Environmental Science & Technology

Article

Cite This: *Environ. Sci. Technol.* 2019, 53, 69−76

pubs.acs.org/est

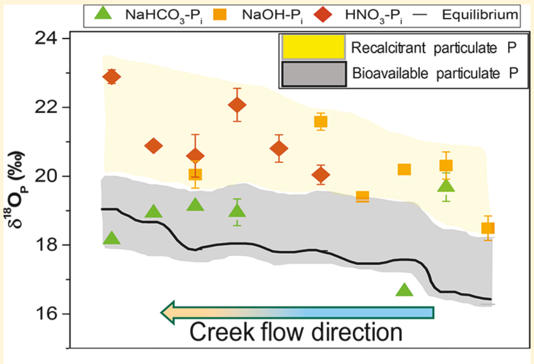
Stable Isotopes and Bayesian Modeling Methods of Tracking Sources and Differentiating Bioavailable and Recalcitrant Phosphorus Pools in Suspended Particulate Matter

Kristi A. Mingus,[†] Xiaomeng Liang,[‡] Arash Massoudieh,[‡] and Deb P. Jaisi*,[†]

[†]Department of Plant and Soil Sciences, University of Delaware, Newark, Delaware 19716, United States
[‡]Civil Engineering Department, The Catholic University of America, Washington, DC 20064, United States

Supporting Information

ABSTRACT: Understanding the sources of different phosphorus (P) pools and their bioavailability under imposed biogeochemical environments in a watershed is limited largely due to the lack of appropriate methods. In this research, phosphate oxygen isotope ratios and Bayesian modeling on fingerprinting elements were applied as two novel methods to identify sources and relative recalcitrancy of particulate P pools suspended in water in the continuum of sources from land to the mouth of a coastal estuary to the Chesapeake Bay. Comparative analyses of sizes, relative ratios, and oxygen isotope values of particulate P pools in the creek water suggested that the $NaHCO_3$−P pool was bioavailable, whereas NaOH−P and HCl−P pools were recalcitrant during P transport along the creek. Agricultural field soil, streambank, and river bottom sediments were major sources of particulate P and their contributions varied significantly at the headwater and downstream regions of the creek. Bayesian modeling based on fingerprinting elements suggested that tides played a major role in forming particulate matter from estuarine sources at the creek mouth region and importing it upstream. These findings provide new insights into the origin and fate of particulate P and the fidelity of isotope and fingerprinting methods in source tracking of P in tidally influenced watersheds.



INTRODUCTION

Nutrient contamination of surface waters has long been a water quality challenge in major rivers and coastal watersheds in the U.S. Surface water eutrophication and dead zones, for example in the Chesapeake Bay and the Gulf of Mexico, caused by excess nutrients derived largely from agriculture are frequently highlighted in news and reports.[1] Restoration of such water bodies is complicated by the various nutrient sources, their temporally and spatially variable inputs, and complex interactions affecting their occurrence, fate, and transport.[2] The current stalement on water quality improvement has raised debates and accountability for nutrient release has remained open-ended.

By virtue of the properties of the phosphate (PO_4^{3-}) anion, which has high affinity for solid surfaces such as soil minerals, particulate matter, and colloidal particles, phosphorus (P) is transported dominantly in the particulate form.[3] Likewise, particulate phosphorus (PP) is the dominant form of P exported by rivers to the Chesapeake Bay.[4] The particulate matter is made up of both inorganic and organic components. The inorganic-rich components such as sand, silt, and clay (aggregates) can settle in water at low flow whereas organic-rich components consisting of phytoplankton, bacteria, and other biological materials typically remain floating.[5] Thus, the composition and relative concentrations of inorganic P (P_i) and organic P (P_o) of suspended particulate matter often vary along a river transect, particularly in estuarine settings. Further, differences in residence time and mobility of P_i and P_o in the particulate matter cause variability of their concentrations along river channels.

Scientific understanding of the role of PP in water quality remains severely limited. For water quality assessment, the bioavailability of particulate matter, defined as the potential plant or microbial uptake of a specific form of nutrient in a particular ecosystem[6] from the point of entry to the ecosystem to the point of export, should be known. However, determining the bioavailability of PP pools in a system is not straightforward because they are impacted by site-specific biogeochemical conditions such as salinity, pH, redox condition, and community structure and activity of (micro)-organisms. Methodological limitation is a major challenge in determining P or PP bioavailability. For example, indirect methods commonly used to quantify bioavailability include

Received: September 14, 2018
Revised: November 30, 2018
Accepted: December 3, 2018
Published: December 3, 2018

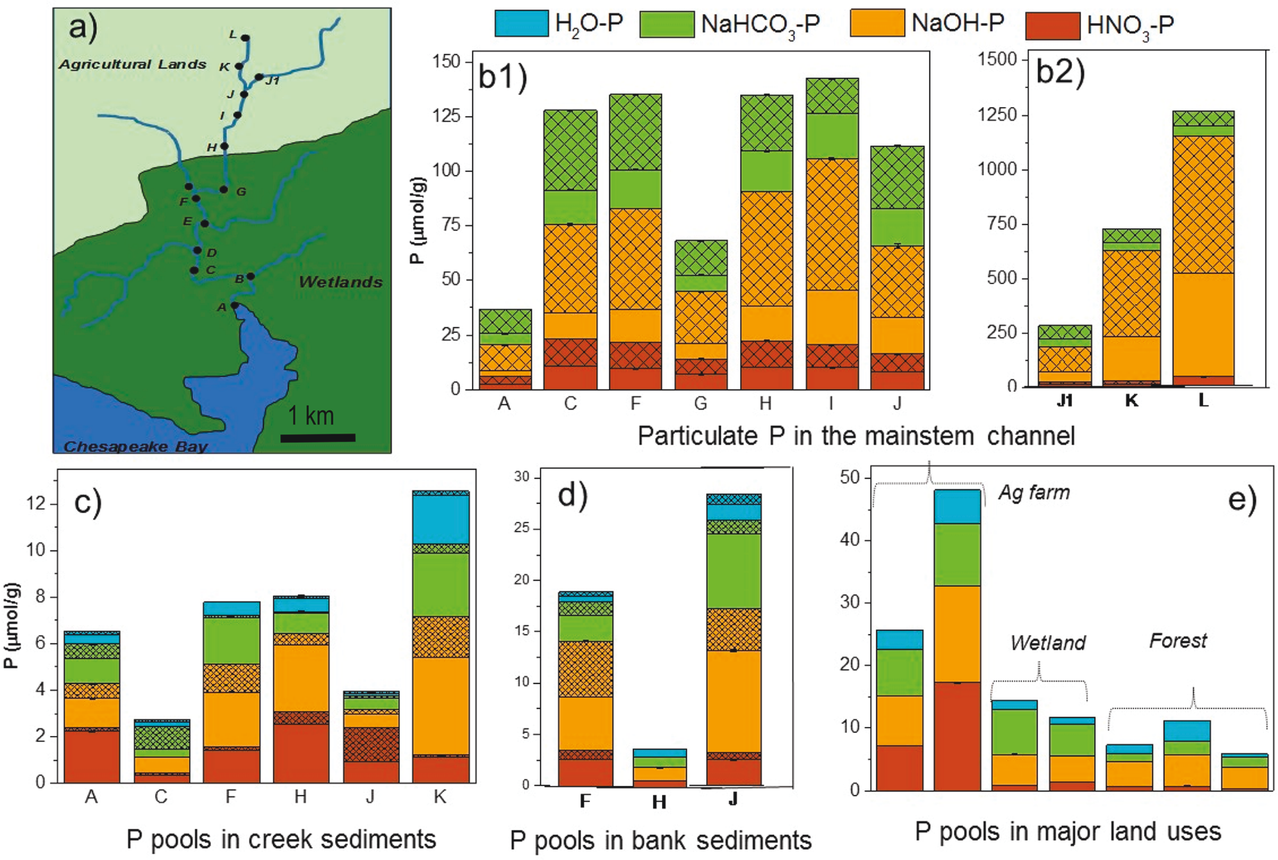


Figure 1. a) Location map of the East Creek watershed. The salinity varies from 0.5 to 17.8 PSU from the ditch (L) to the mouth of the creek (site A). b−e) Speciation of P into different P pools and P_i and P_o in each pool in the main channel of the creek b), surface-sediments (0−2 cm depth) c), creek bank sediments d), and major land use e). Please note the cross-hatching refers to P_o and plain color is for P_i and the same color is used for the same P pool. In the text, P without any subscript means total P (sum of P_o and P_i). Ag farm in figure e refers to agricultural lands.

dissolved/soluble reactive P plus biomass P,[7] bioassays,[8] and sequential extractions.[7,9,10] These operationally defined methods still provide useful information and allow comparisons among literature data but cannot be used to test if particular P pools are bioavailable in a given space and time. Further, multiscale interactions among PP pools and with dissolved P in water and the interplay of physicochemical and biological reactions demand more innovative techniques that go beyond operationally defined methods capable of discriminating bioavailable pools from recalcitrant PP pools. The major research objectives of this study were to (i) identify the sources of particulate P pools in the East Creek watershed and (ii) differentiate bioavailable and recalcitrant inorganic PP pools along an environmental gradient under base flow conditions from the source sites in the watershed to the mouth at the Chesapeake Bay. In this research phosphate oxygen isotopes and multielement sediment fingerprinting methods were used to meet these objectives.

■ MATERIALS AND METHODS

Study Site and Collection of Soil, Sediment, and Waters from Creek and Other Landforms. East Creek is a tidally influenced tributary located in Somerset County in Maryland and it drains to the lower Chesapeake Bay (Figure 1a). The upstream part of the watershed includes agricultural farms and scattered poultry operations with a few forest patches. The southern half of the watershed is primarily surrounded by wetland and remains partly saturated during high tide and after rain events. A total of 14 sampling sites (from A to L, Figure 1a) along the salinity gradient were chosen, which span from a drainage ditch near agricultural fields to the mouth of the creek at the Chesapeake Bay. From each site, 8−64 L of water was collected to achieve sufficient particulate matter for chemical and isotope analyses under baseflow (receding tide) conditions. Conductivity of water was measured using an EC meter (Orion, Beverly, MA) and salinity was measured using a salinity test kit (LaMotte, Chestertown, MA). Paired sediment cores were collected from selected water sampling sites using a suction corer.[11] The top 2 cm of the core, which represents freshly settled particulate or eroded surface and dominates P exchange with the water column, was chosen for further analyses. Streambank sites (next to sites F, H, and J) were selected based on the water flow direction and visible scour channels. After collection, water, sediment core, and streambank samples were stored on ice and placed in coolers and transported to the laboratory for analyses.

Soil samples were collected from major land use types including agricultural farms, forested lands, and wetlands in the watershed. Sampling locations in different land use types and land covers were selected based on current and past land use maps, aerial photographs, and site visits. At least 20 sampling sites per land use/cover were collected and processed separately. From each site, at least two samples were collected from the top-soil (0−5 cm) and composited by thorough mixing. Poultry litter applied in the field was collected from the stockpile in the field.

Processing Suspended Particulate Matter and Soils from Potential Source Sites. Suspended particulate matter in each water sample was separated via centrifugation using Stokes's Law of settling (≥100 nm cutoff size for particulate matter and <100 nm was operationally defined as as dissolved P). Pelleted particulate matter was washed twice with deionized (DI) water to remove variable salt content from different sites for the accurate determination of the particulate mass. Soil pore-water was separated by centrifugation and saved for isotopic analysis. Please note this method extracts mobile water and a small fractionation between mobile and immobile waters in soil pores is reported.[12] The larger time frame used to calculate equilibrium isotope values (see below) is expected to compensate for this potential variability. The pH of creek water was measured directly but the solid samples were mixed with DI water at a 1:1 ratio before pH measurement. After removing porewater, sediment, streambank material, soil, and manure samples were freeze-dried, homogenized, and size-separated (<200 μm) using a mechanical sieve before further analyses.

To separate and quantify different P pools in solid samples (soil, manure, particulate matter, streambank, and sediment), a sequential extraction method developed by Hedley et al.[10] and revised by Tiessen et al.[13] was adopted with slight modifications.[14] To avoid P from any particular pool being carried over to subsequent P pools, supernatants from the extraction and rinsing steps in a particular P pool were collected separately and quantified for both P_i and P_o. Persulfate digestion was used to oxidize P_o to P_i, and the P_o was calculated as the difference between total P and P_i. All extracted solutions were stored at 4 °C for 1 week or less before further processing and purification for isotopic analyses.

Purification of P Pool Extracted Solutions and Isotope Analyses. Dissolved P in creek water (after separation of particulate matter) and all extracted P pools from soil, sediment, and particulate matter were processed for the removal contaminants and to concentrate P_i. The details of processing methods are included in Joshi et al.[15] In brief, different P pools extracted from soils/sediments contain a variable amount of P_o, with high P_o in $NaHCO_3$−P and NaOH-P pools. Therefore, we first pretreated the extracted solution with DAX 8 Superlite resin followed by concentrating P_i using the magnesium induced coprecipitation (MagIC) method. Samples still containing visible impurities after the MagIC dissolution, most notably in the form of dark brown color from acid-insoluble humic acid and other organic matter, required a second DAX treatment. After the volume reduction by evaporation in a water bath at <70 °C, precipitation of silver phosphate (Ag_3PO_4) followed our established method.[15] The recovery of P_i was calculated from the moles of P_i in the starting solution and comparing to that in silver phosphate. Only those samples with ≥90% yield were considered reliable and used for further analysis. Two internal standards with different $\delta^{18}O_P$ values were processed in parallel to confirm the reliability of the processing method and isotope analyses. The $\delta^{18}O_P$ values of silver phosphate were measured in triplicate in a Thermo-Chemolysis Elemental Analyzer (TC/EA) coupled to a Delta V IRMS (Thermo, Bremen, Germany) (precision 0.3‰) using YR series standards. Similarly, the $\delta^{18}O_w$ values of creek and pore waters were measured using a Finnigan GasBench II coupled with IRMS following the CO_2 equilibration method (precision <0.06‰). The $\delta^{18}O_w$ values were calibrated against USGS W67400 (−1.97‰) and W32615 (−9.25‰) standards. The $\delta^{18}O_w$ and $\delta^{18}O_P$ values are presented relative to Vienna Standard Mean Ocean Water (VSMOW) in this communication. The equilibrium isotopic values were calculated using the Chang and Blake[16] equation which is more relevant to P_i precipitation as Ag_3PO_4 and measurement in online TC/EA. To account for the variability in temperature of sampling sites and water isotope values (see above), the range of equilibrium was chosen to include minimum and maximum temperature within a month of sampling date.

Development of Bayesian Source Apportionment Model Based on the Mass Balance of Fingerprinting Elements. The multielement fingerprinting method has been widely used as an independent method to trace sources of elements and particulate matter to their origin.[17−19] In this study, at least 20 samples were collected from each endmember or potential source including agricultural lands, forest patches, wetland, streambanks, and creek. To compare results with particulate matter, DI water rinses were discarded. Concentrations of 39 elements were measured as candidates for fingerprinting sources using inductively coupled plasma optical emission spectrometry (ICP-OES) (Thermo, Bremen, Germany).

A Bayesian model[17,19] was used to infer the contribution of five potential sources including remobilization of deposited sediments or particulate matter entering from the Chesapeake Bay through tidal flow. Briefly, the posterior distribution of contribution of sources, **X**, is determined based on the Bayes Theorem as follows:

$$p(\mathbf{X}, \mathbf{Y}, \boldsymbol{\Gamma}|\tilde{\mathbf{Y}}, \tilde{\mathbf{C}}) \propto p(\tilde{\mathbf{C}}|\mathbf{X}, \mathbf{Y})p(\tilde{\mathbf{Y}}|\mathbf{Y})p(\mathbf{X})$$

where the left-hand side is the posterior distribution of the contribution of sources into the fluvial samples, **Y** a matrix representing the elemental contents in each source, $\boldsymbol{\Gamma}$ is the variance-covariance matrix for observation error of the fluvial samples, $\tilde{\mathbf{Y}}$ is the matrix representing the observed elemental content in each source, and $\tilde{\mathbf{C}}$ is a vector representing the observed elemental contents in the fluvial samples. On the right-hand side of the equation the first term is the likelihood function which measures the likelihood of observing the fluvial elemental profile $\tilde{\mathbf{C}}$ given source contribution **X** and source elemental profiles **Y**, the second term represents the likelihood of the observed source elemental profiles $\tilde{\mathbf{Y}}$, given the inferred elemental profiles **Y**, and the last term is the prior distribution of the source contributions that is considered a Dirichlet distribution to force the sum of the elemental profiles to be equal to one. The details on the form of the likelihood function and the forms of the prior distributions has been provided in past publications.[17,19]

Content of Ca, Ba, La, and Sr in creek sediments are significantly larger than all upstream sources (Figure S1of the Supporting Information, SI). Further, a monotonic increase in the concentrations of these elements from upstream to downstream led us to conclude that the Bay water is the main contributor of these elements. Net import from the estuary to inland water is not surprising and has been reported before in the Chesapeake Bay.[20] Therefore, particulate matter from the furthest downstream sites (A and B) was considered to represent the Chesapeake Bay water. The Mann−Whitney U-test or Kruskal−Wallis H-test was used to verify the ability of individual tracers to discriminate source categories.[18] On the basis of these tests, the following 20 elements were found to be able to discriminate sources: Al, As, B, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Ni, Pb, S, Zn, Cu, Th, and Ga.

The Markov Chain Monte Carlo (MCMC) approach, specifically the Metropolis-Hasting Algorithm,[21] was used to acquire a sequence of random numbers from the posterior probability distribution. A model program using the C++ language was used to perform the MCMC Bayesian inference with posterior moment approach,[22] which was used to evaluate the convergence of the MCMC algorithm. The source code is publicly available on GitHub at https://github.com/ArashMassoudieh/SourceID. For this research, the program generated a total of about 5 000 000 samples with 8 chains for analyzing each particulate matter sample and an average acceptance rate of 0.0976 was achieved. In this study, the first 12 000 samples were ignored as "burn-in".

RESULTS AND DISCUSSION

Phosphorus Transport in the Main Channel and Export to the Chesapeake Bay. Along the salinity gradient in the main channel of East Creek, from the agricultural ditch (site L, salinity 0.5 PSU) to the mouth at the Chesapeake Bay (site A, salinity 17.8 PSU) (Table S1), the mass of particulate matter increased (Figure S2) but the PP concentration decreased (Figure 1b). The relationship of tidal height, P concentration and oxygen isotope ratios show that the incoming tide as major factor to dilute dissolved P (Figure S3). An order of magnitude decrease in PP concentration suggests the contribution of P-rich particulate matter from a critical source area in the upstream region and of P-poor particulate matter from the downstream region. Total P content of particulate matter is high in upstream (Figure 1b) but the mass is low (Figure S4). Among different P pools in particulate matter in the channel, NaOH−P (primarily Fe and Al oxide-bound P) was always the most dominant P pool, similar to results from the Patuxent estuary located at the opposite flank of the Chesapeake Bay.[23] This pool showed a strong positive relationship with Fe and Al concentrations consistent with the fact that Fe and Al oxides and their complexes with organic matter are major carriers of P.[24] $NaHCO_3$−P (primarily loosely sorbed P), the second major form of PP, showed variable concentrations along the channel, possibly reflecting the exchange of this pool with dissolved P in the water column and/or formation/dispersal of particulate matter during transport. The dominance of specific P pools, however, could vary during storm and baseflow conditions and potentially impact the size and bioavailability of PP pools in the main channel.

Organic P (41−80% of total P) was often a dominant P form in the particulate matter, particularly in the NaOH−P pool. Large proportions of PP_o (Figure 1b), however, are not surprising and are expected due to high P promoting assimilation by algae and bacteria and high contribution of biomass. Intriguingly, relative concentrations of P_o for all three P pools increased downstream. One of the potential reasons for this variation could be the dominance of different sources or composition of particulates in upstream and downstream regions of the creek. Among P_o species, phytate is a dominant compound in upstream and ditch sites[25] but monoesters and diesters, reported to be major P_o compounds in the Chesapeake Bay,[26,27] are most likely candidates in the mouth of the creek.

Bioavailable P pools in the Suspended Particulate Matter. In the main channel, P concentration is above the recommended minimum (1 μM SRP) to sustain healthy aquatic life, and this elevated P is rather common in coastal estuaries in the Eastern Shore and other regions in the Chesapeake Bay.[2] The $\delta^{18}O_P$ values of $NaHCO_3$−P_i pool lie within the range of equilibrium at most sites (Figure 2) in the entire stretch of the creek. This demonstrates that this PP_i pool is microbially cycled and at equilibrium in creek water. The $NaHCO_3$−P pool is considered bioavailable in soils[13] and the distinct isotope effect during biological cycling is well-known in laboratory and field studies.[28,14] Further, microorganisms have been found to extensively recycle bioavailable P even in conditions with P in excess of their biological demand, and they can still imprint distinct isotopic signatures on bioavailable P pools.[29] Thus, this result verifies that the $NaHCO_3$−P pool is a more suitable proxy to quantify bioavailable PP than the empirically defined sequential extraction and bioassay methods. This is particularly important because the bioavailability of PP has been scrutinized as a greater concern than quantifying total PP load to water bodies.[30] In some cases, 25−70% of PP from one storm event and 24% under baseflow conditions are empirically interpreted to be either bioavailable or at risk of becoming bioavailable.[8,9] Therefore, isotope values of sequentially extracted P pools in this study provided a constraint to identify whether certain P pools are bioavailable in the site-specific environmental conditions.

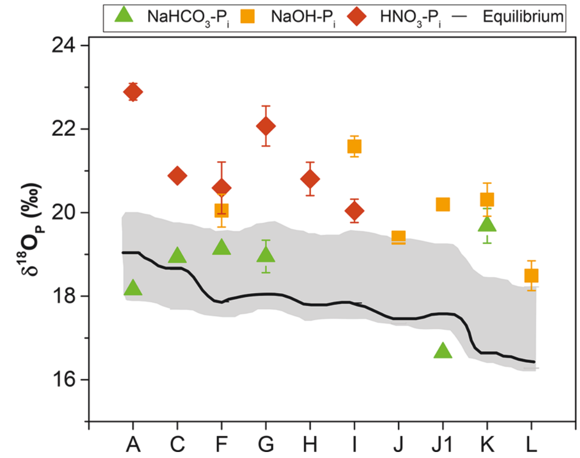


Figure 2. $\delta^{18}O_P$ values of three major P_i pools in particulate P ($NaHCO_3$−P_i, NaOH−P_i, and HNO_3−P_i) in the creek. Equilibrium isotope values (calculated based on the equation derived by Chang and Blake[16]) is represented by a solid black line with the gray region representing variability within a month of PP sampling date.

Recalcitrant P Pool in the Suspended Particulate Matter. The NaOH−P_i pool is generally regarded as moderately or conditionally bioavailable depending on the efficiency of (micro)organisms to access the NaOH−P_i pool and relative concentrations of different P pools. The HNO_3−P_i pool is not considered to be directly bioavailable. However, specific biogeochemical conditions, such as those in oligotrophic waters, reducing environments, or high pH—none of them applicable in the study site—may promote the release of P from these pools and to a bioavailable pool. Interestingly, $\delta^{18}O_P$ values of NaOH−P_i and HNO_3−P_i pools in the particulate matter are much heavier than the equilibrium composition (Figures 2 and S5) and are distinctly different from the bioavailable ($NaHCO_3-P_i$) pool at almost all sites in the main channel. This provides strong evidence that the particulate $NaOH-P_i$ and HNO_3-P_i pools are clearly recalcitrant, i.e., not microbially cycled, during transport through the creek. Furthermore, the $\delta^{18}O_P$ values of these two pools became gradually heavier downstream, likely originating from sources of P from the Chesapeake Bay during incoming tides because the $\delta^{18}O_P$ values of dissolved P in the Bay water in late-spring-summer months are generally heavy (20.81 ± 1.8‰).[31] This interpretation is also consistent with the P content in the particulate matter and results derived from fingerprinting elements (below). Therefore, the possibility of mixing of these sources is more likely than in situ formation of new $NaOH-P_i$ and HNO_3-P_i pools. Questions on the ultimate fate of $NaOH-P_i$ and HNO_3-P_i pools after export from the East Creek watershed (to the Chesapeake Bay) and subsequent processes including deposition, remobilization, and remineralization is out of scope for the creek stretch studied. These processes, however, have been included in other recent studies.[26,31,32] The finding that these pools remained largely recalcitrant to biological cycling in the main channel is significant for two main reasons. First, their isotopic signatures can be utilized for source tracking since they fall out of the range of isotopic equilibrium. Second, they might be of lesser importance from a nutrient management/policy standpoint because they are quantitatively and qualitatively less of an immediate water quality concern in the given stretch of the creek.

Results from Fingerprinting Element based Bayesian Modeling. Contribution of six different potential sources to particulate matter in the water based on Bayesian model analyses of fingerprinting elements is shown (with 95% credible intervals). Please note ditch sites (K and L) are remote and not well connected to the wetlands and therefore the wetland source was not included in their potential sources. The Bay water is estimated to have a major contribution (∼80−97%) into all sites with the exception of J1, K, and L although the contribution into site J1 was also determined to be between 40 and 80%. The data were not able to provide a definitive conclusion on the contribution of the Bay water into ditch sites because the 95% bracket is determined between ∼0−30% and ∼0−55% for sites K and L, respectively. Nonetheless, there is a clear decreasing trend in the contribution of Bay water into particulate matter with moving upstream as the distance from bay increases. Regarding other sources, the data were only able to inform about the upper limits of the contribution. This may be due to either the lack of a large enough difference between elemental profiles of these sources to be discriminated or internal correlation between contributions of some sources. This means that mixing nonunique portions of two or more sources can also result in the same mixture elemental profile or similarly good agreement with the measured elemental data of particulate matter. For sites C to J, the stream bank contribution is inferred to be ∼0−15%, higher for site J1 and for site K and L respectively, between 20−80% and 10−75%. For sites C−J, other sources including wetland, agricultural, and forest contribution are inferred to be up to 10%, 5%, and 5%, respectively, but the lower bracket was found to be close to zero, which means each of these sources could have insignificant contributions. For sites K and L, a higher contribution of agriculture and forest are expected but still the lower bound of the bracket is small. Comparisons of modeled vs measured normalized element content (content for each element divided by the sum of elements) profiles (Figures S6 and S7) for four randomly selected stations show the 95% credible intervals for the normalized elemental contents based on the posterior probability distributions of source contributions and source elemental contents obtained through MCMC analyses. For most elements and in most sites the agreement was acceptable as determined by the measured elemental content lying within the 95% credible intervals of the modeled elemental content, but there are also limited discrepancies for some elements like Cu at site C.

Phosphorus Sources, Sinks, and Cycling. Tracking sources using isotope signatures is based on the fidelity of $\delta^{18}O_P$ values that either (i) remains the same as in the source, or (ii) imprints a new isotope composition that is distinctive of a certain source or enzymatic reaction.[28,33] While identification of source(s) in the first case is direct, the other case requires calculations under specific assumptions.[34] If there is more than one potential P source, or if isotope signatures from different sources overlap, then additional methods are useful to resolve the overlap.

As shown in Figure 2, $NaOH-P_i$ and HNO_3-P_i pools are out of equilibrium and have distinct P source signatures. This means that they have not been cycled by (micro)organisms and thus are suitable for source tracking. Further, there is a gradual enrichment of isotope values of these pools in downstream. This means physicochemical processes such as source mixing and/or partial removal of specific P pools could be major reasons for changes in isotopes of these pools. For example, increased salinity promotes the release of Fe oxide-bound P, and Ca−P is likely to precipitate at high concentrations of P_i and Ca, high pH, and low Mg.[26] Below we discuss the contributions of various potential sources and site-specific physicochemical and biogeochemical conditions based on the results from isotopes and fingerprinting methods.

Topsoil Erosion. The P load contribution from agricultural fields was generally expected to be higher than soils under other land covers due to vulnerability to soil erosion and high P content. For example, Mehlich-3 P, a widely used method to evaluate plant available P, in the agricultural soil near site L was 16.81 μmol/g (521 ppm), much higher than the agronomic optimum. The $\delta^{18}O_P$ values of $NaOH-P_i$ pools in agricultural soil and manure are slightly heavier (∼22−24‰) than that in particulate matter (18−22‰). Shallow subsurface transport has been interpreted to be a major P loss pathway in this flat coastal region.[35] On the basis of the comparison of measured $\delta^{18}O_P$ values of H_2O-P_i pools in agricultural soils and ditch sites, identification of the pathway of dissolved P transport from P rich soil either as surface or subsurface flow is difficult because the ditch P_i was intensively cycled and its original source isotope signature was overprinted. Model results provide strong indication that agricultural sources are more significant in ditch sites. Nonetheless, the $\delta^{18}O_P$ values of HNO_3-P_i pools in particulate matter overlapped with those of the agricultural soils and manure (Figure 3). Since the HNO_3-P_i pool is not expected to be recycled and dissolution and precipitation reactions do not change the isotopic composition of residual HNO_3-P_i,[36] this P pool is ideal for source tracking. However, the precipitation of Ca−P minerals in the two ditch sites (K and L) is highly likely because of very high P_i and elevated pH due to an intense algal bloom, similar to the Chesapeake Bay where a P_i spike caused by degradation of

DOI: 10.1021/acs.est.8b05057
Environ. Sci. Technol. 2019, 53, 69−76

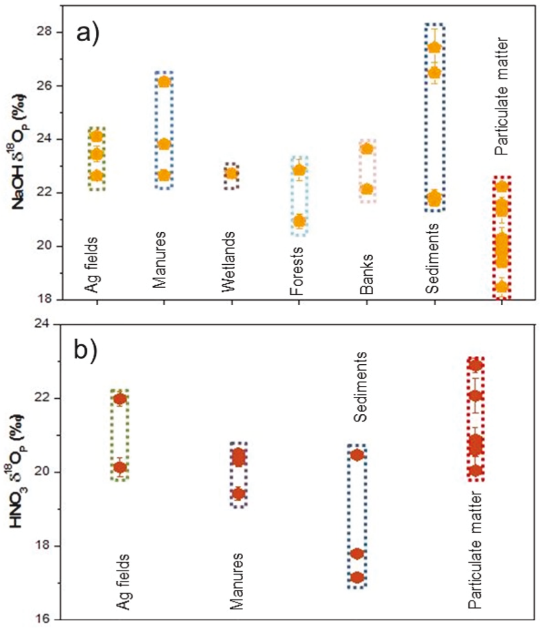


Figure 3. Measured $\delta^{18}O_P$ values of various P sources in the watershed for NaOH–P_i (a) and HNO_3–P_i pools (b). Term "bank" refers to streambank of the main channel and "Ag fields" refer to agricultural lands.

organic debris led to the precipitation of authigenic apatite in the sediment.[31,32] The $\delta^{18}O_P$ values of the HNO_3–P_i pool derived from a remineralized P source are very light and the exact value depends on the composition of P_o species.[32] Relatively lighter $\delta^{18}O_P$ values of the HNO_3–P_i pool from ditch sites (Figure 2) at least are indicative of the precipitation of HNO_3–P_i pools.

Wetland soils may act as a P sink or source, but low P concentrations in wetlands imply that their contribution should be small. In this study, wetlands do not appear to be the significant source of particulate matter, which is supported with both elemental and modeling results (Figure 4). In addition, forest soils have overlapping isotope values of the NaOH–P_i pool with particulate matter but their relative contribution to PP loads is expected to be minimal due to P poor soils and relatively far proximity from the creek.

Streambank Erosion. Erosion and remobilization of streambanks have been reported to contribute P especially under P saturation and in sandy streambanks and have been scrutinized as a dominant source of legacy PP to rivers.[37] In the study site, the concentration of P pools in the streambank was quite variable, but was higher than that in sediment in all cases. Interestingly, the ratio of HNO_3–P_i:NaOH–P_i pools of sediment and streambank material was similar in sites near the bay. This could indicate similar physicochemical processes driving the size of P pools or mobilization of streambank material and deposition in the sediment column, contributing to the sedimentary P pool. Even though a high variability in P content of the bank materials was observed (Figure 1d), which could be due to streambank morphology with respect to interacting/depositing P rich particulate matter, the source identification based on the results from fingerprinting elements indicated that the bank erosion could be a significant factor at upstream sites with contribution ranging from 10–75%. The similarities of $\delta^{18}O_P$ values of NaOH–P_i of streambanks (22–23.5‰) with that of agricultural fields (22–24‰) and comparable to that of particulate matter (18–22‰), also

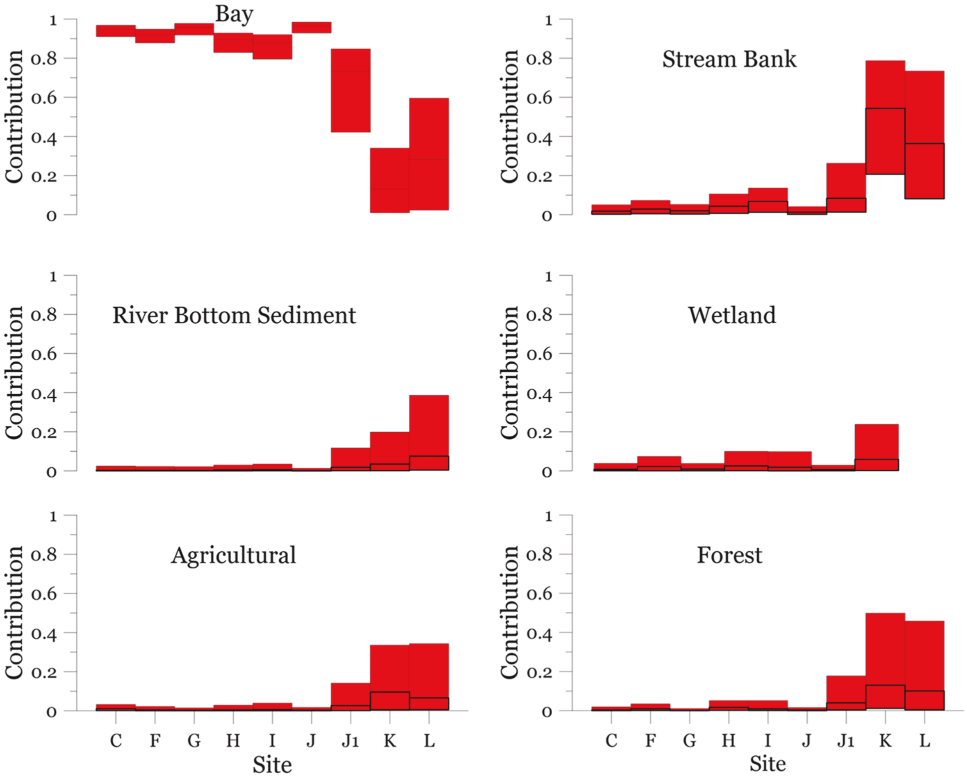


Figure 4. Inferred 95% credible intervals for contribution of different sources in the particulate matter collected from the creek. The brackets indicate the contribution of each source with a 95% probability.

support streambanks in this site as a major source of legacy PP in East Creek.

Remobilization/Remineralization from Sediments. Upward flux of porewater P into the water column could be a significant source of P besides remobilization of sediments. On the basis of the porewater P concentrations[38] and P flux results from controlled laboratory experiments,[11] upward flux of P into the water column is dominant under ambient conditions in this creek. Irrespective of the mode of P release (such as remineralization, reductive or pH promoted dissolution, or ionic exchange), the end result is the net increase of P concentration in the water column but the isotope effect could be different among these processes. The comparison of $\delta^{18}O_P$ values shows that the sediment NaOH−P_i pool is heavier than $NaHCO_3$−P_i values, with $NaHCO_3$−P_i being closer to equilibrium values. One likely reason for heavy $\delta^{18}O_P$ values in the sediment could be kinetic fractionation because P_i with lighter $\delta^{18}O_P$ values tends to desorb from Fe oxides first.[39] A measurable difference in isotope pools might result in a semiopen system such as during constant removal of desorbed P_i by water flow potentially leaving heavier $\delta^{18}O_P$ values in remaining Fe-oxide bound P. Whether such an isotope effect could be significant in the field is yet to be validated. Other factors could be the displacement of P (NaOH−P) with increasing salinity under pH > PZC (point of zero charge). Site F exhibited much lighter $\delta^{18}O_P$ values of HCl−P_i than other sediments, which is suggestive of remineralized source of P (similar to that of ditch sites, see above). This unique finding at site F but not at other sites immediate to upstream or downstream locations is questionable, but most likely resulted from the influence of a tributary joining the main channel at this location. These variations indicate that processes are diverse among sites in a dynamic creek, and data generated from a few sites, while useful to identify local processes, requires careful scrutiny to extrapolate or generalize across the entire creek. Intriguingly, the modeling results suggest that river bottom sediments have a greater contribution at the ditch sites, J1, K, and L, but thier role gradually decreases and becomes insignificant from site J downstream. Nonetheless, results from P pool concentrations, ratios of P pools, isotope values, and fingerprinting elements of suspended particulate matter and sediments indicate that physical remobilization is not likely a significant source of PP in the main channel.

Import from Bay. Relationship of P concentration, tidal height, and $\delta^{18}O_w$ and $\delta^{18}O_P$ values of water and end member sites (Chesapeake Bay and low-tide freshwater in upstream sites)[31] showed that the P dilution due to tide could be three to six times at the middle reaches of the creek.[11] The incoming tide increases salinity which promotes aggregation of biotic and other abiotic components in the water column.[40] While the hydrodynamics related to tide and compositional complexity of aggregates are out of the scope of the current study, it is anticipated that the aggregation of fine particles (colloids and nanosized particles) derived primarily from estuarine sources results in new particulate matter. This means that the inward coming tide contributes significantly to the new source of particulate matter as well as transporting it upstream. While a sizable net landward import of P from the ocean is reported from mass balance analysis in the Chesapeake Bay,[20] our findings provide more definitive information on upstream P transport. Since the particulate P sampling was done during ebb tide, in which land-derived sources are expected to dominate, our results indicate that a good proportion of PP is still present in the water returning to the estuary.

Sources of Particulate Matter. Analyses of P_i and P_o content, size and ratios of P pools, isotope values and their trend along the flow direction, and results from fingerprinting element models allowed us to distinguish among contributions from different P sources or through specific biogeochemical processes that regenerate and remobilize P, albeit positive and negative feedback effects complicate discriminating their relative contributions. A closer look at the particular sources along the creek showed that particulate P in the upstream section was dominated by agricultural sources whereas streambank erosion and tidal input were major sources in the downstream section. While the majority of particulate matter is expected to be derived from land sources and given the fact that $\delta^{18}O_P$ values of NaOH−P_i and HCl−P_i are not expected to vary during transport, the gradually heavier isotopes along the flow direction are likely due to the mixing of new P pools in the water column brought by inward coming tides—which contribute significantly to the new source of particulate matter. Overall, our findings provide valuable information on P removal from sources as well as allowing testing on whether P from specific sources and forms are biologically cycled in the continuum from source to sink.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.8b05057.

> Salinity and pH (Table S1), particulate load, salinity and tides (Figures S2, S3, and S4), isotope values (Figure S5), and concentration and model results of fingerprinting elements (Figures S1, S6, and S7) (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*Phone: (302) 831-1376; e-mail: jaisi@udel.edu.

ORCID

Deb P. Jaisi: 0000-0001-8934-3832

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research was supported by research grants from USDA (NIFA awards 2015-67030-23603 and 2017-67019-26333) and NSF (1738770). K.A.M. would like to acknowledge the basic training on isotopes and handling environmental samples to Sunendra Joshi.

■ REFERENCES

(1) Dzombak, D. A. Nutrient Control in Large-Scale U.S. Watersheds: The Chesapeake Bay and Northern Gulf of Mexico. *Natl. Acad. Eng.* **2011**, *41*, 13−22.

(2) Ator, S. W.; Denver, J. M. Understanding Nutrients in the Chesapeake Bay Watershed and Implications for Management and Restoration—the Eastern Shore; U.S. *Geol Survey* **2015**, *1406*, 72.

(3) Noe, G. B.; Harvey, J. W.; Saiers, J. E. Characterization of suspended particles in Everglades wetlands. *Limnol. Oceanogr.* **2007**, *52*, 1166−1178.

(4) Conley, D. J.; Smith, W. M.; Cornwell, J. C.; Fisher, T. R. Transformation of particle-bound phosphorus at the land-sea interface. *Estuarine, Coastal Shelf Sci.* **1995**, *40*, 161−176.

(5) Fitzsimons, M. F.; Lohan, M.C.; Tappin, A. D.; Millward, G. E. The role of suspended particles in estuarine and coastal biogeochemistry. In *Treatise on Estuarine and Coastal Science, Vol. 4, Geochemistry of Estuaries and Coasts*; Shimmield, G., Ed.; Elsevier, 2012, pp 71−114.

(6) Peijnenburg, W.; Jager, T. Monitoring approaches to assess bioaccessibility and bioavailability of metals: Matrix issues. *Ecotoxicol. Environ. Saf.* **2003**, *56*, 63−77.

(7) Reynolds, C. S.; Davies, P. S. Sources and bioavailability of phosphorus fractions in freshwaters: A British perspective. *Biol. Rev.* **2001**, *76*, 27−64.

(8) Ellison, M. E.; Brett, M. T. Particulate phosphorus bioavailability as a function of stream flow and land cover. *Water Res.* **2006**, *40*, 1258−1268.

(9) Pacini, N.; Gachter, R. Speciation of riverine particulate phosphorus during rain events. *Biogeochemistry* **1999**, *47*, 87−109.

(10) Hedley, M. J.; Stewart, J. W. B.; Chauhan, B. Changes in inorganic and organic soil phosphorus fractions induced by cultivation practices and by laboratory incubations. *Soil. Sci. Soc. Am. J.* **1982**, *46*, 970−976.

(11) Upreti, K.; Joshi, S. R.; McGrath, J.; Jaisi, D. P. Factors controlling phosphorus mobilization in a coastal plain tributary to the Chesapeake Bay. *Soil. Sci. Soc. Am. J.* **2015**, *79*, 826−837.

(12) Newberry, S. L.; Prechsl, U. E.; Pace, M.; Kahmen, A. Tightly bound soil water introduces isotopic memory effects on mobile and extractable soil water pools. *Isot. Environ. Health Stud.* **2017**, *53*, 368−381.

(13) Tiessen, H.; Stewart, J. W. B.; Cole, C. V. Pathways of phosphorus transformations in soils of differing pedogenesis. *Soil. Sci. Soc. Am. J.* **1984**, *48* (4), 853−858.

(14) Joshi, S. R.; Li, X. N.; Jaisi, D. P. Transformation of phosphorus pools in an agricultural soil: an application of oxygen-18 labeling in phosphate. *Soil. Sci. Soc. Am. J.* **2016**, *80*, 69−78.

(15) Joshi, S. R.; Li, W.; Bowden, M. E.; Jaisi, D. P. Sources and mechanisms of formation of acid extractable phosphorus pools in an agricultural soil. *Soil Sys* **2018**, *2*, 45−64.

(16) Chang, S. J.; Blake, R. E. Precise calibration of equilibrium oxygen isotope fractionations between dissolved phosphate and water from 3 to 37 degrees C. *Geochim. Cosmochim. Acta* **2015**, *150*, 314−329.

(17) Stewart, H. A.; Massoudieh, A.; Gellis, A. Sediment source apportionment in Laurel Hill Creek, PA, using Bayesian chemical mass balance and isotope fingerprinting. *Hydrol. Proc.* **2015**, *29*, 2545−2560.

(18) Collins, A. L.; Zhang, Y. S.; Duethmann, D.; Walling, D. E.; Black, K. S. Using a novel tracing-tracking framework to source fine-grained sediment loss to watercourses at sub-catchment scale. *Hydrol. Proc.* **2013**, *27*, 959−974.

(19) Massoudieh, A.; Gellis, A.; Banks, W. S.; Wieczorek, M. E. Suspended sediment source apportionment in Chesapeake Bay watershed using Bayesian chemical mass balance receptor modeling. *Hydrol. Proc.* **2013**, *27*, 3363−3374.

(20) Boynton, W. R.; Garber, J. H.; Summers, R.; Kemp, W. M. Inputs, transformations, and transport of nitrogen and phosphorus in Chesapeake Bay and selected tributaries. *Estuaries* **1995**, *18*, 285−314.

(21) Metropolis, N.; Rosenbluth, A. W.; Rosenbluth, M. N.; Teller, A. H.; Teller, E. Equations of state calculations by fast computing machines. *J. Chem. Phys.* **1953**, *21*, 1087−1092.

(22) Geweke, J.; Tanizaki, H. Bayesian estimation of state-space models using the Metropolis-Hastings algorithm within Gibbs sampling. *Comput. Stat. Data Anal.* **2001**, *37*, 151−170.

(23) Jordan, T. E.; Cornwell, J. C.; Boynton, W. R.; Anderson, J. T. Changes in phosphorus biogeochemistry along an estuarine salinity gradient: The iron conveyer belt. *Limnol. Oceanogr.* **2008**, *53*, 172−184.

(24) Manning, P. G.; Wang, X. W. The binding of Pb, Zn, and other metal-ions in suspended riverine particulate matter. *Can. Miner.* **1995**, *33*, 679−687.

(25) Stout, L. M.; Nguyen, T. T.; Jaisi, D. P. Relationship of phytate, phytate-mineralizing bacteria, and beta-propeller phytase genes along a coastal tributary to the Chesapeake Bay. *Soil Sci. Soc. Am. J.* **2016**, *80*, 84−96.

(26) Li, J. Y.; Reardon, P.; McKinley, J. P.; Joshi, S. R.; Bai, Y. G.; Bear, K.; Jaisi, D. P. Water column particulate matter: A key contributor to phosphorus regeneration in a coastal eutrophic environment, the Chesapeake Bay. *J. Geophys. Res.: Biogeosci.* **2017**, *122*, 737−752.

(27) Li, W.; Joshi, S. R.; Hou, G.; Burdige, D. J.; Sparks, D. L.; Jaisi, D. P. Characterizing phosphorus speciation of chesapeake bay sediments using chemical extraction, P-31 NMR, and X-ray absorption fine structure spectroscopy. *Environ. Sci. Technol.* **2015**, *49*, 203−211.

(28) Jaisi, D. P.; Kukkadapu, R. K.; Stout, L. M.; Varga, T.; Blake, R. E. Biotic and abiotic pathways of phosphorus cycling in minerals and sediments: insights from oxygen isotope ratios in phosphate. *Environ. Sci. Technol.* **2011**, *45*, 6254−6261.

(29) Stout, L. M.; Joshi, S. R.; Kana, T. M.; Jaisi, D. P. Microbial activities and phosphorus cycling: An application of oxygen isotope ratios in phosphate. *Geochim. Cosmochim. Acta* **2014**, *138*, 101−116.

(30) Ishee, E. R.; Ross, D. S.; Garvey, K. M.; Bourgault, R. R.; Ford, C. R. Phosphorus characterization and contribution from eroding streambank soils of Vermont's Lake Champlain Basin. *J. Environ. Qual.* **2015**, *44*, 1745−1753.

(31) Li, J. Y.; Bai, Y. G.; Bear, K.; Joshi, S.; Jaisi, D. Phosphorus availability and turnover in the Chesapeake Bay: Insights from nutrient stoichiometry and phosphate oxygen isotope ratios. *J. Geophys. Res.: Biogeosci.* **2017**, *122*, 811−824.

(32) Joshi, S. R.; Kukkadapu, R. K.; Burdige, D. J.; Bowden, M. E.; Sparks, D. L.; Jaisi, D. P. Organic matter remineralization predominates phosphorus cycling in the mid-bay sediments in the Chesapeake Bay. *Environ. Sci. Technol.* **2015**, *49*, 5887−5896.

(33) Sun, M. J.; Alikhani, J.; Massoudieh, A.; Greiner, R.; Jaisi, D. P. Phytate degradation by different phosphohydrolase enzymes: contrasting kinetics, decay rates, pathways, and isotope effects. *Soil. Sci. Soc. Am. J.* **2017**, *81*, 61−75.

(34) Jaisi, D. P.; Blake, R. E.; Liang, Y.; Chan, S.-J., Exploration of compound-specific organic-inorganic phosphorus transformation using stable isotope ratios in phosphate. In *Applied Manure and Nutrient Chemistry for Sustainable Agriculture and Environment*; Zhang, Z. H., Ed.; Springer: 2014; pp 267−292.

(35) Vadas, P. A.; Srinivasan, M. S.; Kleinman, P. J. A.; Schmidt, J. P.; Allen, A. L. Hydrology and groundwater nutrient concentrations in a ditch-drained agroecosystem. *J. Soil Water Conser.* **2007**, *62*, 178−188.

(36) Liang, Y.; Blake, R. E. Oxygen isotope fractionation between apatite and aqueous-phase phosphate: 20−45 C. *Chem. Geol.* **2007**, *238*, 121−133.

(37) Grundtner, A.; Gupta, S.; Bloom, P. River bank materials as a source and as carriers of phosphorus to Lake Pepin. *J. Environ.Qual.* **2014**, *43*, 1991−2001.

(38) Joshi, S. R. *Biogeochemical Cycling of Phosphorus in the Chesapeake Bay and Its Watershed: Insights from Phosphate Oxygen Isotope Ratios*; University of Delaware: Newark, 2016.

(39) Jaisi, D. P.; Blake, R. E.; Kukkadapu, R. K. Fractionation of oxygen isotopes in phosphate during its interactions with iron oxides. *Geochim. Cosmochim. Acta* **2010**, *74*, 1309−1319.

(40) Stumm, W.; Morgan, J. J. *Aquatic Chemistry*; Wiley: New York, 1996.