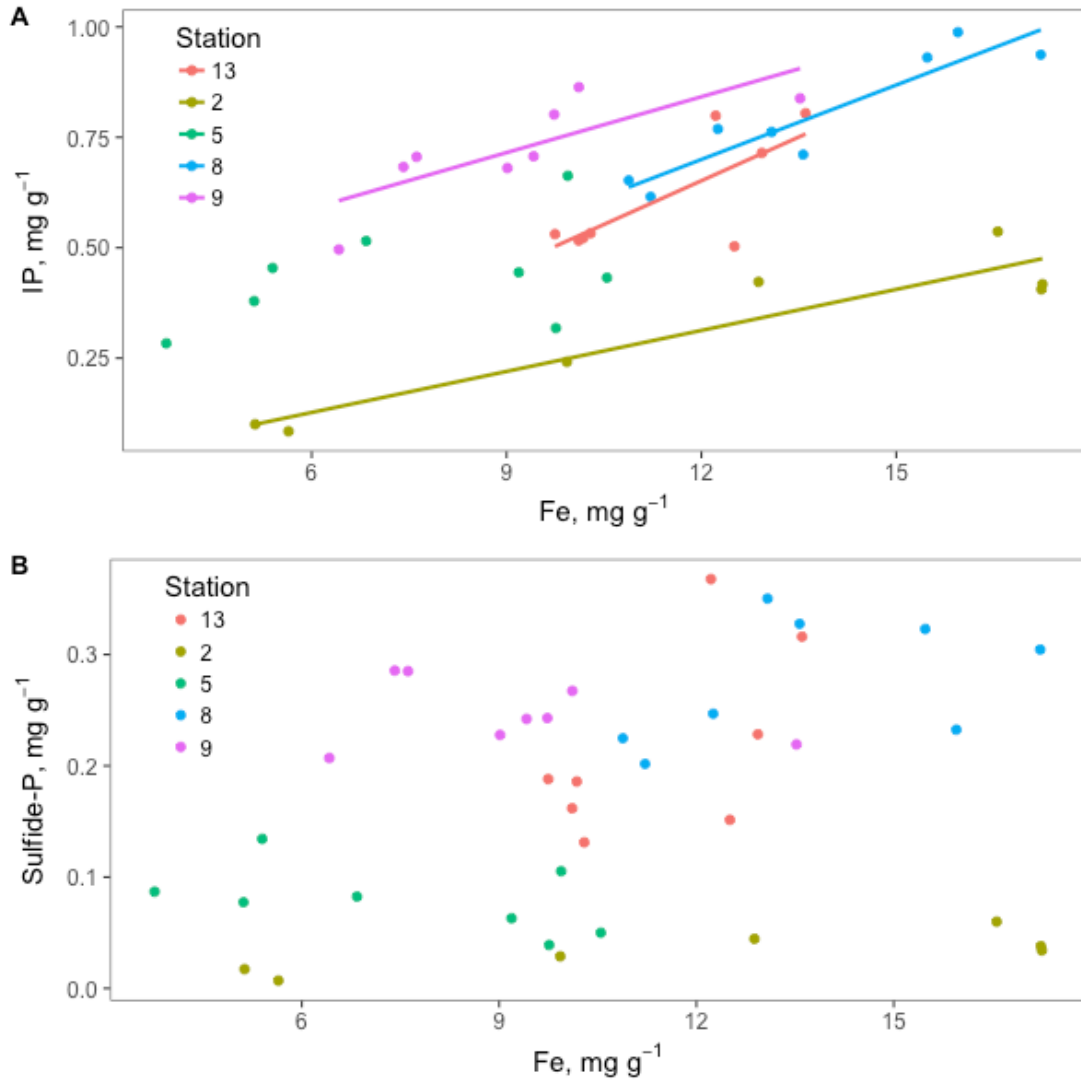


Figure 10. Concentrations of iron (Fe) versus inorganic phosphorus (IP) (A) and sulfide-extractable phosphorus (sulfide-P) (B) in Conowingo Reservoir long cores. Trendlines are included for cores with significant relationships between Fe and P ( $p < 0.05$ ).

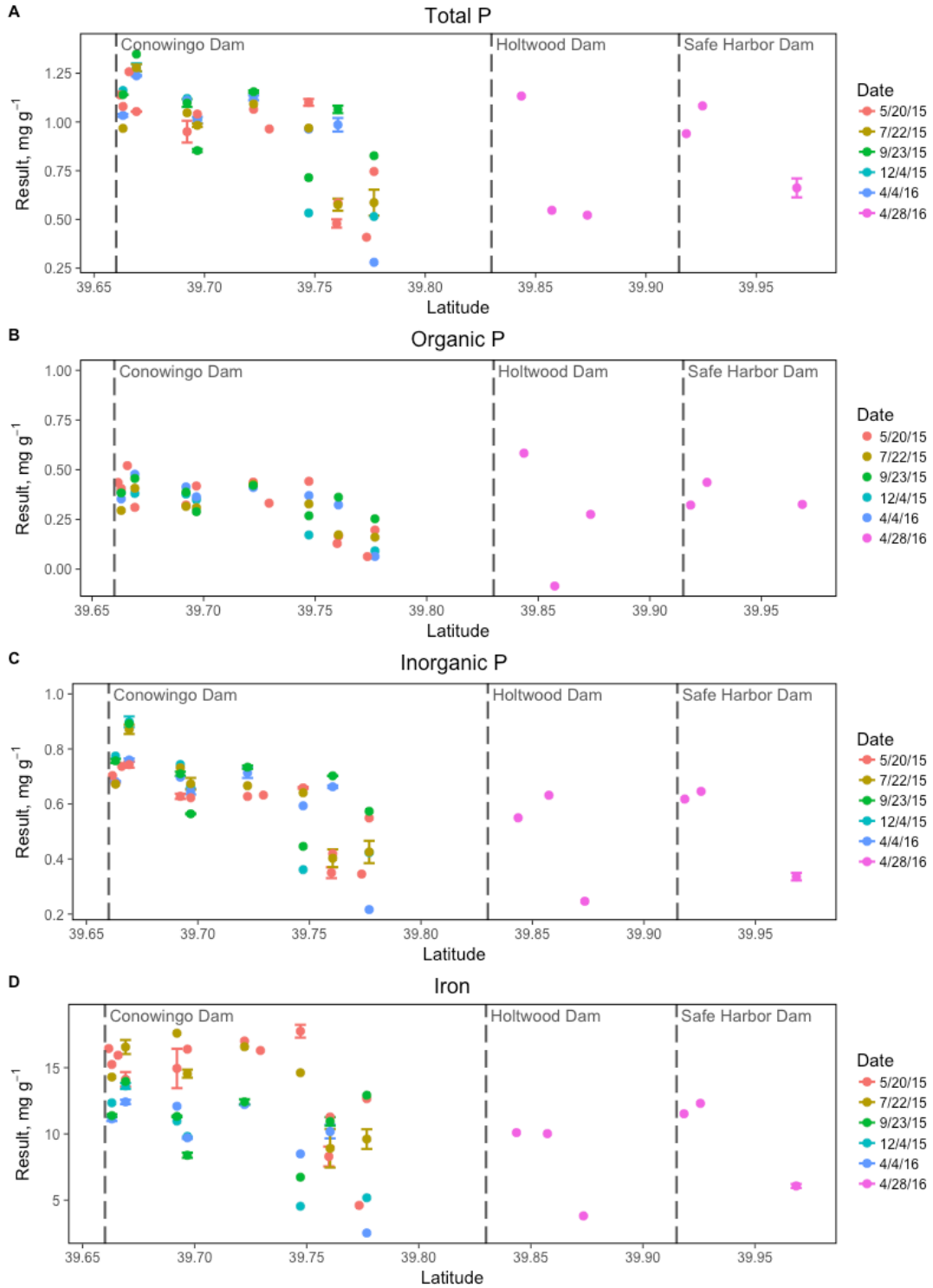


Figure 11. Surface sediment concentrations of different P forms and iron during different seasons along the length of the Lower Susquehanna Reservoir System. For samples with replicates, error bars denote the range of values measured. Sample locations are shown in Figure 5.



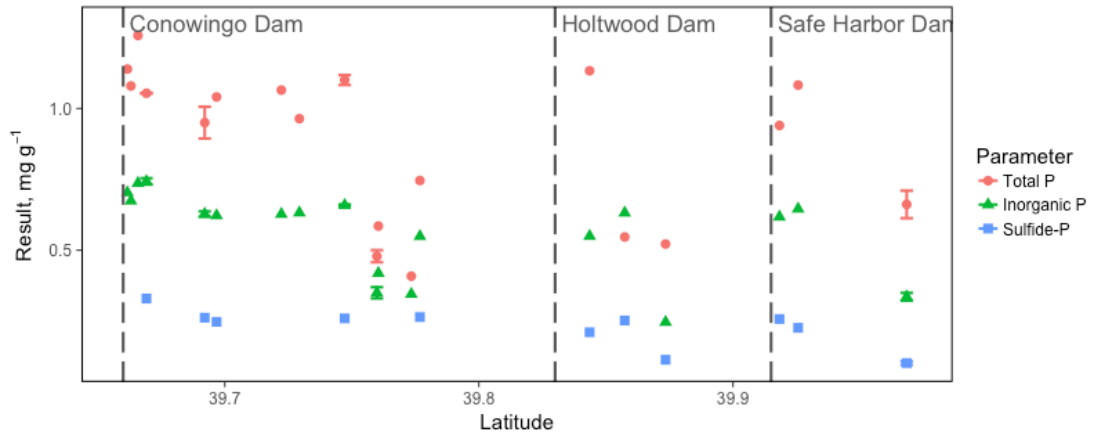


Figure 12. Spring surface sediment concentrations of total, inorganic, and sulfide-extractable P along the length of the Lower Susquehanna Reservoir System. For samples with replicates, error bars denote the range of values measured. Sample locations are shown in Figure 5.

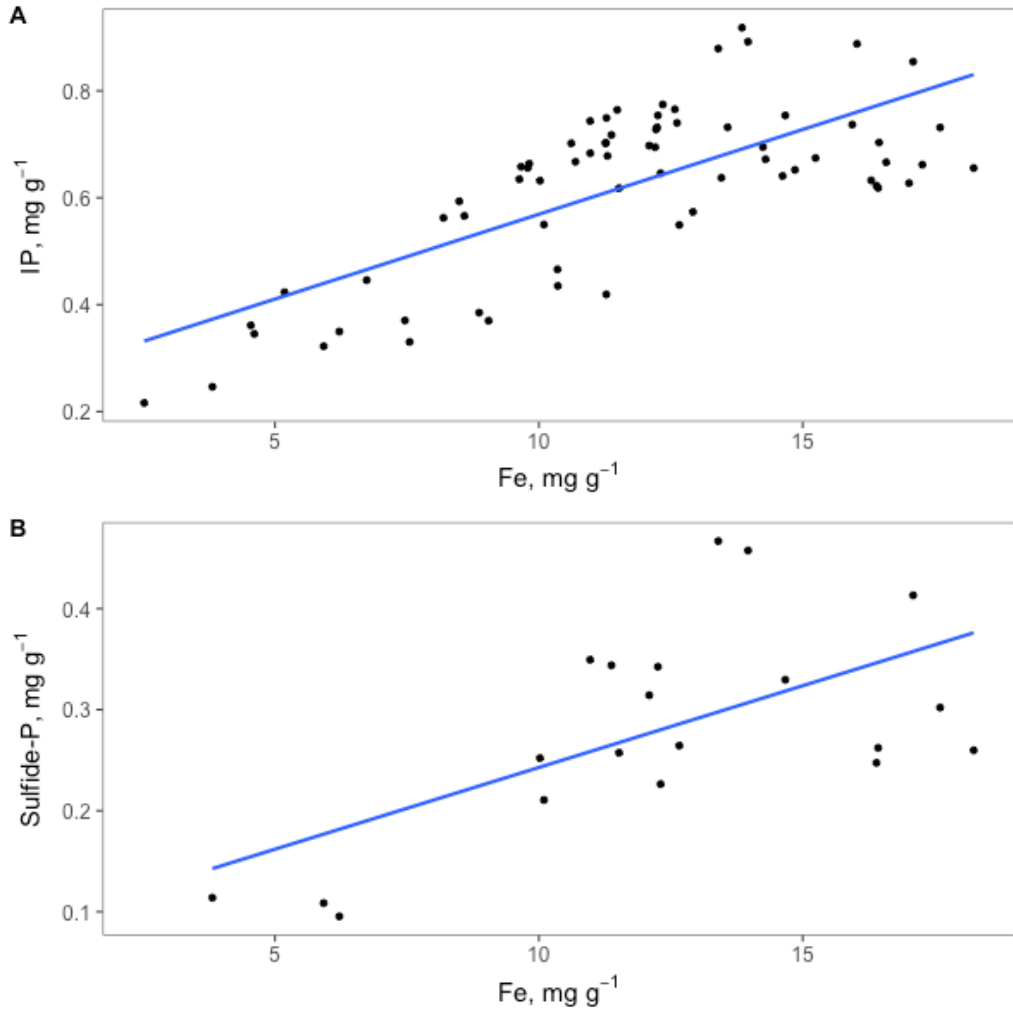


Figure 13. Relationship between concentrations of iron (Fe) and inorganic phosphorus (IP) (A) and sulfide-extractable phosphorus (sulfide-P) (B) in surface sediment from the Lower Susquehanna Reservoir System.



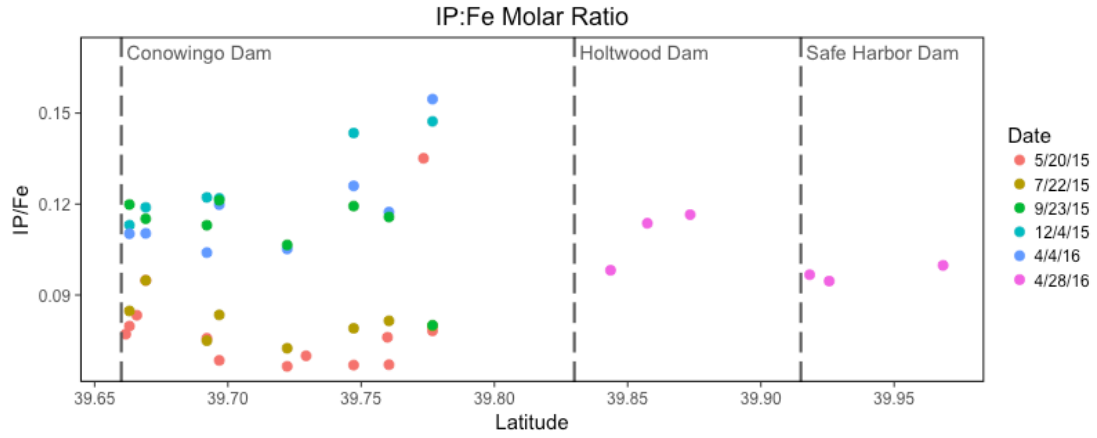


Figure 14. Molar ratios of inorganic P/Fe during different seasons along the length of the Lower Susquehanna Reservoir System. Sample locations are shown in Figure 5.

## Bibliography

- Anschutz, P., Zhong, S., Sundby, B., Mucci, A., & Gobeil, C. (1998). Burial Efficiency of Phosphorus and the Geochemistry of Iron in Continental Margin Sediments. *Limnology and Oceanography*, 43(1), 53–64. Retrieved from <http://www.jstor.org/stable/2838939>
- Aspila, K. I., Agemian, H., & Chau, A. S. Y. (1976). A semi-automated method for the determination of inorganic, organic and total phosphate in sediments. *The Analyst*, 101(1200), 187. <https://doi.org/10.1039/an9760100187>
- Boynton, W. R., Ceballos, M. A. C., Bailey, E. M., Hodgkins, C. L. S., Humphrey, J. L., & Testa, J. M. (2017). Oxygen and Nutrient Exchanges at the Sediment-Water Interface: a Global Synthesis and Critique of Estuarine and Coastal Data. *Estuaries and Coasts*.
- Boynton, W. R., Garber, J. H., Summers, R., & Kemp, W. M. (1995). Inputs, Transformations, and Transport of Nitrogen and Phosphorus in Chesapeake Bay and Selected Tributaries. *Estuaries*, 18(1), 285–314. Retrieved from <http://www.jstor.org/stable/1352640>
- Boynton, W. R., Kemp, W. M., Barnes, J. M., Cowan, J. L. W., Stammerjohn, S. E., Matteson, L. L., ... Garber, J. H. (1991). Long-Term Characteristics and Trends of Benthic Oxygen and Nutrient Fluxes in the Maryland Portion of Chesapeake Bay. In *New Perspectives in the Chesapeake System: A Research and Management Partnership. Proceedings of the Chesapeake Research Conference, 4-6 December 1990, Baltimore, MD* (pp. 339–354). Retrieved from

<http://www.gonzo.cbl.umces.edu/documents/sediments/CBresearchconsort137.pdf>

Capone, D. G., & Kiene, R. P. (1988). Comparison of microbial dynamics in marine and freshwater sediments: Contrasts in anaerobic carbon catabolism. *Limnology and Oceanography*, 33(4), 725–749. Retrieved from <http://www.jstor.org/stable/2837220>

Caraco, N., Cole, J., & Likens, G. E. (1989). Evidence for sulphate-controlled phosphorus release from sediments of aquatic systems. *Nature*, 341. Retrieved from <http://www.nature.com.proxy-um.researchport.umd.edu/nature/journal/v341/n6240/pdf/341316a0.pdf>

Caraco, N., Cole, J., & Likens, G. E. (1990). A Comparison of Phosphorus Immobilization in Sediments of Freshwater and Coastal Marine Systems. *Biogeochemistry*, 9, 277–290.

Cerco, C. F., & Noel, M. R. (2016). Impact of Reservoir Sediment Scour on Water Quality in a Downstream Estuary. *Journal of Environmental Quality*. <https://doi.org/10.2134/jeq2014.10.0425>

Chambers, R. M., Fourqurean, J. W., Hollibaugh, J. T., & Vink, S. M. (1995). Importance of Terrestrially-Derived, Particulate Phosphorus to Phosphorus Dynamics in a West Coast Estuary. *Source: Estuaries*, 18(3), 518–526. Retrieved from <http://www.jstor.org/stable/1352369>

Cloern, J. E. (2001). Our evolving conceptual model of the coastal eutrophication problem. *Marine Ecology Progress Series*, 210, 223–253. Retrieved from <http://www.int-res.com/articles/meps/210/m210p223.pdf>

- Conley, D. J. (2000). Biogeochemical nutrient cycles and nutrient management strategies. *Hydrobiologia*, 410, 87–96. Retrieved from <http://search.proquest.com.proxy-um.researchport.umd.edu/docview/821249268?OpenUrlRefId=info:xri/sid:wediscovey&accountid=14696>
- Cornwell, J. C., & Sampou, P. A. (1995). Environmental controls on iron sulfide mineral formation in a coastal plain estuary. In M. A. Vairavamurthy & M. A. A. Schoonen (Eds.), *Geochemical Transformations of Sedimentary Sulfur* (pp. 224–242). Washington, DC: American Chemical Society.
- Cowan, J. L. W., & Boynton, W. R. (1996). Sediment-water oxygen and nutrient exchanges along the longitudinal axis of Chesapeake Bay: Seasonal patterns, controlling factors and ecological significance. *Estuaries*, 19(3), 562–580. <https://doi.org/10.2307/1352518>
- Fisher, T. R., Gustafson, A. B., Sellner, K., Lacouture, R., Haas, L. W., Wetzel, R. L., ... Karrh, R. (1999). Spatial and temporal variation of resource limitation in Chesapeake Bay. *Marine Biology*, 133, 763–778. <https://doi.org/10.1007/s002270050518>
- Fisher, T. R., Peele, E. R., Ammerman, J. W., & Harding Jr., L. W. (1992). Nutrient limitation of phytoplankton in Chesapeake Bay. *Marine Ecology Progress Series*, 82, 51–63. Retrieved from <http://www.int-res.com.proxy-um.researchport.umd.edu/articles/meps/82/m082p051.pdf>
- Follmi, K. B. (1996). The phosphorus cycle, phosphogenesis and marine phosphate-rich deposits. *Earth-Science Reviews*, 40, 55–124. Retrieved from <http://ac.els->

cdn.com.proxy-um.researchport.umd.edu/0012825295000496/1-s2.0-0012825295000496-main.pdf?\_tid=75422e96-126a-11e7-9988-00000aab0f02&acdnat=1490563590\_c6b3f964c217830731131fc1555909e6

Gibbs, M. M. (1979). A simple method for the rapid determination of iron in natural waters. *Water Research*, 13(3), 295–297. [https://doi.org/10.1016/0043-1354\(79\)90209-4](https://doi.org/10.1016/0043-1354(79)90209-4)

Gurbisz, C., Kemp, W. M., Cornwell, J. C., Sanford, L. P., Owens, M. S., & Hinkle, D. C. (2017). Interactive Effects of Physical and Biogeochemical Feedback Processes in a Large Submersed Plant Bed. *Estuaries and Coasts*, 1–16. <https://doi.org/10.1007/s12237-017-0249-7>

Hartzell, J. L., Jordan, T. E., & Cornwell, J. C. (2010). Phosphorus burial in sediments along the salinity gradient of the Patuxent River, a subestuary of the Chesapeake Bay (USA). *Estuaries and Coasts*, 33(1), 92–106. <https://doi.org/10.1007/s12237-009-9232-2>

Hartzell, J. L., Jordan, T. E., & Cornwell, J. C. (2017). Phosphorus Sequestration in Sediments Along the Salinity Gradients of Chesapeake Bay Subestuaries. *Estuaries and Coasts*, 40(2). <https://doi.org/10.1007/s12237-017-0233-2>

Hirsch, R. M. (2012). Flux of Nitrogen, Phosphorus, and Suspended Sediment from the Susquehanna River Basin to the Chesapeake Bay during Tropical Storm Lee, September 2011, as an indicator of the effects of reservoir sedimentation on water quality. *U.S. Geological Survey Scientific Investigations Report 2012–5185*, (September 2011), 17. Retrieved from <http://pubs.usgs.gov/sir/2012/5185/>

Howarth, R. W., & Marino, R. (2006). Nitrogen as the limiting nutrient for

eutrophication in coastal marine ecosystems: Evolving views over three decades. *Limnology and Oceanography*, 51(1part2), 364–376.

[https://doi.org/10.4319/lo.2006.51.1\\_part\\_2.0364](https://doi.org/10.4319/lo.2006.51.1_part_2.0364)

Huerta-Diaz, M. A., Tovar-Sánchez, A., Filippelli, G., Latimer, J., & Sañudo-Wilhelmy, S. A. (2005). A combined CDB-MAGIC method for the determination of phosphorus associated with sedimentary iron oxyhydroxides. *Applied Geochemistry*, 20(11), 2108–2115.

<https://doi.org/10.1016/j.apgeochem.2005.07.009>

Jordan, T. E., Cornwell, J. C., Boynton, W. R., & Anderson, J. T. (2008). Changes in phosphorus biogeochemistry along an estuarine salinity gradient: The iron conveyor belt. *Limnology and Oceanography*, 53(1), 172–184.

<https://doi.org/10.4319/lo.2008.53.1.0172>

Karl, D. M., & Tien, G. (1992). Magic - a Sensitive and Precise Method for Measuring Dissolved Phosphorus in Aquatic Environments. *Limnology and Oceanography*, 37(1), 105–116. <https://doi.org/10.4319/lo.1992.37.1.0105>

Kemp, W. M., & Boynton, W. R. (1984). Spatial and temporal coupling of nutrient inputs to estuarine primary production: the role of particulate transport and decomposition. *Bulletin of Marine Science*, 35(3), 522–535. Retrieved from <http://www.ingentaconnect.com/content/umrsmas/bullmar/1984/00000035/00000003/art00023?crawler=true>

Kemp, W. M., Boynton, W. R., Adolf, J. E., Boesch, D. F., Boicourt, W. C., Brush, G., ... Stevenson, J. C. (2005). Eutrophication of Chesapeake Bay: Historical trends and ecological interactions. *Marine Ecology Progress Series*, 303, 1–29.

<https://doi.org/10.3354/meps303001>

- Kostka, J. E., & Luther III, G. W. (1994). Partitioning and speciation of solid phase iron in saltmarsh sediments. *Geochimica et Cosmochimica Acta*, 58(7), 1701–1710. [https://doi.org/10.1016/0016-7037\(94\)90531-2](https://doi.org/10.1016/0016-7037(94)90531-2)
- Krom, M. D., & Berner, R. A. (1980). Adsorption of Phosphate in Anoxic Marine Sediments. *Limnology and Oceanography*, 25(5), 797–806. <https://doi.org/10.4319/lo.1980.25.5.0797>
- Krom, M. D., & Berner, R. A. (1981). The diagenesis of phosphorus in a nearshore marine sediment. *Geochimica et Cosmochimica Acta*, 45(2), 207–216. [https://doi.org/10.1016/0016-7037\(81\)90164-2](https://doi.org/10.1016/0016-7037(81)90164-2)
- Langland, M. J. (2009). Bathymetry and Sediment-Storage Capacity Change in Three Reservoirs on the Lower Susquehanna River. *U.S. Geological Survey Scientific Investigations Report 2009-5110*. Retrieved from <https://pubs.usgs.gov/sir/2009/5110/pdf/sir2009-5110.pdf>
- Langland, M. J. (2015). Sediment Transport and Capacity Change in Three Reservoirs, Lower Susquehanna River Basin, Pennsylvania and Maryland, 1900–2012. *U.S. Geological Survey Open-File Report 2014–1235*, 1–18.
- Lehtoranta, J., Ekholm, P., & Pitkänen, H. (2009). Coastal Eutrophication Thresholds: A Matter of Sediment Microbial Processes. *AMBIO: A Journal of the Human Environment*, 38(6), 303–308. <https://doi.org/10.1579/09-A-656.1>
- Leventhal, J., & Taylor, C. (1990). Comparison of methods to determine degree of pyritization. *Geochimica et Cosmochimica Acta*, 54, 2621–2625.
- Li, Z., Sheng, Y., Yang, J., & Burton, E. D. (2016). Phosphorus release from coastal

- sediments: Impacts of the oxidation-reduction potential and sulfide. *Marine Pollution Bulletin*, 113(1), 176–181.
- <https://doi.org/10.1016/j.marpolbul.2016.09.007>
- Linker, L. C., Batiuk, R. A., Cerco, C. F., Shenk, G. W., Tian, R., Wang, P., & Yactayo, G. (2016). Influence of Reservoir Infill on Coastal Deep Water Hypoxia. *Journal of Environment Quality*, 45(3), 887.
- <https://doi.org/10.2134/jeq2014.11.0461>
- Marvin-DiPasquale, M. C., Boynton, W. R., & Capone, D. G. (2003). Benthic sulfate reduction along the Chesapeake Bay central channel . II . Temporal controls. *Marine Ecology Progress Series*, 260, 55–70.
- Marvin-DiPasquale, M. C., & Capone, D. G. (1998). Benthic sulfate reduction along the Chesapeake Bay central channel. I. Spatial trends and controls. *Marine Ecology Progress Series*, 168(Berner 1978), 213–228.
- Mortimer, C. H. (1942). The Exchange of Dissolved Substances between Mud and Water in Lakes. *The Journal of Ecology*, 30(1), 147.
- <https://doi.org/10.2307/2256691>
- Nixon, S., Ammerman, J., Atkinson, L., Berounsky, V., Billen, G., Boicourt, W., ... Seitzinger, S. (1996). The fate of nitrogen and phosphorus at the land-sea margin of the North Atlantic Ocean. *Biogeochemistry*, 35(1), 141–180.
- <https://doi.org/10.1007/bf02179826>
- Nixon, S. W. (1995). Coastal marine eutrophication: A definition, social causes, and future concerns. *Ophelia*, 41(1), 199–219.
- <https://doi.org/10.1080/00785236.1995.10422044>



- Pacini, N., & Gächter, R. (1999). Speciation of Riverine Particulate Phosphorus during Rain Events. *Biogeochemistry*, 47(1), 87–109. Retrieved from <http://www.jstor.org/stable/1469369>
- Palinkas, C. M., Halka, J. P., Li, M., Sanford, L. P., & Cheng, P. (2014). Sediment deposition from tropical storms in the upper Chesapeake Bay: Field observations and model simulations. *Continental Shelf Research*, 86, 6–16. <https://doi.org/10.1016/j.csr.2013.09.012>
- Palinkas, C. M., & Russ, E. (2016). Examining Reservoir Influences on Fluvial Sediment Supply to Estuaries and Coastal Oceans with Sediment Geochronologies: Example from Conowingo Reservoir (Upper Chesapeake Bay, USA). In *American Geophysical Union Fall Meeting*. San Francisco.
- Parsons, T. R., Maita, Y., & Lalli, C. M. (1984). *A manual of chemical and biological methods for seawater analysis* (1st ed.). Oxford [Oxfordshire] ; New York: Pergamon Press.
- Poulton, S. (2005). Chemical and physical characteristics of iron oxides in riverine and glacial meltwater sediments. *Chemical Geology*, 218(3).
- Roden, E. E., & Edmonds, J. W. (1997). Phosphate mobilization in iron-rich anaerobic sediments: microbial Fe(III) oxide reduction versus iron-sulfide formation. *Archiv Fur Hydrobiologie*, 139(3).
- Roden, E. E., & Tuttle, J. H. (1992). Sulfide Release from Estuarine Sediments Underlying Anoxic Bottom Water. *Source: Limnology and Oceanography* *Limnol. Oceanogr*, 37(374), 725–738. Retrieved from <http://www.jstor.org/stable/2837934>

- Ruttenberg, K. C. . (1992). Development of a Sequential Extraction Method for Different Forms of Phosphorus in Marine Sediments. *Limnology and Oceanography*, 37(7), 1460–1482. <https://doi.org/10.4319/lo.1992.37.7.1460>
- Schindler, D. W. (1974). Eutrophication and Recovery in Experimental Lakes: Implications for Lake Management. *Science*, 184(4139), 897–898. <https://doi.org/10.1126/science.184.4139.897>
- Schubel, J. R., & Pritchard, D. W. (1986). Responses of Upper Chesapeake Bay to Variation in Discharge of the Susquehanna River. *Estuaries*, 9(4), 236–249.
- Scicluna, T. R., Woodland, R. J., Zhu, Y., Grace, M. R., & Cook, P. L. M. (2015). Deep dynamic pools of phosphorus in the sediment of a temperate lagoon with recurring blooms of diazotrophic cyanobacteria. *Limnology and Oceanography*, 60, 2185–2196. <https://doi.org/10.1002/lno.10162>
- Stone, M., & English, M. C. (1993). Geochemical composition, phosphorus speciation and mass transport of fine-grained sediment in two Lake Erie tributaries. *Hydrobiologia*, 253(1–3), 17–29. <https://doi.org/10.1007/BF00050719>
- Yao, Q.-Z., Du, J.-T., Chen, H.-T., & Yu, Z.-G. (2016). Particle-size distribution and phosphorus forms as a function of hydrological forcing in the Yellow River. *Environmental Science and Pollution Research*, 23(4), 3385–3398. <https://doi.org/10.1007/s11356-015-5567-3>
- Zhang, Q., Brady, D. C., & Ball, W. P. (2013). Long-term seasonal trends of nitrogen, phosphorus, and suspended sediment load from the non-tidal Susquehanna River Basin to Chesapeake Bay. *Science of the Total Environment*, 452–453, 208–221.

<https://doi.org/10.1016/j.scitotenv.2013.02.012>

Zhang, Q., Hirsch, R. M., & Ball, W. P. (2016). Long-Term Changes in Sediment and Nutrient Delivery from Conowingo Dam to Chesapeake Bay: Effects of Reservoir Sedimentation. *Environmental Science & Technology*, *50*, 1877–1886.

<https://doi.org/10.1021/acs.est.5b04073>