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LINKING SOURCES, TRANSFORMATION, AND LOSS OF PHOSPHORUS IN THE SOIL–WATER CONTINUUM IN A COASTAL ENVIRONMENT

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8.1. PHOSPHORUS: AN ESSENTIAL NUTRIENT TURNED INTO A CONTAMINANT

The agricultural revolution has changed the flow of phosphorus (P) essentially unidirectional – from the exploitation of geologic reserves to produce fertilizers for crop growth and then to foods and fodders for human and animal consumption (Suh and Yee 2011). In this new flow system, driven primarily by human efforts, a significant fraction of the mined P is lost back to the environment. Because of the low stoichiometric need for P compared to other nutritional elements (106C: 16N: 1P; Redfield et al. 1963), small changes in P concentration can cause severe impacts on organism nutrition and water quality (Wetzel 1983). For example, surface water eutrophication and bottom water dead zones in the Chesapeake Bay and the Gulf of Mexico caused by excess nutrients have caught media attention for decades and are still continually highlighted in news and reports such as in the National Academy of Engineering (Dzombak 2011), US Environmental Protection Agency (USEPA) (EPA 2010) and professional magazines (Erickson 2011; Ness 2016). In the 2016 White House report, the National Science and Technology Council (NSTC) highlighted the increasing impacts of harmful algal blooms and hypoxia across hundreds of miles of American coastal and inland waters (WH 2015). Recurring seasonal hypoxia has been one of the lingering problems in the Chesapeake Bay because existing restoration efforts are complicated by the multitude of nutrient sources, temporally and spatially variable inputs, and complex interacting factors affecting their occurrence, fate, and transport (Ator and Denver 2015).

Classically, soil P research centered on agronomic crop yield and developing a robust relationship between available P (e.g. Mehlich, Olsen, or Bray extractable P) and crop yield

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to provide estimates of nutritional needs or fertilizer recommendations (e.g. Syers et al. 2008). On the other hand, geochemical research on water bodies, such as lakes, estuaries, and coastal waters, has historically focused on cycling and transformation of P (Einsele 1936; Ruttenberg and Berner 1993; Hagy et al. 2004). Research efforts that connect processes along transects from agricultural soils to open waters have remained limited. This limitation has caused the knowledge gap to spatially connect P processes from upland soils to open streams and to develop solutions to the complex issue of balancing agronomic P needs and water quality. The current emphasis of US funding agencies (National Science Foundation [NSF] and US Department of Agriculture [USDA]) calling for research at the food–energy–water nexus has aided in catalyzing interdisciplinary research on identifying interrelationships and interdependencies among the three critical resources and help address current challenges on agricultural sustainability and environmental health. In this chapter, we take soil, soil to drainage ditch, and ditch to creek transect approach to identify build-up and transformation of soil P pools as well as loss and transport to the ditch and then to a creek. The seamless research along the transect provides information useful to bridge the competing needs of resources (e.g. crop and water) that are useful to identify ways to evaluate the trade-off and thus to minimize undesirable consequences.

8.2. TRANSFORMATION OF PHOSPHORUS IN SOILS

8.2.1. Transformation of P Pools in Soils Impacted by Agricultural P Loading

Complex interaction between biotic and abiotic processes, which vary both on temporal and spatial scales, controls P dynamics in soils. Plants and microorganisms are two dominant biological drivers that change the concentrations of bioavailable P in soils. Similarly, the major abiotic processes of sorption/desorption and precipitation/dissolution reactions determine the fate of P in soils (e.g. Sharpley 1983; Griffin et al. 2003; Sato et al. 2005). Sequential extraction (Chang and Jackson 1957; Hedley et al. 1982; Ruttenberg 1992) is one of the most widely used operationally defined methods for P research. For example, Hedley et al. (1982) method separates soil P (both organic and inorganic) into H_2O–P, $NaHCO_3$–P, NaOH–P, and HCl–P pools (Figure 8.1). This method is based on the selective properties of reagents used for extracting fairly discrete pools of soil P on the continuum

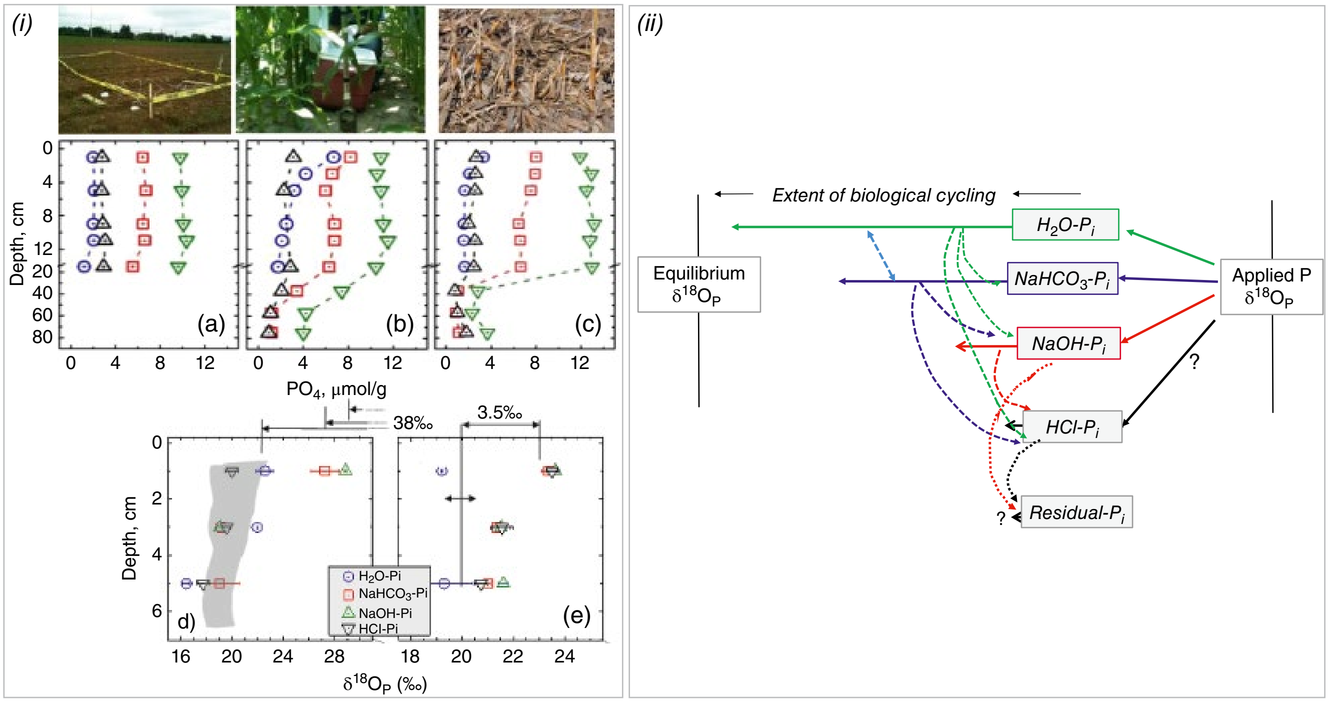

Figure 8.1. (i) Concentrations and isotope values of four P_i pools in an agricultural soil before and after application of ^{18}O-labeled P_i (38‰): (a) 1 day before, (b, d), 18 days after, and (c, e) 155 days after. The shaded region is the average equilibrium isotope composition calculated using equation by Longinelli and Nuti (1973). Equilibrium isotope value is heavier by 0.9–2.3‰ for Chang and Blake (2015) equation. The isotope values of 0–5 cm depth are only shown to highlight the isotope excursion (see Joshi et al. (2016) for additional depths). (ii) Schematic diagram showing biological cycling and transformation of P pools. Different lengths of arrows from P pools to equilibrium isotopes correspond to the relative rate of biological cycling of P pools. The dashed arrows represent the transformation routes of P pools. Source: Revised from Joshi et al. (2016). Reprinted with permission from Wiley.

of increasing bonding energy with soil matrix or minerals. Limited efforts, however, are put into developing relationships among extractability (of reagents) and accessibility and bioavailability (for plants) (Syers et al. 2008). Sequential extraction methods are often criticized for imperfect selectivity, carryover of P pools, lack of independent validation, and methodological artifacts (e.g. Barrow 1986), including the formation of new P pools (e.g. alkaline reagent during NaOH extraction could potentially precipitate new HCl–P pool; Gu et al. 2020). Further user-specified modifications in extraction conditions such as solid-solution ratio, wash step, temperature, time of reaction, and vigor of mixing add complications to compare published databases. These variabilities pose challenge- on relating extracted P pools into corresponding geochemical interpretations. Nonetheless, sequential extraction methods still provide useful information on a relative assessment of P pools that can be empirically related to P forms and used to estimate fate in natural systems. Complementing sequential extraction methods with isotopes (Zohar et al. 2014; Gross and Angert 2015; Pfahler et al. 2017; Helfenstein et al. 2018; Joshi et al. 2018) and spectroscopic methods (solid-state ^{31}P-nuclear magnetic resonance [NMR], P K-edge X-ray absorption near edge structure [XANES] spectroscopy, and X-Ray diffraction) (Shober et al. 2006; Kruse et al. 2015; Liu et al. 2015; Gu et al. 2019, 2020) aid on complement P speciation and can be used to develop a quantitative relationship between P pool and kinetics of biotic and abiotic exchanges (Helfenstein et al. 2018).

Researchers generally agree that inorganic P (P_i) extracted by H_2O (H_2O–P_i) and $NaHCO_3$ ($NaHCO_3$–P_i) represents bioavailable P forms. Conversely, NaOH–P_i and HCl–P_i represent generally unavailable forms that might become partially available depending on various plant- and soil-related factors (e.g. Cross and Schlesinger 1995). NaOH is the most effective reagent to extract organic P (P_o) with minimal hydrolysis and is commonly used in NMR studies (e.g. Cade-Menun 2005). Bioavailability of organic P in agricultural soils is studied much less and is essentially limited to empirical analyses and extrapolation from pure culture or incubation studies. The HCl–P_i is originally thought to represent primary minerals, such as apatite (Tiessen et al. 1984), but the identity of precipitated P minerals in soils has largely been elusive (Joshi et al. 2018).

Formation of one P pool at the expense of other P pools is generally interpreted from changes in the concentration of P pools in spatial and temporal scales (McKenzie et al. 1992; Richards et al. 1995; Lehmann et al. 2005). Those changes, however, could be readily identified from isotope labeling. Recently, a rapid transformation of P pools (applied as ^{18}O labeled P_i) was identified to occur in an agricultural soil (Joshi et al. 2016) (Figure 8.1, i) (see Joshi et al. 2018 for detail analytical methods). The H_2O–P_i pool was found to rapidly exchange oxygen isotopes with water due to biological cycling and thus shifted its phosphate oxygen isotope ($\delta^{18}O_P$) values toward equilibrium (defined by water oxygen isotope ($\delta^{18}O_W$) values and soil temperature) (Chang and Blake 2015; Longinelli and Nuti 1973). This reflects the relative ease of biological cycling of H_2O–P_i pool among all P pools.

The temporal changes in $\delta^{18}O_P$ values of $NaHCO_3$–P_i, NaOH–P_i, and HCl–P_i pools provided information useful to understand the transformation of P pools. For example, a short-term increase in P concentration and simultaneous enrichment of isotopes in H_2O–P_i and $NaHCO_3$–P_i pools toward the isotope value of ^{18}O-labeled P_i (38‰) confirmed that the distribution of labeled P into these two pools. Over time, the labeled P_i was found to be redistributed in all four pools. For example, the $\delta^{18}O_P$ values of $NaHCO_3$–P_i pool became lighter than when it received ^{18}O-labeled P_i at first and calculated from isotope mass balance (in 18 days, Figure 8.1d). This isotope excursion toward equilibrium values suggested that this pool underwent biological cycling. Intriguingly, relatively heavier $\delta^{18}O_P$ values of NaOH–P_i pool than $NaHCO_3$–P_i pool on 18-day time point indicated that the NaOH–P_i received the ^{18}O labeled P but was cycled at the pace slower than $NaHCO_3$–P_i pool. Over a long time (in 155 days), $\delta^{18}O_P$ values of NaOH–P_i pool became slightly lighter (~29–23‰) and closer to equilibrium than 18 days suggesting partial biological cycling of this pool as well. The $\delta^{18}O_P$ value of HCl–P_i pool did not change in a short time (<1 month), which confirms the absence of extraction artifact noted by Gu et al. (2020) that new HCl–P may form from NaOH-desorbed P_i at high pH. However, ~4‰ offset of HCl–P_i in approximately six months is a clear indication that NaOH–P_i or other bioavailable P pools transformed into HCl–P_i. Together, this means that the active transformation of H_2O–P_i and $NaHCO_3$–P_i to NaOH–P_i and eventually into HCl–P_i pool occurs in agricultural soils. Based on these results, a schematic of the pathways of transformation of P pools and concurrent biological cycling can be developed (Figure 8.1, ii).

In summary, results presented above confirmed the progressive transformation of P in soils into less available forms in heavily fertilized soils. This transformation renders original or freshly applied bioavailable P into unavailable forms. Furthermore, some pools showed changes in isotope values without apparent change in concentration (i.e. no net loss or gain) (below the depth not shown in Figure 8.1a; see Joshi et al. 2016). This highlights the need for the isotope method to identify the actual changes in P pools in soils.

8.2.2. Formation of Residual and Recalcitrant P Pools in Soils

Residual P represents the missing piece of the puzzle in the global P crisis (Sattari et al. 2012). The literature often uses multiple definitions for "residual" and "recalcitrant" P. This chapter defines recalcitrant P as the soil P fraction that is not bioavailable but extracted with the stronger reagents during sequential extractions. The residual P is the fraction of P that is not extracted during the sequential extraction method

(Condron and Newman 2011; Read et al. 1973; Sharpe et al. 1984). The residual P pool constitutes a sizeable fraction in soils, ranging from 33 to 51% in a silt loam soil in the Atlantic coastal plain (Joshi et al. 2018) and 45–63% in Chilean Andisol (Velasquez et al. 2015). Quantitation of total P in soils using the most common microwave-assisted acid digestion (US EPA 3051A) method is a gross underestimation because of incomplete dissolution. For example, total P quantified by the microwave method was 64–84% of true total P measured from the complete dissolution of the soil (Joshi et al. 2018). It means the residual P calculated from the difference between the total P quantified from the USEPA method and the sum of sequentially extracted P pools is highly underestimated. Therefore, caution is needed in interpreting total P data and the size of the residual P pool in many past studies.

To understand the long-term P accumulation in soils including the formation of residual P pools, the natural abundance of isotopes is an ideal technique because it does not introduce potential artifacts and perturb physical and chemical equilibria. Most recently, 10 N HNO_3 extraction step was added after the Hedley sequential extraction method to recover a portion of the residual P pool. Comparison of $\delta^{18}O_P$ values of 0.5 M NaOH–P_i, 1 N HCl–P_i, and 10 N HNO_3–P_i pools aided on identifying sources and transformation pathways of residual and recalcitrant P pools (Figure 8.2). The high concentration of Ca in HCl extracted solutions in all soil depths studied suggests that the acid dissolves crystalline Ca–P minerals such as apatite (Tiessen et al. 1983; Cross and Schlesinger 1995), which is consistent with solid-state ^{31}P NMR results (Joshi et al. 2018). The 10 N HNO_3 extract contained a high amount of Fe and Al and overall showed a strong positive correlation with P (R^2 = 0.72–0.95). This result is intriguing because both 1 N HCl and 10 N HNO_3 should dissolve minerals of similar composition, via proton-promoted dissolution, with a difference that 10 N HNO_3 dissolves more crystalline minerals. The similar trends of $\delta^{18}O_P$ values of HNO_3–P_i and NaOH–P_i (closer to fertilizer applied to the field, 22–23.5‰) along with the correlation of elements associated with two pools suggest that NaOH–P_i is a more likely precursor to be transformed into 10 N HNO_3–P_i pool.

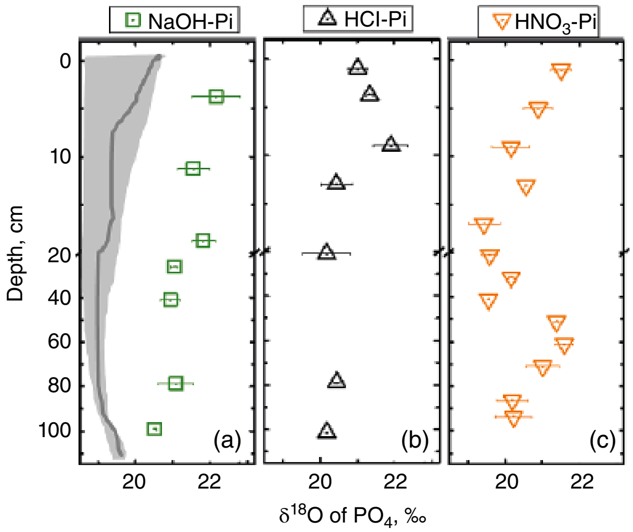

Figure 8.2. Isotope values of three major P_i pools in an agricultural soil as a function of depth: (a) 0.5 M NaOH–P_i, (b) 1 N HCl–P_i, and (c) 10 N HNO_3–P_i. The solid gray line in (a) shows the equilibrium isotope composition and the gray area the variation within the month of soil sampling (Joshi et al. 2018). Source: Joshi et al. (2018). Licensed under CC BY-4.0.

One major limitation of generalizing results from a single time sampling is that it does not capture dynamics of P in soils. For example, there may be several P sources including externally applied fertilizers that contribute to the formation of the HCl–P and HNO_3–P pools. Further, complex interactions among biotic and abiotic reactions could generate and consume P pools. Additionally, various mechanisms by which plant roots and soil (micro)organisms remove P from acid-P pools are known and have been discussed in the past (e.g. Guo et al. 2000; Richardson and Simpson 2011). A possible reverse pathway of forming available P pools from recalcitrant and residual P pools was not considered in this soil because this pathway is expected to be insignificant in agricultural soils where excess P is applied beyond agronomic needs. However, reverse cycling could be significant in nutrient-poor soils such as in forests and prairies.

While the sources of residual P is beginning to be explored, the question on the mechanism of transfer of P between pools has remained essentially unanswered. The literature generally describes P exchange between pools in terms of changes in equilibrium state such as after fertilizer addition or during slow desorption (Hedley et al. 1982; Guo et al. 2000; Syers et al. 2008). The loading of P fertilizer in excess of plant needs results in redistribution P pools by solid-state diffusion (Bolan et al. 1985). The presence of solid-state transfer or transformation can be confirmed from isotopes because neither the slow chemical transformation of the NaOH–P_i pool nor precipitation of HCl–P_i alter the original P isotopic signature, except for minor kinetic fractionation (Jaisi et al. 2010), which is erased quickly. If NaOH–P_i pool remains recalcitrant, its transformation into residual P should lock in its isotopic signatures (e.g. Jaisi and Blake 2010; Joshi et al. 2015). Combining isotope with other research techniques capable of identifying chemical specificity of P such as NMR and synchrotron X-Ray is a way forward for the mechanistic understanding of the formation of residual P in soils.

8.3. SURFACE AND SUBSURFACE FLOW OF PHOSPHORUS FROM AGRICULTURAL SOILS TO OPEN WATER

Chronic loss of P accumulated in agricultural soil over a long time has been increasingly recognized as a major reason for degraded water quality (e.g. Sharpley et al. 2013).

Despite the traditional consideration that leaching is a minor P transport mechanism, subsurface transport of P has been increasingly realized as a primary P transport pathway in artificially drained agricultural soils, such as low lying Mid-Atlantic coastal plain of the Delmarva Peninsula (Djodjic et al. 2000; Kleinman et al. 2015; Shober et al. 2017; NRCS 2019). In such soils, overland flow is suggested to be a minor component of P loss (<8%) (Kleinman et al. 2007; Vadas et al. 2007). Site-specific conditions that delimit pathways of P transport and the magnitude of loss are local hydrology, soil type, pore sizes, and structures (de Jonge et al. 2004), flow regime, catchment size, and storm events (Heathwaite and Johnes 1996), and agricultural practice such as irrigation.

A recent agricultural field-to-ditch transect study analyzed soil P pools, paired them with dissolved P and particulate P (PP) speciation (Bear 2016) (Figure 8.3). Among P pools along the transect, both readily bioavailable (H_2O–P_i and $NaHCO_3$–P_i) and relatively recalcitrant (NaOH–P_i and HCl–P_i) soil P pools were high in agricultural fields. Concentrations of $NaHCO_3$–P_i and NaOH–P_i pools were relatively similar in farm and ditch sites. However, the ditch pH varied from 5.2 to 9.1 depending on the season for the phytoplankton bloom and diurnal cycle. A higher variation of pH is expected in small water bodies (Gao et al. 2014) and P release due to pH change is well documented (Smith et al. 2012). Furthermore, $\delta^{18}O_P$ values of NaOH–P_i of agricultural soil and particulate matter in the ditch were found to be very similar. While it is obvious that particulate matter in the ditch is derived from agricultural soils, the similarity of $\delta^{18}O_P$ values of specific P pools points toward the relative mobility of two recalcitrant P pools. For example, NaOH–P_i is readily mobilized from agricultural soils because Fe and Al oxides are more likely to exist in colloidal form than Ca–P precipitates in HCl–P pool and are selectively transported to the ditch. Here, any contribution of soil H_2O–P_i and $NaHCO_3$–P_i pools to ditch can not be estimated from isotope data because the isotope signatures of these two P pools are often readily overprinted by biological cycling during transport. In-depth research on preferential surface erosion vs. shallow subsurface leaching of P and transport to ditch is required before generalizing P pools selectivity from empirical trends and limited data.

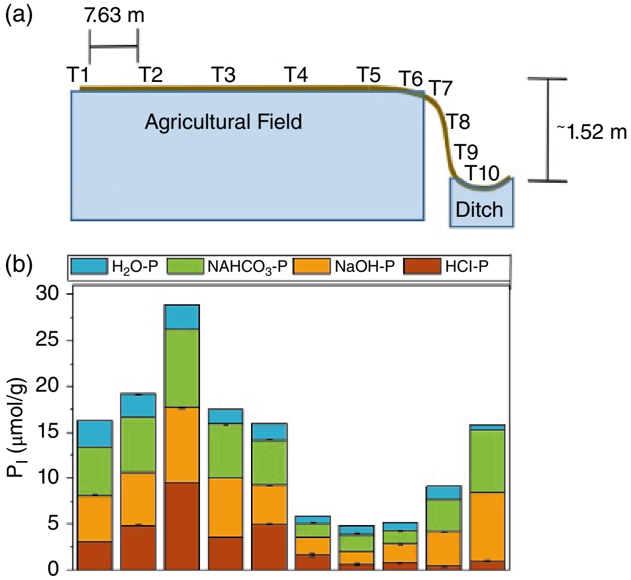

Figure 8.3. (a) Schematics of field-to-ditch transect showing position and spacing of sampling sites in an agricultural field and adjoining ditch. Sites T1–T5 are located on the field, T6–T8 on the ditch slope, and T9–T10 in the ditch. (b) Concentrations of P_i pools at the transect sites. Source: From Bear (2016).

8.4. TRANSPORT OF PHOSPHORUS IN THE MAIN CHANNEL AND EXPORT TO OPEN WATERS

Variation of concentration of P in the creek, measured under the base flow condition, provides information useful for the qualitative evaluation of P hotspots and identifying potential mechanisms. In East Creek, the concentration of dissolved P decreased steadily along the salinity gradient from an agricultural field ditch (site L), the main channel of East Creek, and to the discharge point on the Chesapeake Bay (site A; Figure 8.4) (Upreti et al. 2015). Conversely, the mass of particulate matter increased along the salinity gradient but the P content decreased (Mingus et al. 2019). For instance, the total P_i in the particulate matter was an order of magnitude higher in the ditch than the main channel of the creek, suggesting contribution from critical source areas such as artificially drained fields that have high soil P (Coale and Layton 1999; Stout et al. 2016; Upreti et al. 2015). Temporal analyses of the relationship of tidal height, P concentration, and oxygen isotopes of water identified the tide as the major cause of P dilution downstream, which could be as high as three to six times (Upreti et al. 2015).

Phosphorus in the water column may undergo biological uptake and cycling or sedimentation and that in sediments can be remobilized into the water column as dissolved or suspended forms under imposed physico–chemical and biological conditions. Results from controlled mobilization experiments on creek sediments indicated that under existing field conditions,P was continuously mobilized from the sediments (Figure 8.5) (Upreti et al. 2015). Among the parameters tested, the extent of P mobilization was affected by pH and the effect was most significant under biologically mediated redox changes. The dissolved oxygen (DO) was found to be constant in the water column. Therefore redox-driven P cycling in the water column is not expected. However, Eh decrease to hypoxic level was found in a shallow depth (<1 cm) in the sediment. It means the redox change-related P release could likely happen in the sediment. Assuming $NaHCO_3$–P as the sole P pool in the surface

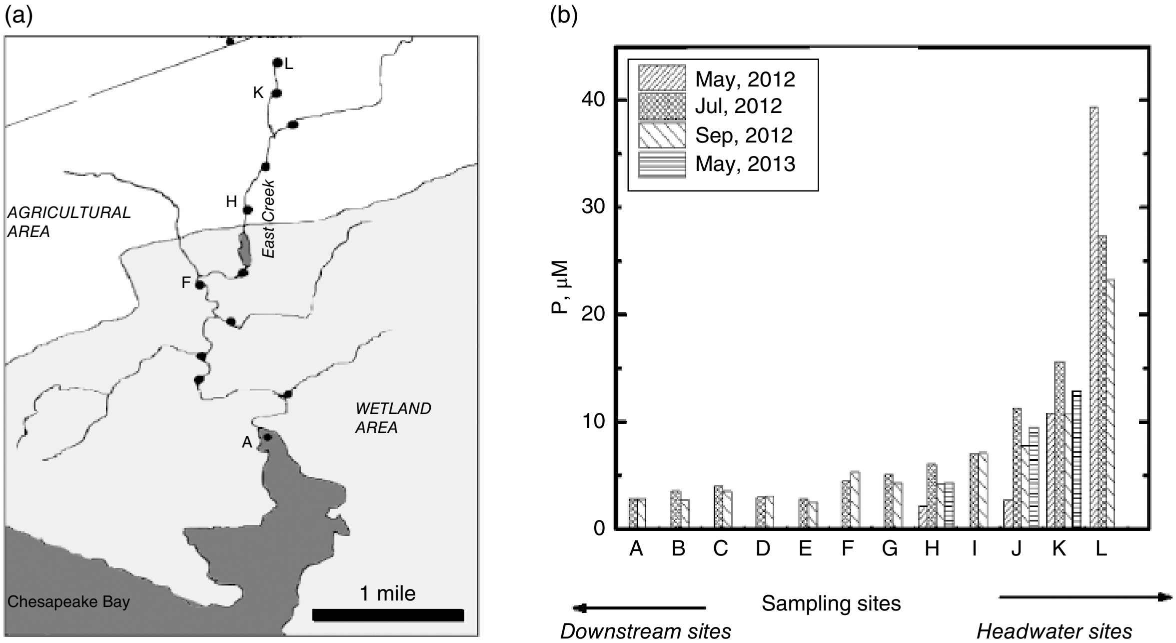

Figure 8.4. (a) Land use map of the East Creek watershed, (b) dissolved P_i concentration over different seasons under base flow condition. The salinity of site L was ~ 0.5 practical salinity unit (PSU) and steadily increased to ~18 at the mouth site (A). Source: From Upreti et al. (2015). Reprinted with permission from Wiley.

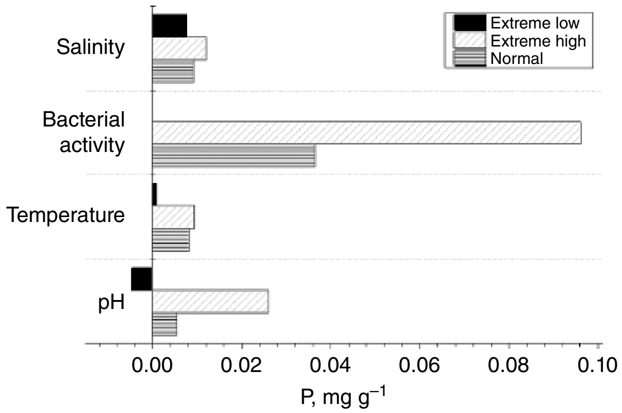

Figure 8.5. Calculated mobilization (positive values) or retention (negative values) of P under field-simulated batch experiments. The normal condition refers to existing field conditions and extreme conditions (both low and high) are likely changes in physicochemical and biological conditions. Source: After Upreti et al. (2015). Reprinted with permission from Wiley.

sediment to be desorbed under the same DO condition, 18–30% of the $NaHCO_3$–P pool may be remobilized if pH were increased from 7.4 to 9.0. Bayesian modeling of fingerprinting elements corroborated these results and predicted up to 5% of the particulate matter in the main channel could be mobilized from the bottom sediment (Figure 8.7). The properties of suspended particulate matter, chemical form of P, and ambient conditions, dominated by pH and salinity, determine the fate of P in the water column.

8.5. SOURCE TRACKING OF P RELEASED FROM SOILS AND UPLAND WATERSHED

Isotopes are useful proxies to identify potential sources of P that forms or releases particulate phosphorus (PP). Analyses of P sources in the watershed including soils from various land cover including forest and agricultural soils, manure, and legacy sources including streambank and sediment sources showed partially overlapping $\delta^{18}O_P$ values in HNO_3–P_i pools (Figure 8.6) (Mingus et al. 2019). A 1.0 N HNO_3 was used in the extraction instead of 1.0 N HCl to avoid the complication that might arise from Cl^- ions during isotope processing. The overlapping isotope signatures of particulate P suggested a mixture of potential P sources. Given variable sources and processes that contribute differently in the upstream and downstream portions of the creek, isotope data can be further scrutinized for different regions or subbasins of the watershed where one source dominate. For example, much lighter $\delta^{18}O_P$ values in 1 N HNO_3–P_i pool were present in ditch sediment, which reflects the likely condition for the precipitation of Ca–P minerals from dissolved P derived primarily from the hydrolysis of organic P (analogous to Chesapeake Bay sediment (Joshi et al. 2015).

To further differentiate the contributions from multiple P sources in this watershed including those with overlapping isotope signatures (Figure 8.6), Bayesian model analyses of fingerprinting elements (e.g. Massoudieh and Kayhanian 2013) were found to be useful. Based on the potential sources in the field and knowledge of site-specific physicochemical and biogeochemical conditions of P release, the contribution

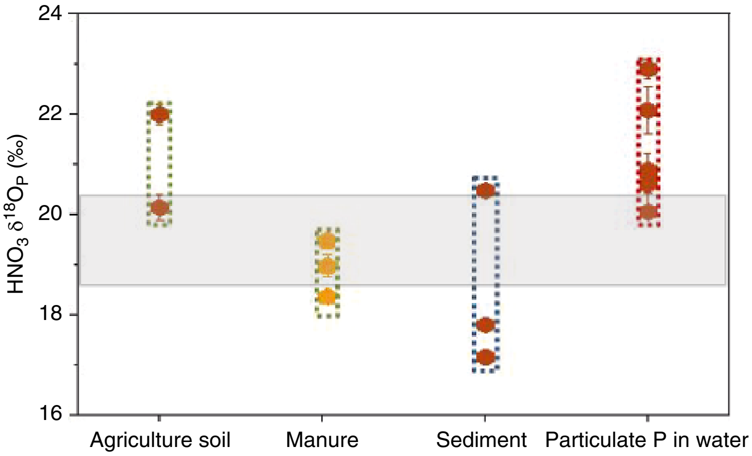

Figure 8.6. Phosphate oxygen isotope values of HNO$_3$–P pool from three possible sources of particulate P in the water column in East Creek watershed. Source: Mingus et al. (2019). Reprinted with permission from ACS.

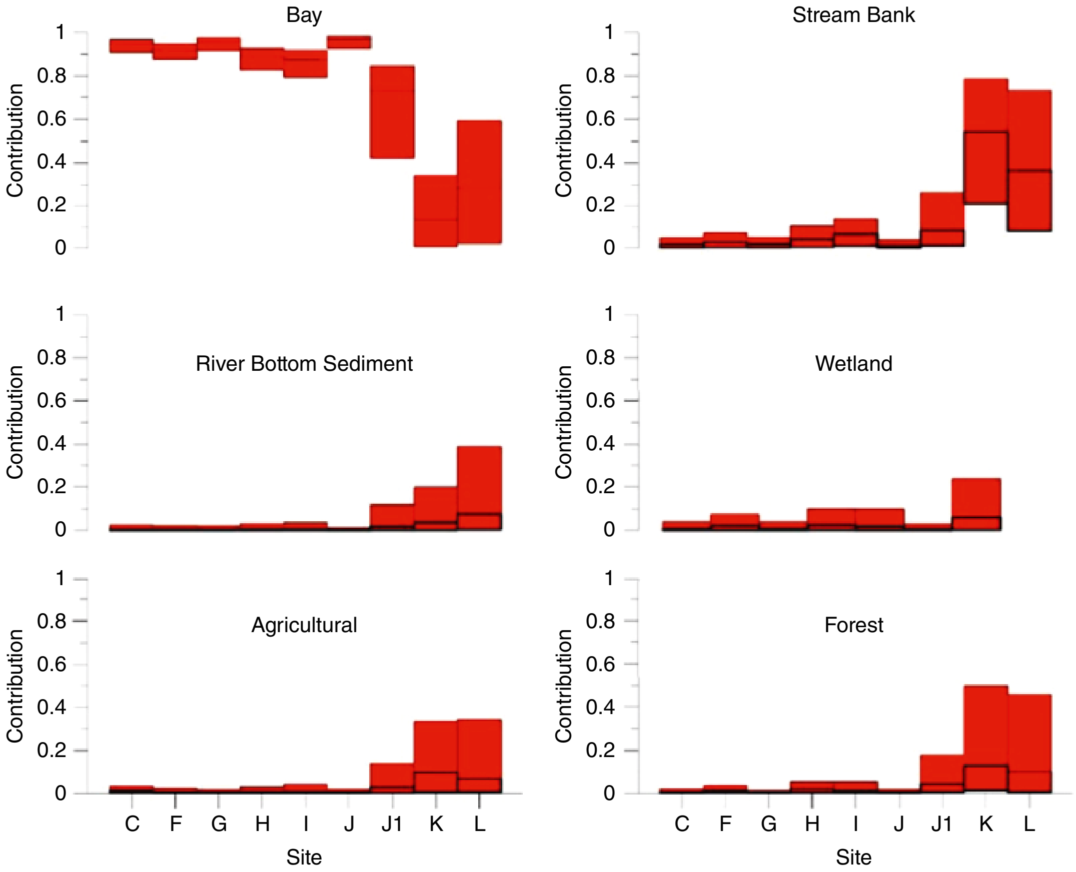

Figure 8.7. Inferred sources in the particulate matter in the creek using fingerprinting elements. The bars shown for each site indicate the range of contribution of each source with a 95% probability (Mingus et al. 2019). The site name corresponds to that listed in Figure 4a. Source: Mingus et al. (2019). Reprinted with permission from ACS.

of six different potential sources to the particulate matter in the water column was model analyzed (Figure 8.7). Among sources, the Bay water was the major contributor (~80–97%) in all sites with the exception of most upstream, freshwater ditch sites (J1, K, and L). The range of contributions from other potential sources varied significantly as well, which increases the uncertainty in discriminating sources. Nonetheless, some trends are conspicuous. For example, a trend of decreasing contribution of particulate matter derived from Bay water source was clear with the tide moving upstream. The incoming tide increased salinity which promoted agglomeration of both biotic and abiotic components

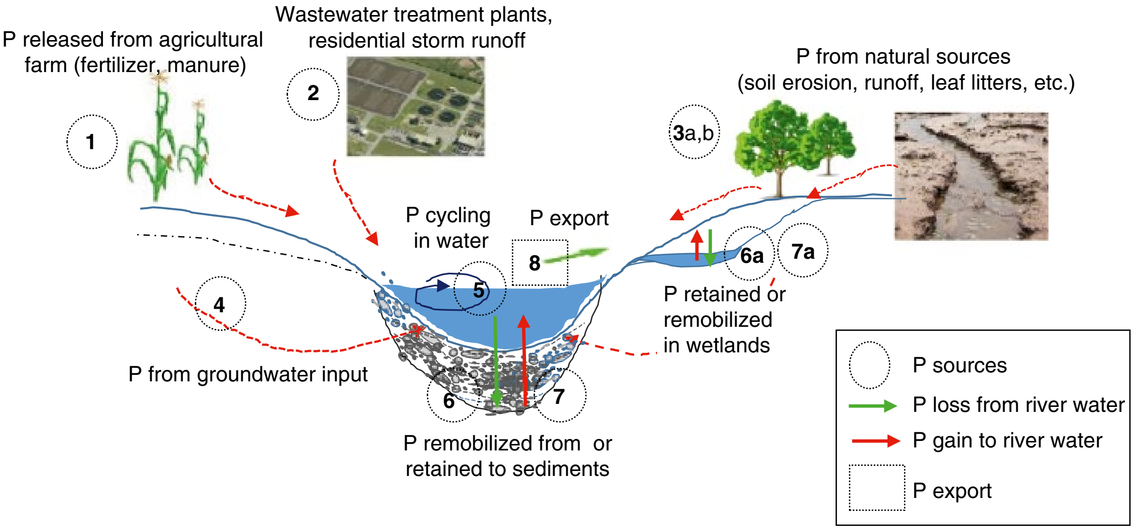

Figure 8.8. A conceptualized transverse cross-section of a water body showing different P sources, internal cycling, input, and output to and from sediments. The potential sources vary based on land use and land application surrounding a water body.

(Stumm and Morgan 1996). Agglomerated inorganic particles and biogenic materials imported from estuarine sources combined with *in-situ* particles and formed new flocs of particulate matter. Since the P content is high in particulate matter compared to dissolved P on mass (of water or solid) basis, P is imported as particulate matter. This result is consistent with past findings that a sizable landward import of P from the ocean occurs in the Chesapeake Bay through tides (Boynton et al. 1995). These results point that the elemental fingerprinting method is useful to estimate P source and transport processes. These outcomes collectively suggest that during the flood tide, when tidal current is flowing inland, the dissolved P in creek water is diluted but the agglomeration of dissolved constituents is enhanced.

8.6. IMPLICATION AND FUTURE RESEARCH DIRECTIONS

Research to identify P sources and biogeochemical processes affecting P in watersheds using tracers is in the early stages. Measured concentration at a particular point in agricultural-runoff dominated creek and river is a function of different sources, processes, and cycling (discussed above) (Figure 8.8). Knowledge of original isotopic signatures of P sources and isotope excursion during pathways of P cycling is necessary to calculate the isotope mass balance and the input and output fluxes from the specific water bodies of interest. This will provide information useful to identify the critical source or sink areas that could potentially promote or inhibit P release to open waters. Application of phosphate oxygen isotopes to track sources of residual and recalcitrant P pools, particularly of Ca–P minerals in soils is relatively straightforward because they retain original source signatures at the time of precipitation and are stable over long time periods (Blake et al. 2010; Jaisi and Blake 2010; Joshi et al. 2015). Furthermore, partial dissolution does not alter the isotopic composition of residual P minerals (Liang and Blake 2007). If an appropriate method is devised to generate equilibria among different P pools based on the measured residual P pool that enables back-calculation of other labile pools in the past, an estimate of historical P loading in a waterbody can be generated. In that regard, isotope signatures serve as a “marker” tool to identify the accumulation of various generations of legacy P in the soil and aid in calculating historical loading. On the other hand, connecting legacy P to the original sources that were used in the agricultural lands in the past will build a framework to comprehend long-term P dynamics in the soil–water continuum. Collectively, it provides a foundation to forecast future scenarios as well as to develop better nutrient management strategies.

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