CHARACTERIZATION OF LEGACY SOIL P AND QUANTIFICATION OF SUBSURFACE LOSSES UNDER ARTIFICIAL DRAINAGE

by

Lauren Rose Mosesso

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Lauren R. Mosesso

Approved: ____

Erik Ervin, Ph.D.
Chair of the Department of Plant and Soil Sciences

Approved: ____

Calvin Keeler, Ph.D.
Interim Dean of the College of Agriculture and Natural Resources

Approved: ____

Louis F. Rossi, Ph.D.
Vice Provost for Graduate and Professional Education and
Dean of the Graduate College

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: ____

Amy L. Shober, Ph.D.
Professor in charge of dissertation

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: ____

Anthony R. Buda, Ph.D.
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: ____

Casey D. Kennedy, Ph.D.
Member of dissertation committee

I certify that I have read this dissertation and that in my opinion it meets the academic and professional standard required by the University as a dissertation for the degree of Doctor of Philosophy.

Signed: ____

Amy S. Collick, Ph.D.
Member of dissertation committee

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ABSTRACT

Phosphorus (P) losses from agriculture can contribute to excess P loading within water bodies and cause eutrophication. Many soils on the Delmarva Peninsula have an increased risk of soil P loss to water bodies due to historical application of poultry litter at N-based rates. The risk for P loss through subsurface pathways is increased due to artificial drainage. However, the mechanisms of soil P loss via subsurface pathways are poorly understood. In addition, there is evidence P solubility in P-enriched soils may decrease with time, especially if P applications are stopped. In this dissertation, we applied methods in chemical and isotope hydrology, soil chemistry and physics, and agronomy to better understand the risk of P mobility and loss through subsurface pathways in soils with a history of P amendment. The objectives of this dissertation project were to: 1) characterize the inorganic P species in agricultural soils amended with various P sources to predict the risk of P mobility 2) determine if soil health practices exacerbate P losses by evaluating soil P stratification and dry aggregate stability in soils with and without a history of soil health practices, and 3) use concentration-discharge (C-Q) relationships, hydrograph separation, and the seasonal origin index (SOI) to identify pathways of subsurface P loss in a ditch-drained field.

Chapters 2 and 3 focused on characterizing the sources and solubility of soil P to predict the risk of P loss. The X-ray absorption near edge structure spectroscopy fitting results identified various aluminum (Al)-, calcium (Ca)-, and iron (Fe) phosphates and P sorbed phases in soils with at least 1% total P and amended with fertilizer, poultry litter, and dairy manure (Objective 1). In drawdown scenarios, we would expect plant P uptake first from semicrystalline Al and Fe phosphates followed by P sorbed phases. Surface P stratification, P accumulation with depth, and soil

aggregate stability was not apparent in selected Delaware soils, which was likely due to significant enrichment of soil P from historical applications of manure prior to the implementation of soil health practices (Objective 2). As such, we saw no evidence that adding soil health practices to these P-enriched soils significantly increased the risk for runoff and leachate dissolved soil P losses as these soils were already a significant potential source of dissolved P.

Chapters 4 and 5 focused on the use of C-Q relationships and the SOI to understand subsurface pathways of P transport and loss. In general, findings from the C-Q study showed that groundwater dilution from matrix flow resulted in low P concentrations within the ditch during small storm events (Q <6.4 L s^{-1}). For large storm events (Q >6.4 L s^{-1}), ditch water P concentrations were elevated due to high water tables interacting with high surface soil P concentrations (averaging 425 mg kg^{-1} in the top 20 cm) and infiltrating precipitation that transported high P soil waters via vertical preferential flow paths (Objective 3). Data from the SOI study revealed that ditch waters were generally synchronized with precipitation at the time of sampling, with wintertime ditch waters exhibiting slight winterlike SOI values (mean daily SOI = -0.20) and summertime ditch waters showing modest summerlike SOI values (mean daily SOI = 0.22). Hence, a relatively equal portion of winter and summer precipitation moved rapidly to the ditch during these seasons, indicating a role for preferential flow (Objective 3). Higher total dissolved P (TDP) concentrations were observed during the summer compared to winter (0.38 vs. 0.13 mg L^{-1}) suggested that antecedent soil moisture may have influenced the amount of P that was lost via preferential flow.

Overall, this dissertation provided insights on how to help land managers make improved nutrient management decisions by predicting P mobility in soils with long-term applications of manure or fertilizers and soil health practices and better understanding pathways of P loss in artificially drained fields.

Chapter 1

LITERATURE REVIEW

1.1 Phosphorus Loss by Subsurface Pathways to Drainage Ditches on the Delmarva Peninsula

1.1.1 Rise of the Delmarva Broiler

The Delmarva Peninsula, consisting of Delaware, nine counties in Maryland and two counties in Virginia, sits between the Delaware and the Chesapeake Bays. Most Delmarva Peninsula soils are Atlantic Coastal Plain soils that are generally sandy, low in cation exchange capacity (CEC) and soil organic matter (SOM), and have high-water tables (Leytem et al., 2003). Starting in the 1700s, flooded soils on the Delmarva Peninsula were drained for agricultural lands by digging open drainage ditches. Drainage ditches increase crop production by lowering the water table and are well suited for very flat landscapes with sandy soils and high lateral hydraulic conductivity (Dunn and Mackay, 1996), like the cropland on the Delmarva (Kleinman et al., 2015). The first known organized drainage ditch project, the Long Marsh ditch in Queen Anne's and Caroline counties in MD, was dug in 1789 (Needelman et al., 2007; Vadas et al., 2007). Twenty years after the first legislation of Delmarva tax ditches in 1793, ditch companies or corporations organized the construction and collection of taxes to create tax ditches under drainage laws in both MD and DE (Ritter, 2010). Around the 1950s, MD and DE passed new drainage laws that created tax collecting, public ditch organizations that oversaw the construction and maintenance of drainage ditches. Today, open ditch drainage is still widely used to drain 25% of DE cropland and 30% of MD cropland (Ritter, 2010).

Commercial broiler production on the Delmarva began in the 1920s and significantly increased during the 1960s. The large production increase in the 1960s was attributed to the combination of broiler production and processing steps with the implantation of vertical integration, processing, and marketing of the broiler (Delmarva Poultry Industry, 2014; Sims et al., 1998). In 2015, high-density broiler production made up 74% of the Delmarva's agriculture sector with eleven million broilers produced a week, or around 600 million broilers a year (Ozbay et al., 2016; Kibet at al., 2011). As a result, the broiler production on the Delmarva Peninsula produces more than 700,000 tons of manure a year (Guo and Song, 2009).

1.1.2 Nutrient Loss and Imbalance on the Delmarva Peninsula

In previous decades, Delmarva farmers faced a lack of economically feasible options to dispose of produced poultry manure. Delmarva farmers turned towards applying poultry litter (bedding and manure) to the agricultural lands surrounding their poultry operations (Leytem et al., 2003; Guo and Song, 2009; Toor and Sims, 2015; Kleinman et al., 2007). Litter was applied to agricultural soils at rates exceeding P crop demand to build up soil P reserves for future use (Vaughan et al., 2007; Ozbay et al., 2016). It was believed that all applied P, including excess, would stay immobile in the soil as soil tightly binds with P and surface runoff is minimal in on the Delmarva (Ritter 2010; Vadas et al., 2007). Due to decades of historical litter application at rates exceeding P crop demand, many areas on the Delmarva now have highly P-saturated soils. In P-saturated soils, all potential P sorption sites (Al and Fe oxides, clays, carbonates) are occupied, and the bound P is immobile (Toor and Sims, 2015). The excess P remains in the soluble solution pool, and, as the soluble P pool grows, P can more easily be lost from soil (Sharpley et al., 2013; Toor and Sims, 2015; Ozbay et al., 2016). Phosphorus draw down of these high-P soils may take 25 years or more under normal cropping conditions with no additional P inputs before soil P concentrations return to the agronomic optimum level (Fiorellino et al., 2017). The reality is that many Delmarva soils continue to receive manure inputs (albeit at lower rates) and are at risk for P losses during storm events or irrigation by way of runoff or subsurface leaching; the problem is exacerbated in areas drained by open ditches (Kleinman et al., 2015a). Drainage ditches act as conduits for P into large water systems, such as the Chesapeake Bay, as water and P collected in the tax ditch drains to larger and larger water bodies (Sallade and Sims, 1997; Vadas and Sims, 1998; Needelman et al., 2007). Excess P within water systems results in degradation of water quality due to eutrophication (Qin and Shober, 2018). Phosphorus lost from agricultural soils will reach waterbodies like the Chesapeake Bay at staggered times due to storage and transport within streams, resulting in a lag in water quality improvement for months to years after initial P application on soil (King et al. 2015; Sharpley et al. 2013).

Both MD and DE require nutrient management plans that generally restrict manure applications to P-based rates in response to P-saturated soils (Perez 2015), resulting in the need for more land base to assimilate the manure. As a result, MD and DE implemented manure transport cost-share programs to reduce manure application to lands nearest the poultry operations, which are more likely to be enriched with P (Perez, 2015; Sims et al., 2016). Nutrient imbalances on Delmarva continue to grow in light of nutrient management regulation due to the need to supplement locally grown grain with grain imported from the Mid-West to support the broiler industry, resulting in poultry litter containing nutrients from both the Delmarva and Mid-west feed (Beegle et al., 2013). This poultry litter is applied to soils on the Delmarva, adding to the nutrient pool in the region (Kellogg et al., 2010; Leytem et al., 2003).

1.1.3 Subsurface Flow and Phosphorus Losses in Coastal Plain Artificially Drained Soils

Prior to the late 1990s, surface runoff was considered the main form of P loss while P loss through leaching and subsurface transport was thought to be minimal on the Delmarva Peninsula (Vadas et al., 2007). Sims et al. (1998) recognized that P leaching and subsurface transport can be significant in fields with preferential flow pathways, sandy soils, and high water tables, long term application of manure/fertilizer resulting in P saturated soils, and artificial drainage, all of which are present on the Delmarva Peninsula (Toor and Sims, 2015). As a result, Delmarva farmers face serious nutrient management issues related to subsurface P loss from agricultural soils enriched with “legacy P.”

Researcher found that around 90% of annual ditch P export (“legacy” and newly applied P) from heavily manured fields occurs in subsurface pathways and reported TDP loss of 0.6-3.6ha^{-1} yr^{-1} at the University of Maryland Eastern Shore (UMES) research farm (Kleinman et al., 2007; Mosesso et al., 2021). Water movement through preferential flow pathways (i.e., macropores) from storm events or irrigation is common (Kleinman et al., 2015a) and accelerate P export to drainage ditches (Toor and Sims, 2015). Vadas et al. (2007) found that the water table at the UMES site is perched on an argillic clay horizon for up one to two days after a storm event. During perching, the stratified top layer of P is saturated, creating reducing conditions and mobilizing oxide-bound P that can potentially be lost from the soil.

Perching ceased when the water infiltrated through the clay layer or moved laterally (Vadas et al., 2007). Robinson et al. (2021) used time-lapse electrical resistivity imaging (ERI) to track the movement of injected KBr on a study field at the UMES Research Farm. They found that the tracer moved quickly by vertical preferential pathways through the argillic horizon and then slowly and laterally by matrix flow pathways through the sand horizon with travel times of years to decades to reach the drainage ditch. Mosesso et al. (2021) developed a conceptual model of water table interactions with stratified P hotspots and preferential flow pathways during storms of varying magnitude on the same UMES study field.

Determining critical source areas (CSA) for subsurface P loss remains a challenge for managing P leaching in flat agroecosystems. Critical source areas are defined as areas with high concentrations of soil P and high transport potential resulting in an elevated risk of leachate P loss due to the interaction between P hotspots and hydrology within the soil. Correctly identifying critical source areas is important for targeting best management practices (BMPs), such as nutrient management, P removal structures, and vegetative buffers (Thomas et al., 2016). Unlike runoff CSAs, which can be identified using tools such as topographic indices (Sharpley et al., 2009; Thomas et al., 2016), CSAs of P leaching are not easily identified. Geophysical tools may be a viable approach to identify areas of high transport potential that could lead to P leaching, as Robinson et al. (2021) was able to estimate that likely CSAs were mainly within several meters (up to 10 m) of the drainage ditch. In addition, determining drainage intensity with open drainage networks proves difficult as ditches vary widely in terms of their widths, depths, spacings, and placement (not all ditches are parallel or perpendicular to one another;

Shober et al., 2017). As with tile drainage, the more intensive the drainage (i.e., closer spacing and deeper ditches), the higher the risk of subsurface P loss (Skaggs et al., 1994). Despite advances in understanding subsurface P transport in flat, artificially drained agroecosystems, more research is needed to understand the processes and pathways (i.e., residence time, degree of mixing; Shober et al., 2017; Robinson et al., 2021; Mosesso et al., 2021) that increase the risk of P loss from these settings.

1.1.4 Chemical Speciation of Legacy Phosphorus Soils

Understanding chemical speciation within legacy P enriched soils is important to predict the transformations and mobility of P, especially under P drawdown scenarios. Multiple tools including chemical extractions and non-destructive spectroscopy have been used to improve our understanding of P speciation and cycling in soils. While a more detailed review of this topic is available in Qin and Shober (2018), we provide a general overview of chemical extraction and non-destructive direct speciation techniques for P impacted soils.

In brief, sequential chemical extraction techniques are used to characterize inorganic and organic P species in soils (Chang and Jackson, 1958; Hedley et al., 1982). Sequential chemical extraction employs reagents of increasing P soil extraction strength to partition P into operational "pools" to predict relative bioavailability (Hedley et al., 1982). While useful, chemical extraction techniques cannot be used to determine the exact chemical P species present in soils, as P species may be altered with the addition of each reagent and there are no standards of P bioavailability collected within each extracted P fraction. As a result of these limitations, researchers often interpret each fraction differently (Kizweski et al., 2011; Condron and Newman, 2011; Lombi and Susini, 2009). Despite these drawbacks, chemical extraction is costeffective and provides useful information on the effects of fertilizer and manure applications on soil P.

X-ray fluorescence analyses (XRF) and direct speciation techniques such as x-ray absorption near edge structure spectroscopy (XANES) are non-destructive and can improve our understanding of the specific P species in legacy P soils (Hesterberg et al., 2017; Peak et al., 2002; Kelly et al., 2008). X-ray fluorescence analyses of soils requires no sample preparation and quantifies the total elemental composition of soils quickly (Kramar, 1997; Kelly et al., 2008); however, XRF does not give information on P species present. Synchrotron-based XANES allows for speciation of P species (including crystalline, poorly crystalline, and amorphous species) in a variety of environmental samples including soils (Beauchemin et al., 2003) and animal manures (Hesterberg et al.,1999; Peak et al., 2002; Toor et al., 2005; Shober et al., 2006) through use of a fingerprinting technique. Fingerprinting techniques, such as principal component analysis (PCA) or linear combination fitting (LCF), compare the spectra of representative standards with the spectrum of an unknown sample to identify P species within the soil (Fendorf & Sparks, 1996; Wasserman, 1997; Ravel and Newville, 2005). Linear combination fitting can identify three to five dominant species present in the weighted-average, or bulk, soil spectra. For good fitting results, a diverse library of high quality standard spectra that are representative of the selected samples is needed (Beauchemin et al., 2003; Kizewski et al., 2011). Although XANES successfully characterizes inorganic P forms, this method is less useful at identifying organic P forms as it is difficult to discern between organic functional groups bonded to P species (Lombi and Susini, 2009). In addition, environmental samples like soil are highly heterogeneous; an analyzed pellet of soil is a weighted-average of the P species present in the pellet, which may not be representative of all P species impacting P solubility at a larger scale. As such, scaling up results from XANES can be potentially problematic.

Until recently, high P concentrations (>1% or >10 g kg^{-1} total P) were needed to produce good XANES spectra for soils. However, recent advancements in beamline detectors are producing cleaner spectra output in soils with lower P concentrations (<1% or <10 g kg^{-1} total P; T. Wu and G. Sterbinsky, personal communication, 2021). These advanced detectors eliminate spectral noise caused by high concentrations of silicon (Si) and aluminum (Al) found in soils. These cleaner spectra improve identification of P species present within the soil using LCF, allowing researchers to speciate soils with lower P concentrations.

1.2 Hydrologic Tools to Characterize Pathways of Subsurface P Loss

Hydrograph separation (Klaus and McDonnell, 2013), concentration-discharge (C-Q) relationships (Walling and Webb, 1986; Evans and Davies, 1998), and seasonal origin index (SOI; Allen et al., 2019a) are tools that use stable water isotopes or geochemical tracers to characterize the sources and pathways of water and solutes. These tools can be applied in flat, artificially drained agroecosystems, like the Delmarva Peninsula to infer the hydrologic mechanisms that induce subsurface P transport from agricultural soils. These tools can be used to corroborate risk assessment tools like P indices and increase our knowledge of P loss pathways that help agronomists and growers better manage P inputs and reduce soil P losses from fields.

1.2.1 Isotopic and Chemical Hydrograph Separation

Hydrogen has two stable isotopes (^{1}H and ^{2}H) and oxygen has three (^{16}O, ^{17}O, and ^{18}O); the most abundant stable isotopes (^{1}H, ^{2}H, ^{16}O, ^{18}O) are measured. Stable isotopes of oxygen and hydrogen are non-reactive and occur naturally in water molecules; these isotopes are ubiquitous in the environment and follow the same processes through the hydrologic cycle as water (McGuire and McDonnell, 2007). As a water molecule travels throughout a watershed, fractionation through physical processes (e.g., evaporation and condensation) and mixing occur. Both the source of the water and fractionation processes acting on the water molecule result in a unique isotopic signature. When waters are not subject to the effects of evaporation, they are assumed to mix conservatively, thus, water isotopes ($\delta^{18}O$ and $\delta^{2}H$ values) can be used as naturally occurring conservative tracers to characterize the hydrologic pathways of water within a watershed (McGuire and McDonnell, 2007).

Hydrograph separation partitions a stormflow hydrograph into "event" and "pre-event" water using two-component mixing models (Klaus and McDonnell, 2013). "Event" water is water newly added to the watershed, while "pre-event" water consists of water already in the watershed. In flat agroecosystems, like those found on the Delmarva Peninsula, "event" water is assumed to be precipitation moving through preferential flow pathways as overland flow is minor in flat landscapes (Vidon and Cuadra, 2011; Klaus et al., 2013), while "pre-event" water represents soil water and groundwater that move thorough matrix flow (Steenhuis et al., 1994; Klaus and McDonnell, 2013). In agricultural landscapes where vertical preferential flowpaths are known to facilitate the transport of soil P to ditches (Kleinman et al., 2015; Toor & Sims, 2015), the fraction of "event water" has been interpreted to represent the relative significance of preferential flowpaths to subsurface P leaching (Klaus et al., 2013;

Vidon & Cuadra, 2011; Williams et al., 2016). The mixed model equation for two-component hydrograph separation is:

$$Q_t = Q_p + Q_e$$

$$C_t Q_t = C_p Q_p + C_e Q_e$$

$$F_p = \frac{C_t - C_e}{C_p - C_e}$$

Where Q_t is the streamflow, Q_p is the contribution from "pre-event" water, Q_e is the contribution of "event" water, C_t, C_p, and C_e are the δ values of streamflow, "pre-event" water and "event" water and F_p is the fraction of "pre-event" water in the stream. Sklash and Farvolden (1979) defined the five underlying assumptions of hydrograph separation as follows: 1) pre-event and event water must be isotopically and geochemically different; 2) event water remains isotopically and geochemically constant during the storm; 3) water within unsaturated and saturated soil zones are isotopically identical; 4) pre-event water remains geographically constant within the system, and; 5) contributions from surface storage are insignificant. If all five assumptions are not met, the mixing models may incorrectly separate the hydrograph.

In addition to stable water isotopes, dissolved solids and base cations can be used as geochemical tracers in two-component hydrograph separation models to better understand the various sources and pathways within a catchment (Hangen et al., 2001; Richey et al., 1998). Because geochemical solute tracers are quasi-conservative and interact with soil, stable water isotopes and solute tracers may not share the same sources and pathways and, therefore, can provide complementary information for pathways of nutrient loss (Moore, 1989; Brown et al., 1999; Kendall and McDonnell, 2006). Silica (SiO_2) is especially useful for understanding differences in surface and subsurface runoff sources and pathways as soil and groundwater have elevated silicate concentrations. In contrast, chloride (Cl^-) is useful for understanding “pre-event” or “event” sources (Klaus and McDonnell, 2013; Pionke et al., 1993). Moreover, Richey et al. (1998) reviewed numerous two-component hydrograph studies and concluded that the calculated “pre-event” fractions from both stable water isotopes and solute tracers were similar, suggesting silicate and chloride may behave conservatively during storm events. However, several researchers found that solute tracers over- or underestimated the “pre-event” fraction contributing to stormflow when compared to the “pre-event” fraction calculated from isotope-based hydrographs; these researchers suggested that solute tracers should not be used by themselves in hygrograph separation mixing models (Obradovic and Sklash, 1986; Wels et al., 1991).

Two-component hydrograph separation can be expanded to three components, but this expansion requires that another tracer (e.g., δD, $\delta^{18}O$, or a geochemical solute tracer) be used (Klaus and McDonnell, 2013). Three-component mixing models are preferred over two-component as the assumption of only two sources or pathways of water within the system is unrealistic. Most commonly, $\delta^{18}O$ and silicate are used in three-component mixing models (Klaus and McDonnell, 2013). However, Kendall and McDonnell (2006) noted weaknesses of two and three-component mixing models, including the models’ inability to incorporate constant or non-stationary transit times, changes in precipitation intensity, and δD and $\delta^{18}O$ value changes within a storm. Two- and three-component hydrograph separation have been applied to tiled-drained fields in the Midwest, USA (Kumar et al., 1997; Vidon et al., 2012; Kennedy et al., 2012; Williams and McAfee, 2021) to investigate water and solute delivery pathways of water of water into the tiles. The use of hydrograph separation to characterize P loss in ditch-drained fields is less common in the literature (Mosesso et al., 2021). When applied in open-drainage systems, hydrograph separation can provide insight into pathways of P loss and can help determine the fraction of P loss from preferential flow pathways during storm and irrigation events.

Recently, automated hydrograph separations have gained popularity to quickly separate base and stormflow components during a study period. For example, Siegert et al. (2021) and Charchousi and Papadopoulou (2019) used the *BaseflowSeparation()* function in the *EcoHydRology* in R (Fuka et al., 2018) to determine baseflow fractions within a study stream or ditch. In addition, nutrient load estimates (which can be calculated in the R *loadflex* package; fuka et al., 2015) can be paired with the flow component fractions to quantity of DP lost from storm and baseflow (Mosesso et al., 2021).

1.2.2. Concentration-Discharge (C-Q) Relationships during Storm Events

Plotting the relationship of a solute concentration versus discharge (concentration-discharge plots or C-Q) within agriculturally drained settings can provide insight into the sources, storage, and pathways of P transport and loss (Osterholz et al., 2020). The long-term slope (β) of C-Q relationships can determine the behavior of solutes with flow in a stream or drainage ditch. In this C-Q relationship, the solute concentration can decrease with increasing discharge (dilution), increase with increasing discharge (enrichment), or remain unchanged (constant; Godsey et al., 2009). Thompson et al. (2011) developed the coefficients of variation of concentration relative to discharge (CV_C/CV_Q) to explore the relationship between solute concentration variability and discharge. The CV_C/CV_Q value can determine if the solute is transport limited (i.e., chemostatic) or source limited (i.e., chemodynamic). Musolff et al. (2017) and Dolph et al. (2019) combined the β and

CV_C/CV_Q to gain insight into P export regimes within a German watershed of varying land use and a Minnesota agricultural field, respectively. In soils with a history of P, P loss from agricultural watersheds is often driven by enrichment (positive β; Dolph et al., 2019) and transport limitation (Basu et al., 2010; Thompson et al., 2011; Rose and Karwan, 2021).

In addition to defining long-term C-Q patterns within a drainage ditch or stream, C-Q patterns during individual storm events can provide insight into the sources and pathways of dissolved P with varying magnitude storm events and antecedent soil moisture conditions. For an individual event, the C-Q relationship may show hysteretic behavior, or plot as a circular shape, when the relationship between the solute, such as dissolved P, and Q differ on the rising limb of a hydrograph than the falling limb (Williams, 1989). The rotation direction of the relationship can be either clockwise or anticlockwise. Clockwise hysteresis occurs when the solute concentrations are highest on the rising limb of the hydrograph, meaning that the solute quickly reaches the drainage ditch due to fast transport pathways or solute proximity to the ditch or stream. Anticlockwise hysteresis occurs when the solute concentrations are highest on the falling limb of the hydrograph, suggesting that there is a delay in solute arrival in the ditch due to distant solute hotspots or the solute is diluted within the ditch (Bowes et al., 2019). Previously, the C-Q relationships were characterized by qualitative measurements such as the rotational direction, curvature size and shape, and slope (Evans & Davies, 1998; Williams, 1989). Researchers have developed two quantifiable indices: 1) the hysteresis index (HI), which estimates the rotation and magnitude of C-Q hysteresis (Lloyd et al., 2016), and 2) the flushing index (FI), which quantifies the C-Q slope (Butturini et al., 2008; Vaughan et al., 2017). Pairing the HI and FI indices (Liu et al., 2020; Vaughan et al., 2017; Wymore et al., 2019; Frazar et al., 2019), can reveal important information regarding the sources and pathways of storm-driven dissolved P losses in drainage ditches and can help to compare C-Q relationships between storms of varying magnitude. As with hydrograph separation, antecedent soil moisture conditions can impact a storm's C-Q relationship by effecting the connectivity between P hotspots and the drainage ditch. Low antecedent soil moisture promotes clockwise hysteresis, but stronger solute flushing, while high antecedent soil moisture promotes anticlockwise hysteresis (Biron et al., 1999; Seeger et al., 2004; Vidon and Cuadra, 2010; Knapp et al., 2020; Rose and Karwan, 2021). The hysteresis and flushing indices have been used by Aguilera and Melack (2017), Vaughan et al. (2017), and Rose and Karwan (2021) at watershed scales to understand pathways of solute loss (e.g., nitrate, P) with various land use covers. Researchers have applied these indices to tile drained landscapes to investigate mechanisms of legacy P loss in drainage waters (Rose and Karwan. 2021); these researchers found that P losses within drainage water were supply limited ($CV_C/CV_Q > 0.5$). Rose and Karwan (2021) found that these landscapes had clockwise hysteresis and with strong P flushing responses. In contrast, Frazar et al. (2019) investigated P loss from two artificially drained agricultural watersheds in Rhode Island and found that C-Q relationships had an anticlockwise relationship, but P had a strong flushing response, indicating P hotspots are not proximal to the stream network.

1.2.3 Seasonal Origin Index

The seasonal origin index is a unitless value that was recently developed by Allen et al. (2019a) and is used to determine if summer or winter $\delta^{18}O$ precipitation values are overrepresented in a system compared their relative volumes. This index uses the strength of the seasonal isotope cycle in precipitation to represent isotopic differences between annual average discharge and annual average precipitation on a unitless scale from -1 to 1. The SOI is calculated using the $\delta^{18}O$ values of typical midwinter (δ_{PW}), typical midsummer (δ_{PS}), and volume-weighted annual precipitation (δ_P) and streamflow (δ_Q) to calculate the volume-weighted annual streamflow $\delta^{18}O$ SOI (SOI_Q), as follows:

$$SOI_{\overline{Q}} = \begin{cases} \dfrac{\delta_{\overline{Q}} - \delta_{\overline{P}}}{\delta_{Ps} - \delta_{\overline{P}}}, if\ \delta_{\overline{Q}} > \delta_{\overline{P}} \\ \dfrac{\delta_{\overline{Q}} - \delta_{\overline{P}}}{\delta_{\overline{P}} - \delta_{Pw}}, if\ \delta_{\overline{Q}} < \delta_{\overline{P}} \end{cases}$$

The SOI was first applied to tree xylem (Allen et al., 2019a) and then to streamflow to determine the fraction of summer and winter precipitation contributing to the study stream after accounting for evapotranspiration (Allen et al., 2019b). Since its development in 2019, the SOI has been used to understand water acquisition by trees (Zhang et al., 2021; Goldsmith et al., 2022) and to ascertain the relative importance of winter versus summer precipitation in surface water and groundwater (Xiao et al., 2022).

Although the SOI is a relatively new concept that has not be applied in many research areas, this tool can be applied to artificially drained agroecosystems to determine if winter or summer precipitation is overrepresented in drainage water and to estimate the relative importance of preferential flow as a rapid pathway of P transport from fields to drainage ditches.

1.3 Need for Model to Quantify Subsurface Phosphorus Loss on the Delmarva Peninsula

As the processes and pathways associated with subsurface P transport into drainage ditches remain poorly understood (Sims et al., 1998; Shober et al., 2017), tools like the Delaware P Site Index (DE-PSI) and Maryland Phosphorus Management Tool (MD-PMT) may not accurately describe the risk of subsurface P loss from agricultural fields. These P Indices are field level risk assessment tools that farmers and consultants can use to determine the risk of "legacy" and new P losses (soil P, manure P, or fertilizer P) from their fields to surface water in order to select and place best management practices that reduce the potential for edge-of-field P losses. However, the subsurface components of the DE-PSI and the MD-PMT require updates in order to reflect the latest science on subsurface P losses (Sims et al., 1998). An evaluation of these P Indices is needed to confirm that their representations of the processes and pathways associated with P loss within the whole field are accurate (Sharpley et al., 2012). Shober et al. (2017) assessed the P Indices used on the Delmarva Peninsula (including DE-PSI and the MD-PMT) and found that these tools could accurately predict P loss through matrix flow in sandy soils but not silt loams soils dominated by preferential flow pathways. Long-term studies that measure P leachate from open drainage fields on the Delmarva Peninsula are needed adequately validate and/or modify these P Indices. However, this research is multifaceted and complex. For example, on the Delmarva there is no standardization for the placement and depth of ditch drains, which makes determining drainage intensity for a field difficult. In addition, determining the subsurface drainage associated with one field is difficult as fields are usually drained from multiple ditches and ditches are linked with ditches draining upland fields, mixing the subsurface drainage from multiple fields (Shober et al., 2017).

As long-term field sampling proves difficult, hydrological models can be used in place of long-term leachate P datasets to estimate P leachate loads from open drained fields and verify the P risk assessment tools (Bolster et al., 2016; Vadas et al., 2013). However, current hydrological models are not equipped to estimate subsurface P losses through preferential flow pathways in open drained agricultural fields. Current hydrological models predict subsurface P losses only by tile drainage (e.g., APEX, SWAT), with only some models accounting for loss by matrix and preferential flow pathways into tile (e.g., HYDRUS, ICECREAMDB; Radcliffe et al., 2015). Models must be developed or modified that can predict subsurface P losses through preferential flow pathways into open ditch drains to improve P risk assessment on the Delmarva Peninsula.

One promising model is DRAINMOD, a field-scale model that simulates the hydrology of artificially drained landscapes on various timescales. This process-based model requires long-term weather data (e.g., precipitation amounts, maximum and minimum temperature, potential evapotranspiration values), soil characteristics (e.g., matric potential and lateral saturated conductivity at various depths), and drainage design characteristics (e.g., tile spacing and depth). Previous version of DRAINMOD versions, including DRAINMOD-NII (Youssef et al. 2005), DRAINMOD-DSSAT (Negm et al., 2014; Negm et al., 2017), and DRAINMOD-FOREST (Tian et al., 2012), were developed to simulate carbon and N cycling and loss and combine the Decision Support System for Agrotechnology Transfer (DSSAT) and Physiological

Processes Predicting Growth (3-PG) forest growth models. More recently, DRAINMOD developers modified the model to simulate P cycling and loss in artificially drained landscapes (DRAINMOD-P; Askar et al., 2021a & b). Within DRAINMOD-P, macropore flow, soil erosion, and sediment loss can also be simulated (Askar et al., 2021a). However, when testing the model performance, DRAINMOD-P overestimated surface runoff. The DRAINMOD-P model was calibrated and validated with a 5-year dataset from Ohio. As DRAINMOD-P is not validated for the unique soil and management characteristics of the Delmarva Peninsula, significant data collection efforts would be required to calibrate and validate the model for use on the Delmarva.

1.4 Research Objectives

Agricultural fields with a history of P application can contribute to excess P loading within water bodies and cause eutrophication resulting in hypoxia. In flat agroecosystems, leaching was determined to be the primary route of P loss; however, these subsurface pathways and mechanisms of soil P loss are poorly understood. In addition, there is evidence that in soils with soil test P concentrations above the agronomic optimum, more soluble P species may become less soluble and more resistant, resulting in difficulties of crop uptake of P. This dissertation took a source-transport approach to better understand soil P solubility and pathways of subsurface P loss from fields to better manage historically and newly applied P within critical source areas. The objectives of this dissertation project were to: 1) characterize the inorganic P species in agricultural soils under varied management to predict P mobility, 2) determine if soil health practices exacerbate P losses by evaluating soil P stratification and dry aggregate stability in soils with and without a history of soil health practices, and 3) characterize pathways of subsurface P loss in a ditch-drained field using C-Q relationships, hydrograph separation, and the seasonal origin index.

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Chapter 2

UNDERSTANDING PHOSPHORUS DYNAMICS IN MANURE AND FERTILIZER IMPACTED DELMARVA SOILS

2.1 Introduction

Historical inputs of animal manures and commercial P fertilizers to agronomic and horticultural crops at rates that exceeded crop P removal led to buildup of soil test P (STP) to concentrations that exceed agronomic optimum levels. As such, yield responses to additional P inputs are not expected in areas of the U.S. with intensive animal agriculture (Feyereisen et al., 2010; Patterson et al., 1998; Vadas & Sims, 1998; MacDonald et al., 2011). Soils with elevated STP concentrations represent a source of "legacy P" that is linked to elevated risk of P loss via erosion, surface runoff, and subsurface flow (e.g., leaching and subsurface lateral flow; Boesch et al., 2001; Jarvie et al., 2017; Osterholz et al., 2020). Erosion and surface runoff losses tend to be the dominant P loss pathways in sloping upland landscapes (Sharpley et al., 1993). In contrast, subsurface agricultural P losses are more common in flat, artificially drained landscapes like those prevalent on the Delmarva Peninsula (King et al., 2015; Kleinman et al., 2015). Drainage networks circumvent natural hydrologic pathways resulting in discharge of stormwater and nutrients directly into sensitive waterbodies like the Chesapeake and Delaware Bays (Sims et al., 1998; Shober et al., 2017; Mosesso et al., 2021), which can cause eutrophication and hypoxia (Bricker et al., 2008; Carpenter et al., 1998).

According to the 2016 State of the Bay Report (Chesapeake Bay Foundation, 2020), P continues to be a major nutrient of concern in the Chesapeake Bay. As such, many growers in the Mid-Atlantic now face restrictions on future applications of P fertilizers and manures due to increased risk of P loss from legacy P soils. Limitations on P applications reduce farmers' ability to recycle locally produced manures and requires that farmers find alternative sources of N and micronutrients to meet crop needs. In addition, even if manure application to P-enriched Mid-Atlantic soils were to stop today, it could take decades to decrease soil test P concentrations under current grain and forage cropping systems to levels where plant response to P would be expected (McCollum, 1991; Fiorellino et al., 2017). Plus, researchers suggested that the equilibrium among soil P pools may shift as soil test (Mehlich-3) P increases, leading to a redistribution of P among the soluble and more resistant pools of P (Reiter et al., 2013). Significant shifts in soil P equilibrium may restrict the amount of soluble soil P available to growing crops should manure or fertilizer applications to high P soils cease (Qin & Shober, 2018). As such, the use of agronomic soil test P (e.g., Mehlich-1, Mehlich-3, etc.) may overestimate the amount of plant available P, as well as the risk of P loss from P-enriched soils. In addition, providing soil and nutrient management guidance to farmers growing in P-enriched soils is difficult because our understanding of the chemical forms and cycling of P in P-enriched soils is incomplete (Lui et al., 2015; Gamble et al., 2020; Doydora et al., 2020). We need a better understanding of the fate, transformations, and availability of P-enriched soils as they are connected to increased edge-of-field P losses (Sharpley et al., 2004; Luo et al., 2017).

Soil test P trends alone do not give researchers enough information to manage legacy soil P (Reiter et al., 2013). Pairing chemical extraction techniques with direct speciation techniques can improve our understanding of P dynamics in P-enriched soils by providing more insight into soil P speciation, transformations, and mobility (Hesterberg et al., 2017; Peak et al., 2002, Kelly et al., 2008; Sui et al., 1999). Chemical extraction including agronomic soil tests and sequential chemical extraction techniques are frequently used to predict probability of crop response (Sims et al., 2000**)** and characterize inorganic and organic P species in soils, respectively (Chang and Jackson, 1958; Hedley et al., 1982). Sequential chemical extraction employs reagents of increasing P soil extraction strength to fractionate P into operational "pools" to predict relative bioavailability (Hedley et al., 1982). Other extracted elements that commonly bind with P (e.g., aluminum [Al], calcium [Ca], and iron [Fe]) can be analyzed to infer P speciation in the soil. In addition, sequential chemical extraction is useful to understand how P pools shift under various management (e.g., change in P input type, cease of P inputs, and long-term manure inputs) to predict P solubility (Reiter et al., 2013; Fiorellino et al., 2017; Abdala et al., 2018).

Unlike chemical extractions, direct speciation techniques non-destructively determine the elemental composition or P species present in the soil (Kramar, 1997; Hesterberg et al., 1999). Synchrotron based X-ray absorption near edge structure spectroscopy (XANES), speciates inorganic P species in environmental samples like soils (Beauchemin et al., 2003) and poultry litters/manures (Hesterberg et al.,1999; Peak et al., 2002; Toor et al., 2005; Shober et al., 2006) by comparing spectra of representative standards with that of an unknown soil (Fendorf et al., 1996). Unlike x-ray diffraction, XANES can identify both crystalline, poorly crystalline, and amorphous species. Using a fitting method called linear combination fitting (LCF), three to five dominant species are identified that are present in the weighted-average soil pellet spectra (Ravel & Newville, 2005). Previously, high P concentrations (>10 g kg^{-1} total P) were needed to produce a good XANES spectra for environmental samples like soils. However, new detectors have allowed for cleaner output of spectra features in environmental samples with lower P concentrations (<10 g kg^{-1} total P) by eliminating spectral noise caused by high concentrations of silicon (Si) and aluminum (Al). A second direct speciation technique, X-ray fluorescence (XRF) analyses, can determine the total elemental composition of soils and other environmental samples (Kramar, 1997; Kelly et al., 2008) and can supplement chemical extraction data to support XANES fitting results.

Our goal was to better understand P chemistry in soils that received long-term applications of manure or fertilizers so we can help land managers make better nutrient management decisions. For this project, we coupled chemical extractions and non-destructive spectroscopic tools to obtain information about past P speciation in eight agricultural soils from the Mid-Atlantic Coastal Plain (Delaware, Maryland, Virginia) with a history of poultry litter, dairy manure, or commercial P fertilizer application. Researchers have previously investigated P speciation in organic amendments (Shober et al., 2006; Seiter et al., 2008) and manure-amended soils (Hill & Cade-Menun, 2008; Gamble et al., 2020). We expand upon past work by comparing P speciation in agricultural soils under varied management (e.g., dairy manure vs. poultry litter; grain rotation vs. forage rotation vs. vegetables, etc.). Results from this study will guide management recommendations for agricultural soils on the Delmarva Peninsula.

2.2 Materials and Methods

2.2.1 Sample Selection and Management History

We selected eight archived agricultural soils from the Mid-Atlantic Coastal Plain region representing common regional cropping management systems (e.g., poultry-grain, dairy-forage, and grain-vegetable; Table 2.1) and with at least 1% total P. Two DE soils were selected from archived samples that were submitted by grain crop producers to the University of Delaware Soil Testing Lab in the late 1990s; both soils had perchloric acid digestible P concentrations that exceeded 1.10 g kg^{-1} (Pautler & Sims, 2000). The first DE sample was collected to a depth of 20 cm in Nov 1996 from a 4-ha field near Greenwood, DE that was planted in a cereal rye (*Secale cereale*) cover crop following conventionally tilled full-season soybean (*Glycine max* L.); the predominant soil type was a Hambrook sandy loam (fine-loamy, siliceous, semiactive, mesic Typic Hapludults; Soil Survey Staff, 2022). The grower indicated that the field received a pre-plant application in 1996 of 1) 0 kg ha^{-1} of N, P, and K, 2) 90, 39, 74 kg ha^{-1} of N, P, K, respectively and 3) 168, 73, and 138 kg ha^{-1} of N, P, K, respectively, with no manure was application. Based on grower supplied information and satellite imagery (2002, 2008-2021; USDA-NASS, 2021), we inferred that the field was used to produced agronomic row crops, with corn (*Zea mays* L.), soybean (full or double-cropped), and double-cropped barley (*Hordeum vulgare* L.) or winter wheat (*Triticum aestivum* L.) as the main crops in rotation.

The DE second sample was collected from a depth of 7.6 cm in Feb 1997 from a 6.7-ha field near Millsboro, DE; the predominant soil series was a Pepperbox-Rosedale complex (Pepperbox: loamy, mixed, semiactive, mesic Aquic Arenic Paleudults; Rosedale: loamy, siliceous, semiactive, mesic Arenic Hapludults; Soil

Survey Staff, 2022). The previous crop was conventionally tilled full-season soybean. The grower reported that the field received 2.24 Mg ha^{-1} of poultry litter crust to the field in the fall of 1996; no other fertilizers were listed on the sample information sheet. Based on grower supplied information and satellite imagery (2002; 2008-present; USDA-NASS, 2021), we inferred that the field was planted in a corn, full-season soybean rotation or corn and double cropped winter wheat and soybean.

A third DE soil was collected in Sept 2015 from 1.6-ha soybean field with a history of poultry litter that was located near Millsboro, DE; the predominant soil series is a Mullica-Berryland complex (Mullica: coarse-loamy, siliceous, semiactive, acid, mesic Typic Humaquepts; Berryland: sandy, siliceous, mesic Typic Alaquods; Soil Survey Staff, 2022). A composite soil sample was collected by sampling to a depth of 15 cm using a shovel from random locations in the field to obtain several kilograms of soil for use in a laboratory study. The field was maintained in a corn, winter wheat, double-cropped soybean rotation between 2008 and 2015; prior to 2008, the field was used to grow various crops including mixed fruits and vegetables and agronomic grain crops (USDA-NASS, 2021).

Composite soil samples were also collected from two row crop fields with a history of poultry litter application near Parsonsburg, MD in May 2014 by collecting subsamples to a depth of 15 cm using a shovel from random locations in field. The predominant soil in both fields is a Mullica-Berryland complex (Soil Survey Staff, 2022). The first field was a 26.8-ha corn field that was planted in a corn, full-season soybean or corn, double-cropped oats (*Avena sativa* L.) and soybean (2012-2013) since 2008 (USDA-NASS 2021). The field was likely managed in row crops or vegetable production prior to 2008 (2002 crop layer; USDA-NASS, 2021). The second

MD soil was collected from a 9.1-ha soybean field that was managed in a corn, full-season soybean rotation from 2008 to 2014; the field contained alfalfa and soybean in 2002 (USDA-NASS, 2021).

A third MD soil was selected from archived samples collected from the Central Maryland Research and Education Center (CMREC) near Upper Marlboro, MD as part of a long-term study on soil test P drawdown (Fiorellino et al., 2017; Kratochvil et al., 2006). Soils were collected (eight soil cores to a depth of 15 cm) from a 4.6-m × 12.2-m research plot prior to planting in spring 2003; the predominant soil type was a Donlonton fine sandy loam (fine-loamy, glauconitic, mesic Aquic Hapludults). This research plot received four annual applications of dairy manure from 1994 to 1997 at a total P rate of 400 kg ha^{-1} (per application) during which time the plot was planted in continuous corn. The field was left fallow in 1998 and no additional P was applied. The site was planted back into corn for the 1999 and 2000 growing seasons; 14 kg ha^{-1} of P was applied once as a starter fertilizer during this period. The plot was subsequently planted in corn silage (spring) and rye haylage (fall) in 2001 and 2002; no additional P was applied to the site after 2000.

Soils were collected in 2018 from a 44.5-ha field at the Eastern Shore Agricultural Research and Extension Center near Painter, VA; the predominant soil is a Bojac sandy loam (coarse-loamy, mixed, semiactive, thermic Typic Hapludults; well drained; Soil Survey Staff, 2022). Between 2015 and 2018, the field was planted with a summer plasticulture crop of tomato, cantaloupe, or watermelon following conventional tillage. Vegetable/fruit crops received triple superphosphate fertilizer (0-46-0) at a P rate of 56 kg ha^{-1}. Winter wheat was also planted annually from 2015 to

2017 after conventional tillage; no P was applied to wheat. The field was not tilled, and no winter crop was planted in 2018.

The final soil sample was collected in 2018 from a 22.2-ha soybean field near Painter, VA; the dominant soil series was Bojac sandy loam. The field had a history of commercial fertilizer and poultry litter application. In 2015, the field was planted in conventionally tilled potato (summer) that received 56 kg ha^{-1} of P as diammonium phosphate, which was followed by conventionally tilled winter wheat. In 2016 and 2018, the field was planted in soybean that received no P application. Corn was planted in 2017 and received poultry litter at a rate of 2.24 Mg ha^{-1} tons/ac P followed by a winter wheat cover crop. The field was primarily cropped in a corn, full-season soybean rotation between 2008 and 2018 (USDA-NASS 2022), with occasional plantings of double-cropped winter wheat and soybean (2008 and 2010) or double-cropped barley and soybean (2013).

2.2.2 Soil Chemical Analysis

Soil samples were analyzed for pH (1:10 soil: deionized water), organic matter (loss on ignition-LOI), using standard testing methods (Northeastern Coordinating Committee, 2011) at the University of Delaware Soil Testing Laboratory. Soils were analyzed for P, aluminum (Al), calcium (Ca), and iron (Fe) by inductively coupled plasma-optical emission spectrometry (ICP-OES) following Mehlich-3 extraction (1:10 soil to solution ratio of 0.2 M CH_3COOH + 0.25 M NH_4NO_3 + 0.015 M NH_4F + 0.13 M HNO_3 + 0.001 M EDTA, 5-min reaction time, filtered through Whatman #42 paper; Northeastern Coordinating Committee, 2011). The Mehlich-3 P saturation ratio (PSR) was calculated using the molar ratio of Mehlich-3 P to Mehlich-3 Al and Fe (Maguire and Sims, 2002; eq 2). In addition, soil samples were analyzed for water extractable P (WEP; Murphy and Riley, 1962) using a GENESYS™ 30 Visible Spectrophotometer (Thermo Scientific, Waltham, Massachusetts) at 882 nm following deionized water extraction (1:10; Self-Davis, 2009).

Total elemental composition P, Al, Ca, and Fe of all soil samples was determined using energy dispersive XRF analysis (S1 Titan 600 Handheld XRF, Bruker, Billerica, MA) following the EPA method SW-846 6200. Prior to analysis, P standards and samples were ground into a fine powder using a mortar and pestle, placed into a 31-mm closed X-CELL sample holder (SPEX SamplePrep, Metuchen, NJ), and covered with 4-μm thick film (3526 Ultralene, SPEX SamplePrep, Metuchen, NJ). We selected a three-phase element scan method with each sample scan lasting 120 s. We also collected XRF data on National Institute of Standards and Technology reference soils (SRM 2710a and SRM 2709a) for quality control.

Samples were also subjected to a modified Hedley sequential fractionation to determine the effect of long-term P applications on the operational P “pools" (Sui et al., 1999). In brief, 0.5 g of each soil was sequentially extracted with: 1) 30 mL of deionized water, 2) 30 mL of 0.5 M $NaHCO_3$, 3) 30 mL of 0.1 M NaOH, and 4) 30 mL of 1 M HCl. Samples were filtered (0.45-μm) following each step and the supernatant was analyzed for P, Al, Ca, and Fe by ICP-OES. Extractable P from each Hedley extractant was summed for each soil to determine the total extractable inorganic P.

2.2.3 X-ray Absorption Near Edge Structure Spectroscopy (XANES)

Phosphorus K-edge XANES spectra were collected for our eight soil samples and 23 reference standards (Figure A.1; Table A.1) at the bending magnet beamline 9-BM at Advanced Photon Source (APS), Argonne National Laboratory in Lemont, Illinois. Prior to analysis, soils were ground with an agate mortar and pestle, hand pressed into a 7-mm pellet, and adhered to a sample holder using double-sided carbon tape. Spectra were collected for each soil in fluorescence mode using a silicon (Si) double crystal monochromator with a 4-element Vortex silica drift detector that was calibrated to 2149 eV using a P_2O_5 standard. For each sample, we collected three to five scans over an energy range of 2109 to 2286 eV with the following step sizes: 2.0 eV from 2109-2139 eV, 0.12 eV from 2139-2174 eV, and 0.05 eV from 2174-2286 eV. Spectra of synthesized or purchased reference standards were collected using total electron yield to minimize the effect of self-absorbance in fluorescence mode and preserve the integrity of the white line peak (Hesterberg et al., 1999; Shober et al., 2006). Standard spectra were collected along various ranges of energies and step sizes over multiple beam visits (Table A.2).

The XANES data was processed using Athena software (Ravel & Newville, 2005). Artifacts from individual scans were removed (deglitched) if necessary. Individual scans for each sample or standard were then merged and calibrated to the maximum peak energy of the first derivative. The merged scans were normalized following the protocol of Werner et al. (2015) by correcting our spectra pre-edge range within -25 to -10 eV, while normalizing our edge-step within the range of 35 to 65 eV.

Phosphorus K-edge XANES spectra of soil samples were compared with spectra of P reference standards using the linear combination fitting (LCF) data analysis tool in Athena (Ravel & Newville, 2005) to identify the predominant P species and their respective contributions in each soil. Reference standards with molar ratios of P to Al, Ca, or Fe (based on XRF, data not shown) that were higher than molar ratios of these elements in the soil sample were considered unlikely to be present at significant quantities in the soil and were excluded from LCF analysis. The remaining standards were fit against the sample spectrum and removed if the standard was not present in the spectrum (weight equaled 0). We then evaluated all the fitting combinations from the final five standards. The LCF fitting range was -5 to 50 eV for all soils except the Bojac-fertilizer and Mullica-Berryland-MD2, which were fitted in the range of -5 to 40 and -5 to 30 eV, respectively. If needed, we allowed the calibration energy (E_0 = 2149 eV) to shift up to ±1 eV during LCF to account for slight variations in beam calibration across different data collection visits. Final LCF fits were selected based on the residual factor (R-factor) and (chi) $\chi 2$ values for each fit, as smaller values indicate a better fit.

2.3 Results and Discussion

2.3.1 Soil Chemical Analysis

Seven of our soils were acidic with pH ranging from 4.7 to 5.8; the Donlonton soil was mildly acidic (pH of 6.5). Organic matter ranged from 9.0 (Bojac-fertlizer) to 62 g kg^{-1} (Donlonton). Mehlich-3 P concentrations ranged from 54.1 to 697 mg kg^{-1} (Table 2.1), which was representative of the region. For example, Mullica-Berryland-MD1 and 2 were collected from Wicomico County, MD soils, where 12% of soils have Mehlich-3 P concentrations that exceed 488 mg kg^{-1}. The Donlonton soil was collected from Prince George's County, MD, where 19% of soils have Mehlich-3 P concentrations ranging from 142 to 492 mg kg^{-1} (Maryland Department of Agriculture, 2016). Mehlich-3 P concentrations for all soils, except for Hambrook, were above the University of Delaware agronomic critical soil test concentration (50 mg kg $^{-1}$ Mehlich-3 P) and considered to be within the “excessive” soil test range (>101 mg kg $^{-1}$ Mehlich-3 P), which indicates that P concentrations are more than adequate to support crop growth and that crops are unlikely to respond to additional P applications. In fact, additional applications of P to soils with “excessive” soil test P results in wasted resources and can increase the risk of negative environmental impacts (Sims et al. 2002). The soil Mehlich-3 PSR values ranged from 0.06 (Hambrook) to 0.55 (Pepperbox) with an average of 0.35. All soils, except for Hambrook, had PSR values above the environmental threshold of 0.20, indicating that the soil poses a very high risk for P loss by runoff, erosion and leaching to water bodies (Maguire and Sims, 2002). The Hambrook soil had a PSR value of 0.06, which suggests that the soil can still retain high concentrations of P. The Hambook soils also had the largest sample P:Al and P:Fe molar ratios, which is likely due to the soil mineralogy and lack of manure applications (Table 2.2). Other soils (e.g., Mullica-Berryland-DE and Donlonton) had higher total Al and Fe concentrations but lower P:Al and P:Fe ratios (Table 2.2), which was likely due to increased P concentrations from repeated manure application. Water extractable P concentrations ranged from 2.51 (Hambrook) to 31.1 mg kg^{-1} (Donlonton), with an average of 14.7 mg kg^{-1}. Six out of eight soils had WEP concentrations above the environmental threshold of 8.6 mg kg^{-1} and pose a high risk of dissolved P loss during runoff or leaching events (Maguire and Sims, 2002).

We aimed to collect soils with over 1 g kg^{-1} P. Based on XRF analysis, the total P in our selected soils ranged from 0.98 (Hambrook) to 6.26 g kg^{-1} (Mullica-Berryland-DE). Total Al and Fe concentrations ranged from 31.3 to 42.0 g kg^{-1} and 4.22 to 30.3 g kg^{-1}, respectively. Total Ca ranged from 2.14 to 4.36 g kg^{-1} (Table 2.2).

2.3.2 Chemical Fractionation

Our chemical fractionation data showed that the total extractable P in the H_2O-extractable P pool ranged from 14.4 (Hambrook) to 89.1 mg kg^{-1} (Donlonton). The total extractable P in the $NaHCO_3$-extractable pool ranged from 52.8 to 280 mg kg^{-1}. Within the NaOH-extractable pool, the total extractable P ranged from 273 to 690 mg kg^{-1}, while the total extractable P in the HCl-extractable pool ranged from 41.7 to 117 mg kg^{-1} (Figure 2.1a). Our finding that P was most abundant in the NaOH-extractable pool are consistent findings with other studies that investigated the chemical fractionation in P-enriched soils (Beauchemin et al., 2003; Sharpley et al., 2004).

Researchers previously reported that repeated applications of manure (Qian et al., 2004; Shafqat & Pierzynski, 2010; Sharpley et al., 2004) or commercial fertilizer (Koch et al., 2018; Luo et al., 2017) led to increases in total soil P, with significant shifts in the distribution of P toward more resistant soil pools (e.g., NaOH- and HCl-extractable pools in the Hedley fractionation). Several researchers also noted significant increases in labile P pools following years of manure or biosolids application (Qian et al., 2004; Shafqat & Pierzynski, 2010; Sharpley et al., 2004). While we are unable to compare the P fractionation of our eight P soils with unamended soils, we are confident that manure and fertilizers applications also resulted in a build-up and redistribution of P compared to unamended soils (Figure 2.1). The Hambrook soil, which was the least impacted by P applications had the largest proportion of P in the HCl-extractable pool and lowest in the H_2O-extractable pool. Koch et al. (2018) also found that compost and fertilizer (TSP) increased total P fractions, with the largest increases in the moderately labile and stable P fractions and little to no increase in labile P fractions.

We also measured Al, Ca, and Fe within each extractable pool and the distribution between the operational pools helped us determine the general solubility of P and of the potential for the presence of Al-, Ca-, or Fe-P species in our eight soils (Table A.3). As expected, our data showed that Al concentrations were highest in the NaOH-extractable pool (870–1424 mg kg^{-1}; 52–82%). In contrast, extractable Ca was equally distributed in the $NaHCO_3$- (236–1,095 mg kg^{-1}; 37–61%) and HCl-extractable (149–508 mg kg^{-1}; 27–47%) pools. Extractable Fe was found mainly in the HCl-extractable P pool (288–1,350 mg kg^{-1}; 58–83%). The Hambrook soil contained the highest concentrations of soil Fe, with 97% extracted (7,964 mg kg^{-1}) by HCl.

2.3.3 Phosphorus K-XANES

We determined that all or most Fe-P minerals were not likely present in four of the soils (Pepperbox, Mullica-Berryland-MD1, MD2, and DE) based on the total P:Fe ratios by XRF (Table 2.2). The molar ratio of P:Fe in most Fe-P standards was >1.33 (Table A.2). Similarly, the molar P:Ca ratios of five of the selected soils (Pepperbox, Mullica-Berryland-MD2 and DE, Bojac-manure) suggested that Ca-P species including apatites, β-TCP, monetite, and brushite were most likely not dominant species in the soil samples. As such, these standards were not included in the LCF analysis for the specified soils. Although we have a large standard library, each of our soils showed residual in the fitting results due to a bulk XANES analysis, meaning that LCF could not account for all the spectra variability. In addition, it is difficult to ensure a representative sample of the field with the small sample size needed for XANES. Gamble et al. (2020) conducted micro-focused XANES on high STP soils on the Mid-Atlantic soils and identified clusters of Ca phosphates, Fe phosphates, and P sorbed Fe and Al-oxides, highlighting soil P distribution heterogeneity. As such, bulk

XANES is best suited to identify dominant species and the presence of other P species at lower concentrations cannot be confirmed or denied using this technique.

Phytic acid was not found in any of our soils (Figure 2.2). Monoesters, such as phytic acid, are a commonly found organic P species in manure-amended soils (Turner, 2005) but are not considered bioavailable from binding to soil particles (Gerke 2015), specifically clay particles in acid soils (Doydora et al., 2020). Dou et al. (2009) and Hill and Cade-Menun (2009) also saw little phytate accumulation within manured soils, even though poultry litter has up to 80% phytic acid (Turner, 2004; Maguire et al. 2004; McGrath et al., 2005), as phytic acid may have transformed or been transported within the soil. Low concentrations of phytate within the soil and limitations of the XANES method in identifying organic P species likely explains why our XANES fits did not identify phytic acid our soils, even though six of our soils were amended with poultry litter or dairy manure (Lombi and Susini, 2009). Solution ^{31}P liquid nuclear magnetic resonance (NMR) is a more appropriate method to identify organic P species in soil than XANES (Cade-Menun 2005).

2.3.3.1 Aluminum Phosphates and Phosphorus Sorbed to Al (hydr-)oxides

Aluminum was the most abundant element in all soils; soil P:Al ratios were an order of magnitude higher than P:Fe and P:Ca ratios (Table 2.2). Based on LCF results, Al phosphate (Al-P) minerals or sorbed phases (e.g., P sorbed to boehmite) were common in soils with "excessive" soil test P due to applications of poultry litter or dairy manure, as Al-P species accounted for 59% or more of the total P in these soils **(**Figure 2.2). Aluminum phosphates were also found to contribute to the sample spectra for soils that received commercial fertilizer applications; however, Al-P species typically represented < 20% of the total P in these fertilized soils.

Non-crystalline and poorly crystalline Al-P species (i.e., Al phosphate 3-, 10-, and 30- d) were identified in all eight of our soils. Aluminum phosphates have been found in soils with histories of manure (Abdala et al., 2015) and fertilizer application (Koch et al., 2018). Abdala et al. (2015) found an increase in amorphous Al and Fe minerals after continuous manure application. Both poorly crystalline Al-P and P sorbed to Al (hydr-)oxides were identified in fertilizer amended soils, Hambrook and Bojac-fertilizer soil (Figure 2). Luo et al. (2017) and Koch et al. (2018) found that commercial fertilizers minimally altered soil P species in soils averaging 0.70-0.90 g kg^{-1} total P compared to an unamended soil. As the Hambrook soil had similar total P concentrations (0.98 kg^{-1}) to the soils investigated in Luo et al. (2017) and Koch et al. (2018), Al-P and Al (hydr-)oxides may have been present due to the soil mineralogy. Aluminum (hydr-)oxides, like boehmite and gibbsite, are naturally found in soils (Sparks, 1995) and have been identified in alum-amended poultry litter (Peak et al., 2002) and manure-amended soils (Abdala et al., 2015). Phosphorus binds to Al and Fe (hydr-)oxides through an inner-sphere complexation reaction at the surface site that can be reversed through ligand exchange (Van Riemsdijk and Lyklema, 1980; Gamble et al. 2020). Variscite, a stable Al-P, was identified as the dominant P species in the dairy manure-amended Donlonton soil thorough LCF. The Donlonton soil pH of 6.5 indicates the potential for dissolution of semi-crystalline Al-P minerals (sample contains less than 10% of semicrystalline Al-P), resulting in the persistence of less soluble Al-P species like variscite.

In P drawdown scenarios, we would expect that plants would likely mine poorly crystalline Al-P from our soils before poorly crystalline Fe-P and more crystalline Al-P and Fe-P. Armstrong et al. (1993) found that amorphous or semicrystalline Al-P and Fe-P were more available for plant uptake due to increased surface area, and increased solubility, compared to more crystalline variscite and strengite. The authors also found that corn plants preferred P uptake from poorly crystalline Al-P over poorly crystalline Fe-P. In addition, Armstrong et al. (1993) compared corn P uptake labelled amorphous Al-P and variscite and found that amorphous Al-P was over fifteen times more plant available than variscite. As such, we expect low potential for variscite dissolution in the Donlonton soil until more soluble Al-P species are depleted.

2.3.3.2 Iron Phosphates and Phosphorus Sorbed to Fe (hydr-)oxides

Iron phosphate (Fe-P) minerals or sorbed phases accounted for 43% or less of the total P identified by LCF in most of our soils (Figure 2.2). The main species identified by XANES LCF were semi-crystalline or amorphous Fe-P and phosphosiderite, with P sorbed to ferrihydrite found in the dairy manure-amended Donlonton and poultry litter-amended Mullica-Berryland-MD2 soils. Fitting results found P sorbed to hematite accounted for 69.4% of the spectra within the Hambrook soil, which received commercial fertilizer application only and had soil Mehlich-3 P concentrations within the optimum range.

Iron phosphates have been previously found in manure-amended soils (Lindsay et al., 1979; Sato et al., 2005; Gamble et al., 2020). Iron phosphates play a major role in P solubility in P saturated soils (Lindsay et al., 1989). Long-term manure application promotes the transformation of crystalline Fe minerals to amorphous Fe minerals (Abdala et al. 2015), like the poorly crystalline Fe-P identified in two of our study soils that received poultry litter or commercial fertilizer applications. Amorphous and poorly crystalline Fe-P minerals are 10 to 100 times more soluble than crystalline Fe-P minerals (Lindsay, 1979) and these species would dissolve and replenish P within the soil solution before Fe (hydr-)oxides. Phosphorus sorbed to iron (hydr-)oxides, like hematite and ferrihydrite, is commonly found in manure-amended soils (Sato et al., 2005; Shober et al., 2006; Gamble et al., 2020) and was found in three of our eight soils; two of which had total Fe concentrations (by XRF) above 30.3 g kg^{-1}. Phosphorus sorbed to hematite was identified in Hambrook; fractionation data support this as HCl-extraction yielded 7.96 g kg^{-1} of Fe (Table A.3). The Hambrook soil was the least impacted by P additions, having a history of commercial fertilizer applications rates designed to support crop growth. The relatively high concentrations of extractable Fe (especially in the HCl-extractable pool), the low concentrations of H_2O-, $NaHCO_3$- and Mehlich-3 extractable P as compared to total extractable P, and the low Mehlich-3 PSR (0.06) demonstrate the high fixation potential of this soil, which is likely due to natural mineralogy and low historical applications of P (Figure 2.1b). These data suggest that soluble P is quickly fixed by soil Fe when incorporated into the Hambrook soil, hence the accumulation of P in the HCl-extractable pool that Hambrook had a large reserve of more crystalline, stable minerals like. Phosphate sorb to Fe (hydr-)oxides through outer or inner sphere complexation (both monodentate and bidentate; Sparks, 2003); Dimirkou et al. (2002) found that P adsorption to hematite increases with lower pH as there is an increase in proton availability. In addition, P sorbs to poorly crystalline ferrihydrite through an inner-sphere bidentate complex (Khare et al., 2007; Gypser et al., 2018) and P desorption from ferrihydrite requires 400 to 500 times more energy than P desorption from more crystalline Fe-oxides and amorphous Al-oxides (Gypser et al., 2018). As such, P sorbed to ferrihydrite in Mullica-Berryland-MD2 and Donlonton soils is a more resistant form of P and will remain after Al and Fe-P dissolve, and potentially after other P sorbed to Al and Fe(hydr)oxides desorb. However, prolonged raised water tables during winter months may promote P loss from Fe-P and Fe (hydr-)oxides by reductive dissolution of Fe, especially for the Donlonton and Hambrook soils, which have the highest Fe concentrations (Ponnamperua, 1972; Sallade and Sims, 1997). Tully et al. (2019) found that Fe species in the ditch and flooded field were non-crystalline, which may be due to reductive dissolution of Fe and a release of P as Fe preferentially binds with sulfide.

2.3.3.3 Calcium Phosphates

Fitting results identified calcium phosphate (Ca-P) minerals in two of our soils, both with “excessive” soil test P concentrations that received heavy applications of poultry litter or commercial fertilizer (Figure 2.2). Fluorapatite was identified as a minor component (4.3% of total P) in the Bojac-fertilizer soils that received TSP fertilizer to support vegetable production. Hydroxyapatite was also identified as a minor component (7.5% of total P) in the Mullica-Berryland-MD1 poultry litter amended soils; this soil had the highest total Ca concentration by XRF (4.36 g kg^{-1}). Fluorapatite is the least soluble Ca-P and is from natural bedrock (Dixon et al. 1989) and TSP (Henstra et al., 1981). After the continual addition of TSP to the Bojac-fertilizer soil, fluorapatite present in the TSP may not have fully dissolved or highly soluble Ca^{2+} within TSP may have dissolved and precipitated, increasing in stability (Essington, 2015; Penn and Camberato, 2019). Hydroxyapatite is a stable and crystalline Ca-P that has been found in animal manures (Shober et al. 2006) and in P-saturated, acid soils (Beauchemin et al., 2003). Sato et al. (2005) investigated the speciation of Ca-P in soils with short- and long-term manure application in slightly calcareous soils (pH ~7). The authors found that more soluble Ca-P species were present after short-term manure application and Ca-P species were more stable in long-term fields. Due to the acidic conditions of Mullica-Berryland-MD1 (pH of 5.0), more soluble Ca-P (monetite and brushite) may have dissolved preferentially, leaving behind less soluble Ca-P minerals, such as hydroxyapatite. The Donlonton soil had the highest M3 Ca and second highest total XRF Ca concentrations (Figure 2.1; Table 2.2), suggesting the potential for the presence of Ca-P minerals. However, no Ca-P species were identified in this soil using LCF (Figure 2.2). This Donlonton soil had a soil pH of 6.5 and several years with neither dairy manure nor fertilizer application; as such, Ca-P minerals deposited during dairy application may have dissolved and been taken up by crops (Penn and Camberato, 2019).

2.3.4 Observations on Management History Impacts on P Dynamics

In this section, we established qualitative comparisons between our eight legacy P soils with various trends in management history. We did not make direct comparisons between soils because of variability in the soil type and management, which will ultimately influence the dominant P species found in our soils (Shober and Sims, 2007; Penn and Sims, 2002).

2.3.4.1 Soils Amended with Poultry Litter

Poultry litter-amended Mullica-Berryland-MD1 and Mullica-Berryland-DE soils had similar dominant P species based on LCF results (Figure 2.2). Both soils were planted with row crops, had excessive soil test P concentrations, and had similar soil pH, Mehlich-3 Al, Ca, Fe concentrations, and chemical extraction data. The dominant species for these soils were Al-P and P sorbed to Al (oxy-)hydroxides (over

90% total P); specifically, semicrystalline Al-P and P sorbed to boehmite. Fitting results identified hydroxyapatite in Mullica-Berryland-MD1, the sample with the highest total Ca concentrations, but not in Mullica-Berryland-DE. Only hydroxyapatite was identified by linear combination fitting in the Mullica-Berryland-MD1 soil, possibility because the analyzed soil pellet did not accurately represent field heterogeneity or because the Mullica-Berryland-MD1 soil had a larger reserve of stable Ca-P species. While both soils had similar M3 Ca concentrations and chemical extraction data distribution, Mullica-Berryland-MD1 had more total Ca by XRF (5.36 g kg^{-1}) compared to the Mullica-Berryland-DE soil (2.41 g kg^{-1} Ca, Table 2.2), supporting the presence of a larger stable Ca-P mineral reserve.

2.3.4.2 Soils with High Total Fe Concentrations

Based on fitting results, P sorbed to Fe (hydr-)oxides dominated both the Hambrook and Donlonton soils. These soils had the highest total Fe concentrations by XRF (30.3 and 30.5 g kg^{-1}, respectively; Table 2.2). Linear combination fitting identified semicrystalline Al-P minerals in both soils (8.8- 13.6%), with a higher proportion of Al-P species in the Donlonton soil when compared to the Hambrook soil (58.2 and 31.3%, respecitvely). The higher proportion of Al-P species in the Donlonton soil may be due to soil minerology (e.g., higher total P, Mehlich-3 P, and Mehlich-3 Al concentrations; Table 2.1 and 2.2) and differences in management. Although both soils had very similar total Fe concentrations, the Hambrook soil had lower Mehlich-3 P concentrations than the Donlonton soil (345 and 514 mg kg^{-1}, respectively). However, the Hambrook soil had higher concentrations of total extractable Fe was within the HCl-extractable pool than the Donlonton soil (7,965 vs. 1,352 mg kg^{-1}; Table A.3); these results support the high percentage of P sorbed to hematite found in in the Hambrook soil by LCF. The Hambrook soil had a low risk of P loss with high concentrations of total Fe and Al (30.3 and 46.3 g kg $^{-1}$, respectively) with WEP (2.51 mg kg $^{-1}$) and M3 P concentrations (54.1 mg kg $^{-1}$, PSR = 0.06) within the optimum range and under the environmental threshold. However, Donlonton had a higher risk of P loss with WEP concentration of 31.1 mg kg $^{-1}$ and a PSR value of 0.43. In addition, the pH of the Donlonton soil was within the range where P is most available in the soil solution and available for plant uptake or leaching (Lindsay et al., 1979; Penn and Camberato, 2019). The Donlonton soil solution P availability was reflected in the high WEP concentration (31.1 mg kg^{-1}), the largest percentage of total extractable P in the H_2O-extractable pool (19.5%) of our eight samples (Table 2.1; Figure 2.1b). The Donlonton soil had the smallest percentage of total extractable P in the $NaHCO_3$-extractable pool (11.6%), but the distribution between total extractable P in the NaOH and HCl-extractable pools were comparable to our other samples. This distribution of P within operational soil P pools suggests that P with the $NaHCO_3$-extractable pool (labile P sorbed to soil surfaces; Hedley et al. 1982) was dissolving and replenishing the soil solution P; as such, LCF identified mostly stable P species.

2.3.4.3 Soils Amended with Manure + Fertilizer and Only Fertilizer

The Bojac-manure and Bojac-fertilizer soils contained semicrystalline Al-P species (30.1 and 18.3%, respectively) and P sorbed to or boehmite (59.3 and 48.8%, respectively), as determined by LCF **(**Figure 2.2). Interestingly, LCF results identified amorphous Fe-P in Bojac-fertilizer soil and crystalline phosphosiderite in the Bojac-manure soil. Both soils had similar chemical fractionation of Al, Ca, and Fe concentrations, Mehlich-3 Al concentrations, and total P, Al, Ca, and Fe concentrations (Table 2.1, Figure 2.1). Based on our records, Bojac-fertilizer consistently received 56 kg ha^{-1} of TSP, unlike Bojac-manure that received diammonium phosphate (56 kg ha^{-1}) or poultry litter (4,483 kg ha^{-1}) every two years. Bojac-fertilizer's higher P loading rate likely resulted in a higher Mehlich-3 P concentration in the Bojac-fertilizer soil (371 and 267 mg kg^{-1}), larger WEP concentration (9.41 and 4.59 mg kg^{-1}, respectively), and PSR value (0.35 and 0.24, respectively). In addition to a lower P loading rate, soil mineralogy or organic matter content likely played a role in Bojac-manure's lower risk of P loss compared to Bojac-fertilizer as Bojac-manure had double the concentration of Mehlich-3 Fe (301 and 165 mg kg^{-1}, respectively) and OM (18.0 and 9.0 mg kg^{-1}, respectively), and slightly higher total Fe concentrations (9.73 and 8.11 g kg^{-1}).

2.4 Implications

Under P drawdown scenarios, we would expect plants to uptake P first from semicrystalline Al-P followed by semicrystalline Fe-P. Following depletion of these P species, more crystalline Al and Fe-P species, like variscite and phosphosiderite, would dissolve to replenish the P within the soil solution. Lastly, as P sorbs to Al and Fe (hydr)oxides through inner sphere complexes; as such, P sorbed to Al-hydroxide, ferrihydrite, and hematite will likely remain in the soil longer than secondary Al- and Fe-P minerals, as plant-induced desorption through ligand exchange requires more energy than Al and Fe-P dissolution. However, a changing climate could exacerbate coastal flooding and saltwater intrusion and promote reductive dissolution of Fe, especially in coastal fields adjacent to tax drainage ditches or natural streams (Tully et al., 2019).

Future research should compare dominant P species in P-enriched soils with various management practices to adjacent unamended soils to determine the influence of management versus soil mineralogy. Moreover, this analysis will be facilitated by improvements in x-ray absorption spectroscopy detectors. In addition, investigating P species in soils impacted by saltwater intrusion will help researchers better managed P in these fields experiencing repeated flooding.

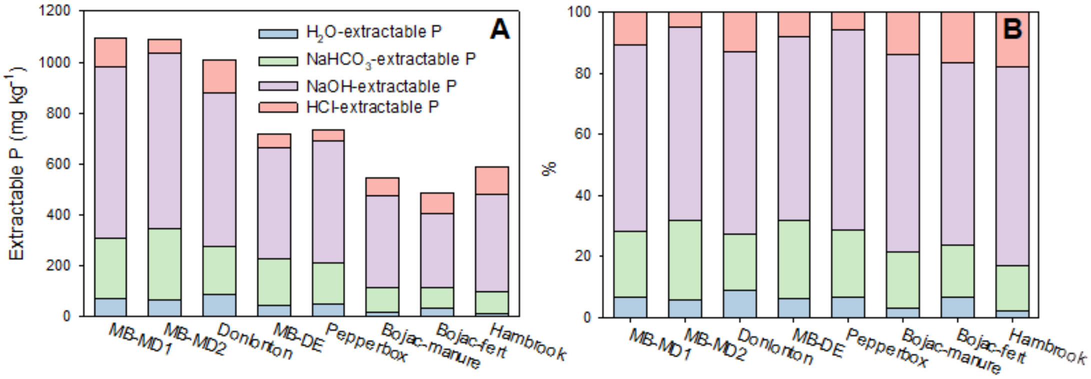

Figure 2.1 A) The extractable P (mg kg $^{-1}$) B) The percentage of total extractable inorganic P solubilized by H_2O, $NaHCO_3$, NaOH, and HCl for all eight legacy P soils.

Table 2.1 Management history, pH, organic matter (OM; loss on ignition in g kg $^{-1}$), water extractable P (WEP; mg kg $^{-1}$), Mehlich-3 P, Ca, Fe, and Al concentrations (mg kg $^{-1}$), and the P Saturation Ratio for eight legacy P soils.

Dominant Soil Series	Management History	pH	OM	WEP	Mehlich-3				
					P	Ca	Fe	Al	P Sat. Ratio
			g kg^{-1}	——— mg kg^{-1} ———					
Mullica-Berryland-MD1	Poultry manure, row crops (corn/soybean)	5.0	29.0	19.8	697	772	187	1134	0.50
Mullica-Berryland-MD2	Poultry manure, row crops (corn/soybean)	4.7	34.0	9.87	431	515	228	1100	0.31
Mullica-Berryland-DE	Poultry manure, row crops (corn/soybean)	5.1	42.0	27.4	492	751	115	1037	0.39
Pepperbox	Poultry manure, row crops (corn/soybean)	5.5	10.0	13.3	629	371	222	894	0.55
Hambrook	TSP fertilizer, row crops (corn/soybean/rye)	5.7	4.9 (49)	2.51	54.1	1261	345	608	0.06
Bojac - manure	Poultry manure, row crops (corn/soybean/wheat)	5.4	18.0	4.59	267	450	301	840	0.24
Donlonton	Dairy manure, forage rotation	6.5	6.2 (62)	31.1	451	1715	514	669	0.43
Bojac - fertilizer	TSP fertilizer, vegetables (tomato) and row crops (corn/soybean/wheat)	5.8	0.9	9.41	371	577	165	839	0.35

Table 2.2 Total P, Al, Ca, and Fe concentrations (g kg $^{-1}$) and molar ratios of P to Al, Ca, and Fe as determined by X-ray fluorescence analysis of eight Mid-Atlantic soils.

	Total Elemental Analysis				Molar Ratios		
Soil Series	P	Al	Ca	Fe	P:Al	P:Ca	P:Fe
	g kg^{-1}						
Mullica-Berryland-MD1	5.00 ± 0.15	31.3 ± 1.75	4.36 ± 0.06	4.22 ± 0.05	7.20	0.67	0.47
Mullica-Berryland-MD2	3.31 ± 0.13	31.3 ± 1.75	3.05 ± 0.05	4.78 ± 0.05	10.9	0.71	0.80
Mullica-Berryland-DE	6.26 ± 0.16	42.0 ± 1.96	3.92 ± 0.06	4.95 ± 0.05	7.72	0.01	0.44
Pepperbox	2.80 ± 0.13	42.8 ± 1.06	2.23 ± 0.05	4.66 ± 0.05	17.56	0.61	0.92
Hambrook	0.98 ± 0.09	46.3 ± 1.09	3.40 ± 0.05	30.3 ± 0.13	54.29	2.68	17.12
Bojac-manure	1.27 ± 0.10	36.0 ± 0.98	2.14 ± 0.05	9.73 ± 0.08	32.58	1.30	4.24
Donlonton	1.73 ± 0.11	32.4 ± 0.97	4.16 ± 0.06	30.5 ± 0.13	21.56	1.86	9.78
Bojac-fertilizer	1.30 ± 0.10	37.6 ± 1.00	2.93 ± 0.05	8.11 ± 0.07	33.40	1.75	3.47

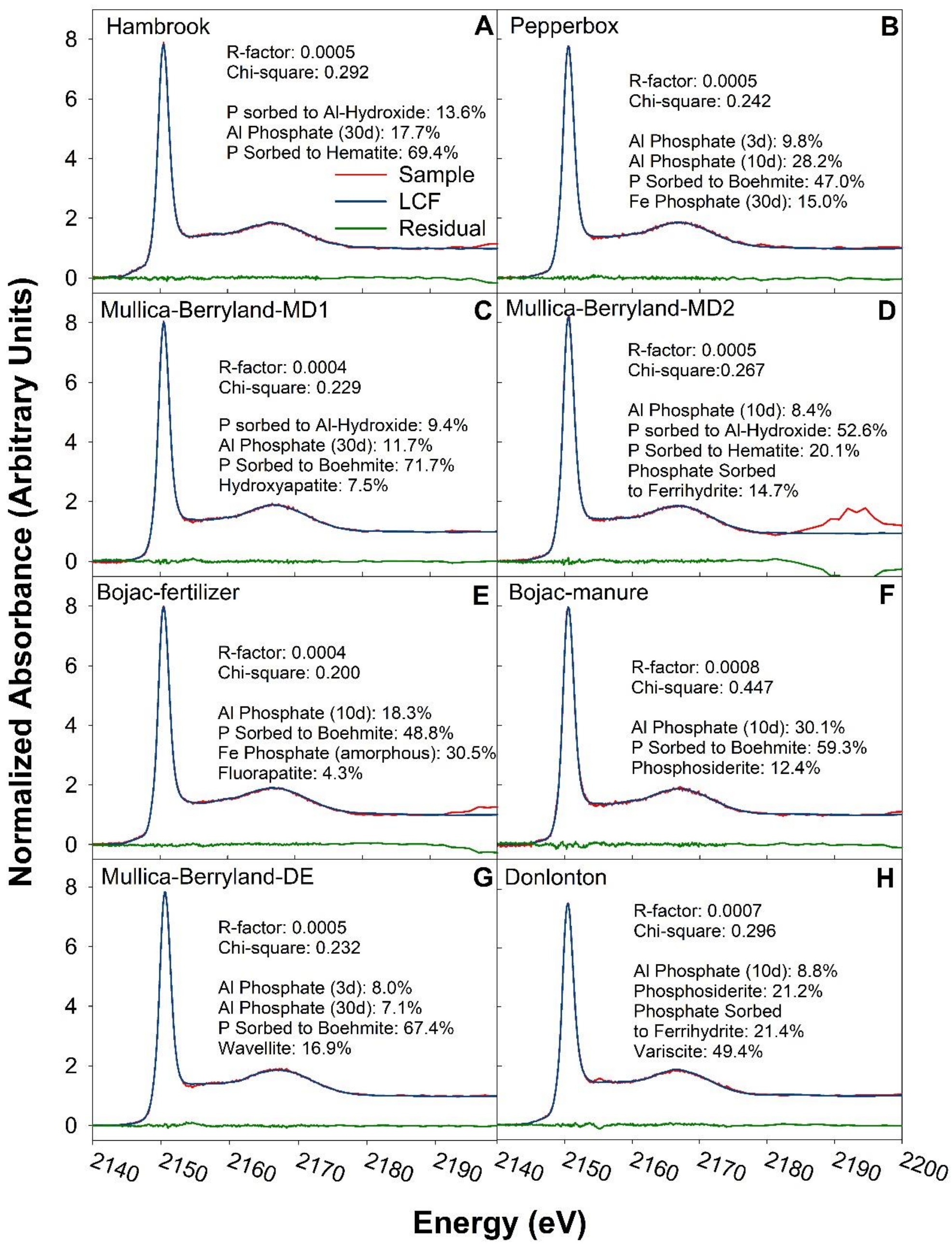

Figure 2.2 Phosphorus K-XANES spectra linear combination fit R-factor, chi-square, and residual for eight legacy P soils.

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Chapter 3

SOIL HEALTH TRADEOFFS MAY BE MINIMAL WHEN SOILS ARE SEVERELY ENRICHED WITH PHOSPHORUS

3.1 Introduction

Phosphorus (P) losses to water bodies from agricultural fields with elevated soil test P concentrations are linked to water quality degradation (Patterson et al., 1998; Feyereisen et al., 2010). Soil health practices, including no-tillage, conservation tillage, and cover crops, are increasing in popularity as farmers seek to conserve soil and improve soil conditions (e.g., fertility, organic matter, infiltration, etc.; USDA-NRCS, 2022). Conservation tillage and cover crops often increase infiltration, soil aggregation, and aggregate stability while reducing particulate P loss (Liu et al., 2014; Dodd & Sharpley, 2016). However, conservation tillage can have unintended trade-offs by promoting dissolved P (DP) losses resulting from surface soil P stratification or preferential flow pathway formation (Zhao et al., 2001; Jarvie et al., 2017; Pease et al., 2018) while cover crop residue can release DP during freezing and thawing (Messiga et al., 2010; Duncan et al., 2019). Scientists warn that potential increases in DP losses can counteract positive impacts of soil health practices (Duncan et al., 2019).

The potential for dissolved P losses from agricultural soils is a significant concern in areas of intensive animal production, where historical applications of animal manures at nitrogen-based rates resulted in the build-up of soil test P to concentrations that exceed agronomic need (Vadas & Sims, 1998; Sims et al., 2002).

To our knowledge, no studies have investigated the potential for P stratification and the formation of preferential flow pathways after implementing soil health practices like conservation tillage and cover crops on soils with elevated soil test P concentrations. Delaware offers an ideal environment for evaluating of soil health practices under elevated soil P concentrations, as soil test P concentrations commonly test within the agronomic "excessive" category (Mehlich-3 P > 100 mg kg^{-1}; Sims et al., 2002) due to historical application of poultry litter and the flat, sandy soils of the region have a propensity for the formation of preferential flow pathways (Kleinman et al., 2015). In this study, we evaluated soil P stratification and dry aggregate stability in soils with and without a history of soil health practices. Results from this study will improve our understanding of how implementing soil health practices may change the risk of P losses from soils enriched in P.

3.2 Materials and Methods

3.2.1 Site Selection and Soil Phosphorus Characterization

We selected ten working agricultural fields in Sussex County, Delaware with 0 to 15 years of soil health practice implementation (e.g., conservation tillage, no-tillage, cover crops). Each field was managed in a grain crop rotation that included corn (*Zea mays* L.) and soybean [*Glycine max* (L.) Merr.]; some fields were double cropped with wheat (*Triticum aestivum* L.) following the corn crop. Fields with cover crops were planted with wheat.

Fields were sampled between 23 Jan and 24 Feb 2020 prior to spring planting. Seven soil cores were collected using a 10-cm bucket auger to a depth of 0.97 m from each field. Each soil core was divided into 11 depth increments (ranging from 5- to

15-cm in depth), with the smaller increments (5 cm) taken near the soil surface and the depth to seasonal high-water table (University of California Davis, 2019). All 770 soil samples were air-dried, ground, sieved (2 mm), and bagged prior to analysis of Mehlich-3 extractable P, Al, and Fe (NECC-1312, 2011) by inductively coupled plasma optical emission spectroscopy (ICP-OES). Mehlich-3 P saturation ratio (PSR) was calculated using Mehlich-3 P, Fe, and Al concentrations expressed on a molar weight basis (Maguire & Sims 2001; eqn. 2). Subsamples from four depth increments (0–5 and 5–10 cm; ±5 cm from the seasonal high-water table) from two cores per field (80 total) were analyzed for water extractable P (WEP; Murphy & Riley, 1962) by spectrophotometer (GENESYS™ 30 Visible Spectrophotometer) following deionized water extraction (Self-Davis, 2009). For each field, we averaged the chemical data above from the field's seven cores. We then determined the chemical properties of larger depth increments by a chemical data weighted average of smaller depth increments.

3.2.2 Dry Aggregate Stability

We determined the size distribution of dry aggregates (modified Kemper and Rosenau, 1986) from selected depths (0–5, 5–10, and 10–25 cm) from three cores per field. Dry aggregate samples were stored in plastic cups and allowed to air dry to prevent the crushing of soil aggregates. Dry aggregate samples were transferred from the storage cup to a Ro-Tap Sieve Shaker (W.S. Tyler Ro-TAP Sieve Shaker RX-29) containing a nest of sieves (no. 4, 8, 16, 30, 50, 100, 200). Dried soils were shaken for 5 min and the aggregates retained on each sieve were weighed.

3.2.3 Phosphorus Risk Assessment

One field level risk assessment tool, the North Carolina P Loss Assessment Tool (NC-PLAT; NC PLAT Committee, 2005), was run to estimate the annual particulate, runoff, and leachate P concentrations loads (lb P/ac/yr) from each site under two scenarios without additional P additions: 1) corn, wheat, double cropped soy; no-tillage and 2) corn, full season soy; clean tillage corn, conventional soybean. We also included a soil (Quindocqua soil series) from the University of Maryland Eastern Shore Research Farms (See Chapter 4.2.1 for more information) in this risk assessment. We inputted the surface (0-5 cm) and subsurface (30 cm) M3 P concentrations and the appropriate values of the Revised Universal Soil Loss Equation (RUSLE) and curve number for the cropping system. We followed the supplemental methods from Shober et al. (2017) to determine transmissivity and drainage intensity calculations for each soil. In addition, annual runoff and leachate volume was estimated using annual precipitation and curve numbers. As the data were not normally distributed, we ran a Wilcoxon signed-rank test in SAS to compare P loads between scenarios.

3.3 Results and Discussion

3.3.1 Phosphorus Characterization

Mehlich-3 P concentrations in surface soils (0–5, 5–10, and 10–15 cm) ranged from 19.7 to 431 mg kg^{-1} (Figure 3.1a; Table B.1). Eight of 10 sites had surface Mehlich-3 P concentrations that were above the agronomic “optimum” (>100 mg kg^{-1} P; Sims et al., 2002), indicating a low probability of plant response to P applications. Moreover, seven fields had surface Mehlich-3 P concentrations above the environmental threshold (>150 mg kg^{-1} P), indicating increased risk of P losses that may impact water quality (Sims et al., 2002; Figure 3.1a). Soil test P concentrations that exceed the 150 mg kg^{-1} Mehlich-3 P threshold are common in the Delmarva region. For example, Maryland Department of Agriculture (2019) reported that 59% Mehlich-3 P concentrations of soils in the Lower Easter Shore counties (adjacent to Sussex County, DE) were above 142 mg kg^{-1}. Mean Mehlich-3 P concentrations in surface soils were 270 mg kg^{-1} for fields with >5 years of soil health practices compared to 246 mg kg^{-1} for soils with no history of soil health practices.

Only the no-till Downer soil, which had surface Mehlich-3 P concentration that were below the agronomic optimum (≤ 50 mg kg^{-1}), showed evidence of soil P stratification (Figure 3.1a). Mehlich 3 P concentrations were 60.8, 32.6, and 19.7 mg kg^{-1} at the 0–5, 5–10, and 10–15 cm, respectively. Mehlich-3 P concentrations in the top 25 cm of the remaining fields tended to be homogenous in both the soil health and conventionally tilled fields (Figure 3.1a). As such, there is little evidence to suggest that implementation of soil health practices was increasing stratification of soil P. Overall, our M3 P results widely contradict those of past researchers who reported stratification of soil test P in the surface layers of fields managed under conservation or no-till due to surface applications of manure or fertilizer (Table B.1; Baker et al., 2017; Cade-Menun et al., 2015; Daryanto et al., 2017, Duiker & Beegle, 2006). We hypothesize that the lack of P stratification in our study was likely due to the adoption of conservation tillage or no-till practices in these fields years after soils were enriched with P from historical manure applications prior to the requirement for P-based manure management with the 1999 Delaware Nutrient Management Act (Sims et al., 2002).

Five of the seven fields (3 soil health, 2 conventional) with "excessive" surface Mehlich-3 P concentrations also had Mehlich-3 P concentrations within the agronomic optimum range (50-100 mg kg^{-1}) at the 36-49 cm depth (Figure 3.1a); three of these seven fields (1 soil health) had Mehlich-3 P concentrations > 50 mg kg^{-1} at the depth to seasonal high water table (up to 97 cm below the soil surface). Enrichment of soil P at depth is indicative of an increased risk of subsurface P loss; however, subsurface P enrichment did not appear to be driven by the implementation of soil health in our fields.

Six of our fields had surface WEP concentrations (0–5 cm) above the environmental threshold of 8.6 mg kg^{-1} (Figure 3.1b) and posed a high risk of P loss, especially through surface runoff (Maguire and Sims, 2002; Kleinman et al., 2011).

Seven of the fields (4 soil health) had surface PSR values (0-5 cm) above the environmental threshold of 0.20, indicating that the soil poses a very high risk for P loss by runoff, erosion and leaching to water bodies (Table B.1; Maguire and Sims, 2002). Three soils (2 soil health) had PSR values above the environmental threshold at a depth of 36 cm, evidence of P leaching at depth.

3.3.2 Dry Aggregate Stability

We compared fields of varying soil health implementation from only the Pepperbox-Rosedale soil series to minimize changes in aggregate size due to different soil types. All Pepperbox-Rosedale soils followed a similar dry aggregate distribution (Figure B.1). The smallest fraction sizes for all Pepperbox-Rosedale soils were sieve sizes 4 and 8 (> 4.76 and 2.38 - 4.75 mm, respectively) and two largest fraction sizes were sieve sizes 50 and 100 (0.297 - 0.594 and 0.149- 0.296 mm, respectively). Although not significantly different from dry aggregate distribution percentages of conventional tillage fields, there is evidence that larger dry aggregates formed in Pepperbox-Rosedale-4 (15+ years of no-till and cover crops) in surface soil layers (0-25 cm) compared with other Pepperbox-Rosedale conventional tillage and soil health fields (Figure B.1). There was also evidence that improved aggregation occurred at depth (86- 97 cm) for Pepperbox-Rosedale-4 (Figure B.2). Soils with a wider size distribution of soil aggregates, suggest the formation of preferential flow pathways (Shipitalo et al., 2000) which may increase the connectivity between the field and drainage ditch, increasing the risk of subsurface P loss (Vadas et al., 2007).

3.3.3 Soil Phosphorus with Soil Health Scenarios

Particulate P, runoff dissolved P, and leachate P loads between scenario #1, cover crops and no-tillage, were significantly different (P value = 0.002 for all three P sources) from scenario #2, conventional tillage (Table 3.1). In the cover crops and no-tillage scenario, PLAT estimated particulate and runoff dissolved P loads decreased on an average of 0.01 and 0.70 lb P/ac/yr, respectively, compared to conventional tillage. Leachate P loads were on average 0.36 lb P/ac/yr higher with cover crop implementation and no-tillage compared to conventional tillage (Table 3.1). However, this tradeoff is minimal because PLAT load estimates showed that soil health practices reduced runoff dissolved P loads, the largest source of P loss. Assuming PLAT accurately modeled P loss within our study fields, soil health practices do not increase P loads, and may in fact slightly decrease P loads from these ten fields. More fields are needed to determine if the tradeoff of increased PLAT leachate P loads is minimal compared to the decrease in particulate and runoff dissolved P loads in fields with high M3 P (>100 mg kg^{-1} P) and soil health implementation.

3.4 Conclusions

We posit that the lack of clear evidence for surface P stratification, P accumulation with depth, and soil aggregate stability in our study was due to significant enrichment of soil P due to historical applications of manure prior to the implementation of soil health practices. As such, we see no evidence that adding soil health practices significantly increased the risk for dissolved soil P losses (both surface and subsurface) in most of our study fields because the soils themselves were already considered a significant potential source of dissolved P. If anything, adopting conservation tillage or no-till and planting cover crops likely reduced runoff dissolved P losses from our study fields when compared to conventional tillage and winter fallow when soil test P concentrations are already many times higher than needed to support plant growth. As with other researchers, evidence of surface P stratification at the site with "optimum" soil test P concentrations continues to support the notion that soil health practices can cause P tradeoffs under certain conditions (i.e., when the risk of P loss from surface soils was "low" at the time of soil health practice adoption). However, our results reflect a very small dataset consisting of primarily coarse-textured, high P soils from flat landscapes. Future studies should focus on sampling from fields with a variety of textures and soil test P concentrations that were collected across various landscape positions and cropping systems to better quantify the potential for changes in P loss risk under soil health management.

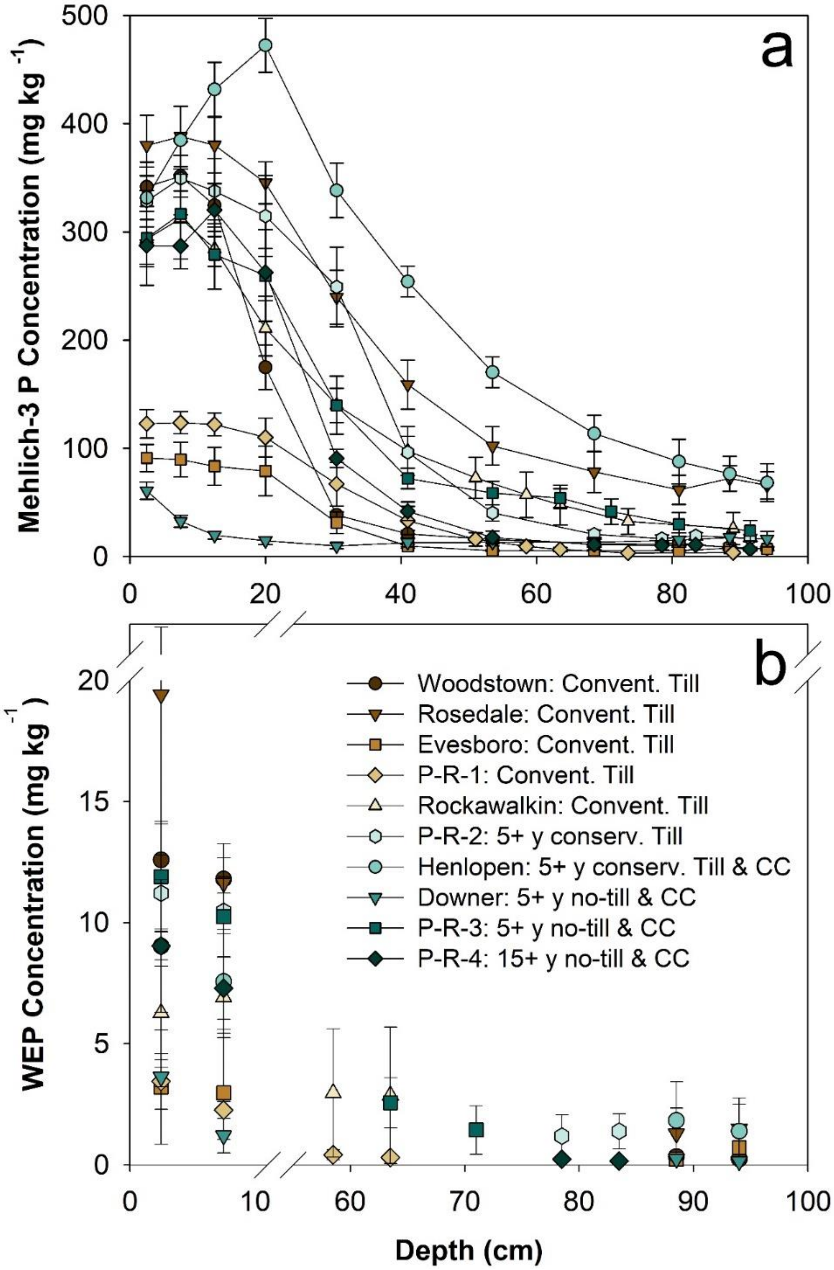

Figure 3.1 **a**) Mehlich-3 P concentrations (mg kg^{-1}) for all ten study fields. Water extractable P (WEP) concentrations (mg kg^{-1}) for all ten study fields. **b)** Water extractable P (WEP) concentrations (mg kg^{-1}) for all ten study fields. Pepperbox-Rosedale fields are abbreviated to "P-R-#" and cover crops are abbreviated to "CC."

Table 3.1 Particulate P, runoff dissolved P, and leachate P loads (lb P/ac/yr) estimated from the NC Phopshorus Carolina P Loss Assessment Tool (NC-PLAT) under two scenarios: 1) corn, wheat, double cropped soy; no-tillage (no-tillage and cover crops) and 2) corn, full season soy; clean tillage corn, conventional soybean (conventional tillage).

Dominant Soil Series	**No-Tillage and Cover Crops**	**Conventional Tillage**
Particulate P Loss (lb P/ac/yr)		
Evesboro	0.00	0.01
Pepperbox-Rosedale-4	0.01	0.05
Woodstown	0.00	0.01
Pepperbox-Rosedale-3	0.00	0.02
Pepperbox-Rosedale-1	0.00	0.00
Downer	0.00	0.00
Henlopen	0.00	0.01
Rosedale	0.00	0.00
Pepperbox-Rosedale-2	0.00	0.01
Rockawalkin	0.00	0.03
Quindocqua	0.14	0.14
Soluble P in Runoff (lb/ac/yr)		
Evesboro	0.17	0.33
Pepperbox-Rosedale-4	0.53	1.03
Woodstown	2.79	4.58
Pepperbox-Rosedale-3	0.55	1.06
Pepperbox-Rosedale-1	0.23	0.44
Downer	0.11	0.22
Henlopen	0.62	1.19
Rosedale	0.70	1.36
Pepperbox-Rosedale-2	0.61	1.18
Rockawalkin	0.54	1.05
Quindocqua	3.07	5.03
Leachate P (lb/ac/yr)		
Evesboro	0.62	0.56
Pepperbox-Rosedale-4	1.78	1.63
Woodstown	0.51	0.31
Pepperbox-Rosedale-3	2.74	2.50
Pepperbox-Rosedale-1	1.32	1.20

Downer	0.19	0.17
Henlopen	6.65	6.06
Rosedale	4.71	4.30
Pepperbox-Rosedale-2	4.90	4.47
Rockawalkin	2.75	2.51
Quindocqua	3.79	2.30

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Chapter 4

EXAMINING SOURCES AND PATHWAYS OF PHOSPHORUS TRANSFER IN A DITCH-DRAINED FIELD

4.1 Introduction

The eutrophication of water bodies from excess phosphorus (P) inputs is a global water quality concern (Oelsner & Stets, 2019). In the eastern United States, agricultural lands receiving manure or fertilizer are a significant source of P loading to estuaries like the Chesapeake Bay (Boesch et al., 2001). These non-point P losses contribute to the growth of potentially toxic algal blooms and lead to dead zones from hypoxia within the water column (Bricker et al., 2008; Carpenter et al., 1998). Phosphorus losses from agricultural soils on the Delmarva Peninsula are linked to high-intensity broiler production, historical manure applications to soils at rates that exceeded crop P removal (Feyereisen et al., 2010; Patterson et al., 1998; Vadas & Sims, 1998), and regional nutrient imbalances (Beegle, 2013). Notably, Delmarva fields with open drainage to facilitate farming operations are often affected by “legacy P” (Ritter, 2010) and therefore are susceptible to significant P losses during storms (Sallade & Sims, 1997; Mozaffari & Sims, 1994).

Although the importance of storms as drivers of P transport is widely acknowledged (Pionke et al., 1999; Sharpley et al., 2008), the processes that mobilize P and the flowpaths that deliver P to surface waters in ditch-drained settings are somewhat less clear. Broadly, surface runoff is considered the prevailing pathway of P loss in sloping landscapes (Sharpley et al., 1993), although subsurface flowpaths are increasingly common in flat landscapes with artificial drainage (Sims et al., 1998; Shober et al., 2017). For example, researchers attributed up to 92% of P losses to subsurface drainage from flat fields (slopes <3%) on the lower Delmarva Peninsula, with dissolved P being the dominant P fraction (Kleinman et al., 2007). In these landscapes, subsurface drainage reflects contributions from vertical preferential flows through fine-textured soils (Kleinman et al., 2015; Toor & Sims, 2015) or from rising water tables that intersect high P soils near the surface (Vadas et al., 2007). In order to better inform P management in flat agroecosystems, we need a more complete understanding of how these subsurface P mobilization and transport processes shape dissolved P dynamics in ditch drainage.

Concentration–discharge (C-Q) relationships can provide important insight into the processes that mobilize and transport solutes like dissolved P. For instance, the long-term slope (β) of C-Q relationships can reveal whether solutes decrease with increasing flow (dilution), increase with increasing flow (enrichment), or remain unchanged (constant) (Godsey et al., 2009). Moreover, the coefficients of variation of concentration relative to discharge (C_{VC}/C_{VQ}) can be used to ascertain if solutes are transport limited (chemostatic) or source limited (chemodynamic) (Thompson et al., 2011). Combining β and C_{VC}/C_{VQ} metrics provides insight into solute export regimes (Musolff et al., 2017). In "legacy P" landscapes, P loss from agricultural watersheds is often driven by enrichment (positive β) (Dolph et al., 2019) and transport limitation (Basu et al., 2010; Thompson et al., 2011). Based on field-scale studies in artificially drained settings (Osterholz et al., 2020; Plach et al., 2018), researchers have suggested that P losses from tile drains are supply limited ($C_{VC}/C_{VQ} > 0.5$), whereas P losses in surface runoff are transport limited ($C_{VC}/C_{VQ} < 0.5$). Solute export regimes can also differ above and below discharge thresholds, as shown with segmented regressions on long-term C-Q data (Moatar et al., 2017; Rose et al., 2018). Such discharge thresholds might be expected in ephemeral ditches that frequently oscillate between hydrologic connection and disconnection with the adjacent field.

Although composite C-Q patterns are useful tools for assessing long-term average watershed behavior, C-Q patterns for individual storms can provide greater insight into the sources and pathways for event-based transport of dissolved P. Hysteresis occurs when C-Q relationships on the rising limb of the hydrograph differ from those on the falling limb. In general, clockwise hysteresis arises from higher solute concentrations on the rising limb due to rapid solute mobilization or proximal solute source areas (Bowes et al., 2009). In contrast, anticlockwise hysteresis emerges when solute concentrations are higher on the falling limb, indicating delayed inputs from distant high-solute sources or rapid influxes of waters with low solute concentrations (Bowes et al., 2009). Although early studies categorized C-Q behavior using observations of rotational patterns, curvature, and slope (Evans & Davies, 1998; Williams, 1989), recent work has relied on two quantifiable indices: the hysteresis index (HI), which estimates the rotation and magnitude of C-Q hysteresis (Lloyd et al., 2016), and the flushing index (FI), which quantifies the C-Q slope (Butturini et al., 2008; Vaughan et al., 2017). When paired (Liu et al., 2020; Vaughan et al., 2017; Wymore et al., 2019), these indices can reveal important information regarding the sources and pathways of storm-driven dissolved P losses in drainage ditches.

Chemical and isotopic hydrograph separation can complement C-Q interpretations by providing additional information on dissolved P sources and pathways during storms. In particular, two-component hydrograph separation involves partitioning drainage water into time components of "event water" added to the watershed (in our case, precipitation from storm events) and "pre-event water" stored in the watershed, primarily as soil water and groundwater (Klaus & McDonnell, 2013). Although stable water isotope ratios of oxygen ($\delta^{18}O$) and hydrogen ($\delta^{2}H$) are commonly applied due to the natural isotopic variation between event and pre-event waters (Klaus & McDonnell, 2013), dissolved solids, such as silica (SiO2) and base cations (Ca2+ and Mg2+), have also proven useful end-members in storm hydrograph separation (Kennedy et al., 2012; Wels et al., 1991). In agricultural landscapes where vertical preferential flowpaths are known to facilitate the transport of soil P to ditches (Kleinman et al., 2015; Toor & Sims, 2015), the fraction of "event water" has been interpreted to represent the relative significance of preferential flowpaths to subsurface P leaching (Klaus et al., 2013; Vidon & Cuadra, 2011; Williams et al., 2016).

In this study, we examined the sources and pathways of dissolved P transfers in a ditch-drained field situated within the poultry-producing region of the lower Delmarva Peninsula. The study field drains agricultural soils with excessive levels of soil test P. Previous research at the study site showed P losses from nearby ditches as high as 20 kg ha^{-1}, posing concerns for water quality protection (Kleinman et al., 2007). Over a 14-mo period, we monitored flow and collected samples of drainage water, soil water, and groundwater for analysis of dissolved P concentration (a) to characterize the temporal variability of dissolved P in hydrologic source waters (soil water, groundwater) and in ditch drainage (baseflow and stormflow) and (b) to use C-Q relationships and hydrograph separation to identify the factors contributing to temporal variability in dissolved P export by ditch drainage. By coupling these two analytical approaches, we advance a conceptual model of dissolved P sources and pathways in low-gradient agricultural landscapes with ditch drainage in the Chesapeake Bay watershed.

4.2 Materials and Methods

4.2.1 Site Selection and Characterization

The study site is a 1.5-ha agricultural field that is located on the University of Maryland Eastern Shore (UMES) Research and Teaching Farm in Princess Anne, MD (Somerset County). The study field is situated near the headwaters of the 24,000-ha Manokin River watershed, a sub-watershed of the Chesapeake Bay (Figure 4.1). An open ditch drains water from the study field to the Manokin River approximately 10 km upstream of the outlet to Chesapeake Bay (Kibet et al., 2011; Kleinman et al., 2011). Historical application of poultry litter at rates that exceeded crop demand contributed to surface (0–20 cm) Mehlich-3 soil P concentrations (Mehlich, 1984) averaging 425 mg kg^{-1}, approximately 10-fold higher than the agronomic critical level of 42.5 mg kg^{-1} (Maryland Department of Agriculture, 2019).

The study field is flat (<1.5% slope) and is artificially drained through an open ditch network designed to lower seasonal high water tables (Figure 4.1) (Vaughan et al., 2008). The dominant soils in the study field are poorly drained Quindocqua series (fine-loamy, mixed, active, mesic Typic Endoaquults; Soil Survey Staff, 2019). Quindocqua soils consist of silt loam topsoil that sits above a 1-m-thick argillic horizon (0.1–1 m depth); the argillic horizon is underlain by coarse marine sediment (around 1 m depth). Electromagnetic induction surveys conducted in 2018 suggested that the argillic horizon is thinner (≤0.2 m) or absent in a small (20% by area) section of the field (Robinson et al., 2020). The presence of an argillic horizon and the occurrence of a seasonally high water table require open ditches to enhance drainage of the field. At the beginning of the study, we collected a set of 10 50-cm-long soil cores that were subsampled in 10-cm increments (50 samples total). These core samples were collocated with our piezometers and lysimeters. The average Mehlich-3 soil test P concentration was 425 mg kg^{-1}, and the average pH was 4.9 in surface soils (0–20 cm). The average soil test P concentration was 133 mg kg^{-1}, and the average pH was 4.4 in deeper soils (21–50 cm), showing evidence of vertical P stratification between surface and subsurface soils.

4.2.2 Hydrologic Monitoring and Water Sampling and Analysis

The study ditch was instrumented with two H-flumes that measured discharge at 5-min intervals. One flume was located at the bottom of the ditch near the road. The second flume was located roughly 220 m upstream near the western edge of the field (Figure 4.1).

We instituted a 14-mo sampling program (29 July 2017–8 Sept 2018) to characterize the isotopic and chemical signatures of the hydrologic pools of P that contribute to P losses in drainage waters under baseflow and stormflow conditions. Groundwater samples were collected monthly (except for April, July, and August 2018) starting in November 2017 from shallow (122 cm depth) short-screened piezometers. In summer months, groundwater sampling occurred shortly after storm events. Soil water was collected from suction cup lysimeters (0.3 m depth) quarterly and during or shortly after several storm events starting in January 2018. Groundwater and soil water samples were collected in 15-ml centrifuge tubes, which were immediately sealed with Parafilm to prevent evaporative fractionation of water isotopes. We used four automatic samplers (900Max, American Sigma) to collect drainage water at a range of different flow conditions. Two time-paced samplers collected samples during baseflow conditions (12-to-72-h intervals), and two additional samplers provided higher resolution (1-to-2-h intervals) samples immediately preceding and during storms. Mineral oil was added to the Sigma bottles used to collect samples for water isotope analysis, whereas standard acid-washed bottles were used to collect samples for analysis of P. Precipitation was sampled at a weather station located 0.35 km northwest of the study ditch; the station featured a heated tipping bucket rain gauge that provided precipitation measurements at 5-min intervals. Composite precipitation samples were collected in a 1-L bottle with added mineral oil, and within-storm samples (1-to-2-h intervals) were collected with a time-paced sampler fitted with a rain collection plate.

Ditch water and precipitation samples designated for nutrient analysis were transferred from automatic sampler collection bottles into two 50-ml tubes to generate an unfiltered and a filtered subsample in the laboratory (0.45-µm Supor filter with hydrophilic polyethersulfone membrane) and then stored in a cold room (4 °C). Filtered subsamples were analyzed for total dissolved P (TDP), $Ca2^{+}$, and $Mg2^{+}$ using inductively coupled plasma–mass spectroscopy (iCAP-RQ, Thermo-Fisher) or inductively coupled plasma–optical emission spectroscopy (720-OES, Agilent Technologies).

Mineral oil was removed with a separatory funnel from ditch pre-storm baseflow, stormflow, and precipitation samples designated for isotopic analysis. These unfiltered samples were then transferred to 15-ml plastic vials, capped, and sealed with Parafilm prior to analysis for $\delta^{2}H$ and $\delta^{18}O$ by cavity ring-down spectroscopy using an isotopic water analyzer (L2140-i, Picarro, and 912-0032, Los Gatos Research). Three working standards were run after every five samples, and quality assurance standards were run every seven samples. Raw isotope ratios were normalized and corrected with a standard, yielding a sample accuracy of ±0.2‰ for $\delta^{18}O$ and ±1.5‰ for $\delta^{2}H$.

4.2.3 Characterization of Concentrations and Loads

The TDP concentrations of groundwater, soil water, ditch stormflow, and ditch baseflow were plotted in box plots and compared for the whole study period and by meteorological seasons (spring, March–May; summer, June–August; fall, September–November; and winter, December–February). Concentrations of TDP were compared across water pools using nonparametric Kruskal–Wallis multiple comparison tests (R Core Team, 2019) with a Dunn's post hoc test (Dinno, 2017). Samples were determined to be significantly different at $\alpha = .05$.

We used the *loadflex* package (version 1.1.11; Appling et al., 2015) in R (version 3.6.3) to estimate TDP loads in the drainage ditch at an hourly resolution as well as for the whole study period. Previously, researchers found the composite method (Aulenbach & Hooper, 2006) was most appropriate for load estimation in small watersheds (Coble et al., 2018; Kelly et al., 2019; McDowell et al., 2019) because it combines a regression-based approach with interpolation. We also used the *BaseflowSeparation()* function in the *EcoHydRology* package (version 0.4.12.1; Fuka et al., 2018) in R (version 3.6.3) to separate hourly discharge into baseflow and stormflow components. Baseflow and stormflow TDP loads were then estimated following the approach outlined by Vanni et al. (2001).

4.2.4 Concentration-Discharge Analyses

We used the full dataset (baseflow and stormflow measurements) to assess long-term C-Q trends in the drainage ditch. Total dissolved P concentrations and discharge were log-transformed (base 10) prior to analysis. Using linear regression, we estimated the slope (β) of the log(C)-log(Q) model to determine the direction of the long-term trend. We then estimated CV_C/CV_Q and paired it with the slope value (Musolff et al., 2017) to ascertain whether TDP exhibited long-term dilution, enrichment, or constant C-Q patterns and if TDP export was chemodynamic (source-limited) or chemostatic (transport-limited). We also used the "segmented" package (version 1.2-0; Vito & Muggeo, 2008) in R (version 3.6.3) to determine if C-Q relationships differed above and below a discharge threshold. Statistical differences in slope above and below the discharge threshold were assessed with the pseudo-score test (Muggeo, 2016). Following the approach of Rose et al. (2018), we then used an F-test on the residual sum of squares to judge whether the segmented regression model provided a significantly better fit to the C-Q data than the linear regression model (Vieth, 1989).

In addition to long-term C-Q trends, we analyzed C-Q hysteresis patterns during seven storms that were successfully sampled during the study period. First, we normalized dissolved P concentrations and discharge measurements for each storm following the approach of Lloyd et al. (2016). We then quantified the direction and magnitude of event hysteresis with the HI (Lloyd et al., 2016) and estimated the C-Q slope with the FI (Vaughan et al., 2017).

4.2.5 Chemical and Isotopic Hydrograph Separation

We used hydrograph separation to provide insight into the possible flow pathways of water and TDP during storm events. Water isotopes (δ^2H and $\delta^{18}O$) and a suite of geochemical tracers (e.g., SiO_2, Ca^{2+}, Mg^{2+}) in baseflow, stormflow, and precipitation were used in two-component mixing models to determine the fraction of "event" water and "pre-event" water in the drainage ditch. To capture variation in precipitation throughout the storm event, we used the bulk incremental weighting approach of McDonnell et al. (1990). Total dissolved P concentrations during storms were paired with mixing model results to investigate the relationship between peak TDP concentrations and peak "event" water, which was assumed to be sourced from rapid preferential flowpaths (Stone & Wilson, 2006; Vidon & Cuadra, 2011).

4.3 Results and Discussion

4.3.1 Climatic and Hydrologic Conditions

Climatic and hydrologic conditions (Figure 4.2a) at the onset of the study (fall 2017) were slightly wetter than normal (1,197 mm) when compared to 30-yr (1981–2010) average precipitation (1,129 mm) for the region (PRISM Climate Group, 2020). Conditions were much wetter (1,561 mm) in 2018 because storms increased in frequency and magnitude toward the end of the study period. In fact, 2018 was among the top three wettest years since 1895 (PRISM Climate Group, 2020). Thirty-five rainfall-runoff events were observed during the 14-mo study. Hydrologic records from the ditch were too short to characterize runoff magnitudes; however, longer-term records from the nearby gauging station (1.2 km northwest of study site) on the Manokin River (USGS Gauge# 01486000; Dillow, 1996) provided evidence that most storms during the study had recurrence intervals of less than 2 yr. Only two storms had recurrence intervals greater than 5 yr. Notably, we captured 11 storm events in the drainage ditch during our automatic sampling campaign, including the largest storm of the study period, a roughly 10-yr event that occurred on 18 May 2018. We present data from the seven largest storms that were sampled (representing 20% of the total rainfall-runoff events that occurred during the study period), because these storms yielded data with sufficient temporal resolution to assess C-Q relationships and conduct isotopic hydrograph separation.

4.3.2 Patterns in TDP Concentrations and Loading

During the study period, TDP concentrations in ditch drainage ranged from below detection (< 0.001 mg L^{-1}) to 1.8 mg L^{-1} (Figure 4.2b), with a median TDP concentration of 0.25 mg L^{-1}. Median TDP concentrations in our study ditch were broadly consistent with Kleinman et al. (2007), who reported average dissolved reactive P concentrations (colorimetric analysis) of 0.25–0.90 mg L^{-1} in a set of nearby nonpoint source ditches on the UMES field site. In both studies, P concentrations in ditch drainage typically exceeded P concentrations expected from background sources (0.06 mg P L^{-1}) (Smith et al., 2003) and the freshwater eutrophication threshold (0.02 mg P L^{-1}) (Dodds et al., 1997, 1998). As expected, high TDP concentrations in drainage supported TDP loading patterns that mirrored discharge patterns (Figure 4.2c). In total, ditch TDP exports were 128 kg during the 14-mo study, with 31.1 kg of TDP exported in May 2018. Annual TDP losses were about 3.3 kg ha^{-1} yr^{-1} in our study (assuming an approximate drainage area of 33 ha determined with high-resolution digital elevation models), whereas Kleinman et al. (2007) reported dissolved reactive P losses of 0.6–3.6 kg ha^{-1} yr^{-1} in 2005.

Analyzing TDP concentrations and loads under different flow conditions further revealed the importance of stormflow in TDP export. For instance, we found that median TDP concentrations during stormflow periods (0.28 mg L^{-1}) were 1.6 times higher than median TDP concentrations in baseflow (0.17 mg L^{-1}) (Figure 4.3). In addition, quarterly surveys of source waters (Figure 4.3) showed the highest median TDP concentration in shallow (0.3 m) soil water (0.89 mg L^{-1}) and a significantly lower median TDP concentration in deeper (>1 m) groundwater (0.04 mg L^{-1}). The vertical stratification of TDP at our site aligns with the findings of Vadas et al. (2007), who reported high dissolved P concentrations (0.65 mg L^{-1}) in shallow (<0.5 m) groundwater and much lower dissolved P concentrations (0.14 mg L^{-1}) in deeper (>1 m) groundwater. Indeed, higher TDP concentrations in stormflow could be sourced from shallow soil waters that are mobilized during storms, although the significance of this mechanism would likely be dictated by seasonal high water tables and temporal variations in TDP in soil water and groundwater. With stormflow accounting for roughly 78% of TDP export (Figure 4.2c) in the drainage ditch, there is a clear need to further examine the processes that mobilize P sources and deliver TDP to drainage ditches.

4.3.3 C-Q Discharge Threshold

By applying a segmented regression model to analyze C-Q relationships for TDP in drainage water (Diamond & Cohen, 2018; Hensley et al., 2019; Rose et al., 2018), we found a C-Q discharge threshold of 6.4 L s^{-1} (95% confidence interval, 3.1–13.4 L s^{-1}). Using the pseudo-score test (Muggeo, 2016), slopes below (β_1 = -0.06) and above (β_2 = 0.30) the discharge threshold were significantly different ($p < .001$). The existence of a discharge threshold in the C-Q relationship for TDP implies differential export regimes at low and high discharges. Notably, the discharge threshold (6.4 L s^{-1}) was roughly equivalent to the median discharge in the ditch (6.8 L s^{-1}); the significance of median discharge thresholds is well established in the C-Q literature (e.g., Diamond & Cohen, 2018; Meybeck & Moatar, 2012; Moatar et al., 2017). For discharges below the discharge threshold of 6.4 L s^{-1} (27% of samples), we found a C-Q slope (β) of -0.06 and a CV_C/CV_Q of 0.43, which indicated a dilution pattern and a somewhat chemostatic (transport-limited) export regime for TDP. Above the discharge threshold (73% of samples), the C-Q slope (β) increased to 0.30 and CV_C/CV_Q equaled 0.32, suggesting an enrichment pattern and slightly stronger evidence for chemostasis ($CV_C/CV_Q < 0.5$) (Musolff et al., 2017). Although the "down-up" C-Q pattern we observed for TDP in drainage water has been reported periodically (Moatar et al., 2017; Underwood et al., 2017), the "flat-up" pattern appears more frequently for TDP (Moatar et al., 2017). Even so, the shift from slight dilution (or even constant) C-Q patterns below the discharge threshold to enrichment above the threshold, along with evidence for transport limitation, suggests greater hydrologic connectivity between the field and ditch at higher flows. In essence, discharges above the 6.4 L s^{-1} threshold point to the likely onset of shallow subsurface flows that connect elevated TDP soil waters with drainage waters.

4.3.4 Concentration–Discharge Analyses

The seven intensively sampled storms spanned a range of flow conditions and TDP concentration patterns (Figure 4.4; Table 4.1). Notably, two of the storms (12 and 19 Aug. 2017) had mean discharges that were below the threshold of 6.4 L s^{-1}, whereas the remaining five storms had mean discharges above the threshold. Mean discharges for the three largest storms (29 Oct. 2017, 18 May 2018, and 8 Sept. 2018) were equal to or greater than the upper 95% confidence interval bound of the discharge threshold (13.4 L s^{-1}). Collectively, these three storms contributed 13 and 27% of the flow and TDP load, respectively, during the study period; smaller storms only accounted for 1 and 2% of the flow and TDP load, respectively.

Four storms exhibited clear, clockwise TDP hysteresis (HIs ranging from 0.23 to 0.54), whereas the other three storms showed more complex patterns (e.g., figure-of-eight; HIs ranging from -0.14 to 0.08) (Figure 4.4; Table 4.1). Complex hysteresis tended to occur in smaller storms with multi-peaked hydrographs, whereas clockwise hysteresis occurred in much larger storms with single-peaked hydrographs. Notably, P hysteresis patterns during storms are typically clockwise (Bowes et al., 2005, 2015; Donn et al., 2012). Yet, Bieroza and Heathwaite (2015) noted a strong control of storm size (indicated by runoff volume) on P hysteresis during their study of 61 storms in a small catchment in the United Kingdom. In their study, large storms tended toward clockwise hysteresis patterns and small storms yielded anticlockwise patterns. As such, the indication of clockwise TDP hysteresis during larger storms in our study ditch is potentially important because it suggests TDP is rapidly transported to the ditch (Bowes et al., 2009). Faster flow pathways that arrive early in these large storm events are likely enriched in TDP (Hensley et al., 2017).

Flushing indices also appeared to vary as a function of storm size. The three largest events (29 Oct. 2017, 18 May 2018, and 8 Sept. 2018) exhibited a strong flushing response (FIs ranging from 0.44 to 0.62), whereas two of the smaller storms (19 Aug. 2017 and 21 July 2018) presented dilution (FIs ranging from -0.60 to -0.98). Other researchers have also observed flushing responses when using the FI approach to analyze dissolved P export during storms, reporting dissolved P concentrations reaching a maximum concentration just prior to the hydrograph peak or in concert with peak flow (Aguilera & Melack, 2018; Rose et al., 2018). When coupled with HI results, the large positive FIs for large storm events provide strong evidence that TDP mobilization was transport limited, with near-ditch sources of P activated by shallow subsurface flow pathways that rapidly responded to precipitation. In contrast, FIs that indicated dilution or indeterminate responses provide evidence of supply-limitation during smaller storm events. During smaller events, high TDP concentrations within the ditch are likely diluted by late-arriving groundwater with lower TDP concentrations.

4.3.5 Chemical and Isotopic Hydrograph Separation

Chemical and isotope hydrograph separations provided additional detail on the sources and pathways of TDP export during storms. Hydrograph separation could be applied to four of the seven storms (Table 4.1) because these storms exhibited event and pre-event end-members that were chemically or isotopically distinct (Genereux, 1998). Consistent with previous studies (Stone & Wilson, 2006; Vidon & Cuadra, 2011), we assumed that event water fractions during storms were delivered to drainage water by rapid preferential subsurface flow pathways. Because the topography of the field and surrounding area is relatively flat (slopes <3%), overland flow is a minor component of discharge (<8%) (Kleinman et al., 2007). Moreover, site-specific estimates of subsurface matrix flow of 0.05 m d^{-1} (Robinson et al., 2020) could not reasonably account for the rapid event water responses observed in the ditches. Likewise, direct channel precipitation to the surface of the ditch accounted for less than 1% of discharge. These multiple lines of evidence suggest that rapid subsurface transport of event water to drainage water is due to preferential flowpaths.

As noted with HIs and FIs, storm size appeared to affect the relative fractions of pre-event and event water in drainage water. For instance, pre-event water was the dominant fraction (56–63%; Table 4.1) of drainage water during two small storms (12 Aug. 2017 and 21 Aug. 2017), which had peak discharges roughly equal to the discharge threshold of 6.4 L s^{-1}. Assuming pre-event waters were largely sourced from groundwater (median TDP, 0.04 mg L^{-1}), it seems likely that significant pre-event baseflow contributions with low TDP concentrations diluted initially high TDP levels in drainage water, as suggested by the negative FI values for these small storms. In contrast, event water represented most of the drainage water (59–68%; Table 4.1) during two large storms (29 Oct. 2017 and 18 May 2018). Notably, the event water peak during these larger storms was roughly concurrent with the peaks in discharge and TDP concentration, especially for the 29 Oct. 2017 storm. The coherence between peak event water and peak TDP provided strong evidence for rapid subsurface transport of P via preferential flowpaths. This finding is consistent with our observations of clockwise flushing responses in the C-Q patterns for TDP during these larger storms, and with other studies identifying preferential flow pathways as the major transport process for TDP in artificially drained landscapes (Vidon & Cuadra, 2011; Williams et al, 2016).

4.4 Conceptual Model of P Transport During Storms

In this section, we synthesize long-term and within-storm C-Q patterns along with chemical and isotope hydrograph separations to elucidate processes affecting TDP dynamics in ditch drainage. We recognize that seven storms represent a small sample of storm events that occur in a given year. However, a number of overlapping factors limited our capacity to capture additional events, including: (a) the logistics of storm sampling (e.g., sudden onset of storms and/or unpredicted storm events that precluded proper set up and programming of equipment, unavailability of field sampling personnel on short notice), (b) shutdown of equipment during winter months to protect electronics from freezing temperatures (n = 12 storms that occurred in the wintertime), and (c) autosampler malfunctions during storms. Yet we are confident that the seven storm events presented in this manuscript (which included the largest storm event on 18 May 2018) were representative in magnitude and duration of the 35 storm events that occurred during the study period. As such, we feel the results enable us to generate a conceptual model of TDP mobilization and transport that can help advance the science and management of water quality in ditch-drained settings. We anticipate that the conceptual model will be most relevant to flat, ditch-drained landscapes on the lower Delmarva Peninsula but also point out that the methods used in our study could be applied to other artificially drained settings to further evaluate our interpretations.

Prior to all seven storm events, TDP concentrations were typically elevated, with median pre-storm TDP concentrations (0.46 mg L^{-1}) exceeding median TDP concentrations across all flows (0.25 mg L^{-1}). Based on previous work, there is sufficient evidence that P dissolution from P-enriched ditch sediments can support high P concentrations in drainage waters at baseflows (Sharpley et al., 2007; Smith et al., 2005). Using a relationship between depth to groundwater and discharge data from the study site in 2015-2016, the water table likely never rose to a height that intercepted high-TDP soil water during these small storms. Considering the evidence from hysteresis and flushing patterns during these small storms, as well as the prevalence of pre-event waters, we believe that the initially high TDP concentrations in pre-event drainage waters were likely diluted by low TDP groundwater that was discharged to the ditch by translatory processes such as matrix flow (Figure 4.5a).

Vertical stratification of soil TDP in the saturated zone, which has been well documented at the UMES field site (Vadas et al., 2007), would be expected to yield increasing solute concentrations with increasing flow as shown in a riparian zone modeling study by Seibert et al. (2009). Two recent studies by Zhi et al. (2019) and Botter et al. (2020) further indicate that the ratio of concentrations in soil water and groundwater (C_{sw}/C_{gw}) explains the observed C-Q patterns at the UMES field site. That is, when C_{sw}/C_{gw} is less than 0.6, dilution is present, whereas when C_{sw}/C_{gw} is greater than 1.8, flushing is dominant; chemostasis occurs when C_{sw}/C_{gw} is between 0.6 and 1.8. Using TDP measurements in soil water and groundwater, we estimated a C_{sw}/C_{gw} ratio of roughly 6.3, which suggests that TDP flushing would be expected if high P source waters were delivered rapidly to the ditch. We propose two transport mechanisms by which this occurs. First, water-table response to large storms results in the direct connection between groundwater and shallow soil water elevated in TDP (Vadas et al., 2007), which would explain the relatively high TDP in drainage water during the three largest storms. Alternately, rapid preferential flows could also transfer high P soil waters to shallow groundwater through discontinuities in the argillic horizon as was indicated by time-lapse geophysical studies in the same study ditch (Robinson et al., 2020). Of course, these are not independent processes, and the preferential flowpaths would enhance the effect of water-table fluctuations on P losses in drainage water.

Nevertheless, the relative importance of preferential flowpaths and water table fluctuations does have important management implications with respect to curtailing P losses from agricultural fields. Although vertical P stratification appears to play an important role in regulating TDP at our study site, the mechanism by which these sources of P are transported to the ditch may be more tightly coupled to water table fluctuations than preferential flowpaths (Figure 4.5b). As such, drainage water management practices may play a critical role in controlling TDP losses in the near term (Ross et al., 2016) by allowing ditch drains to function properly. Other strategies, like occasional deep tillage (Sharpley, 2003), could also be used to remediate P stratification in soils and to disrupt macropores that promote rapid preferential transfers of TDP to ditch drainage. Over the long term, however, nutrient management strategies will need to focus on drawing down legacy soil P reserves to mitigate TDP losses from drainage ditches to surface waters.

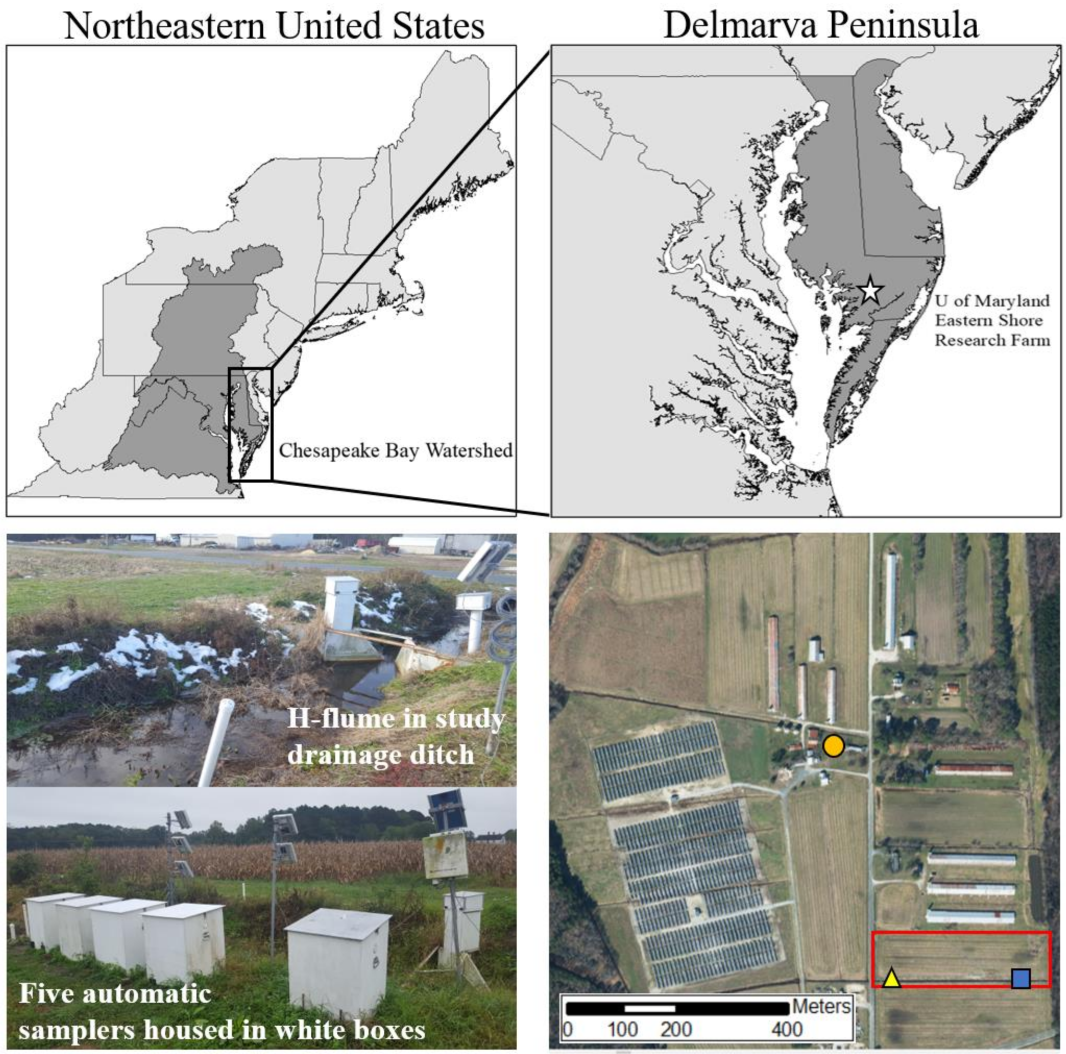

Figure 4.1 The University of Maryland Eastern Shore Research Farm (white star) lies within the Chesapeake Bay watershed in Princess Anne, MD. The study area (red box) is a 1.5-ha field. The yellow triangle designates the location of the H-flume and five automatic water samplers that were used to collect ditch water during baseflow and stormflow periods. The blue square designates the location of the upstream H-flume. Precipitation samples were collected using an automated SIGMA sampler (orange circle) that was installed 0.36 km northwest of the study ditch.

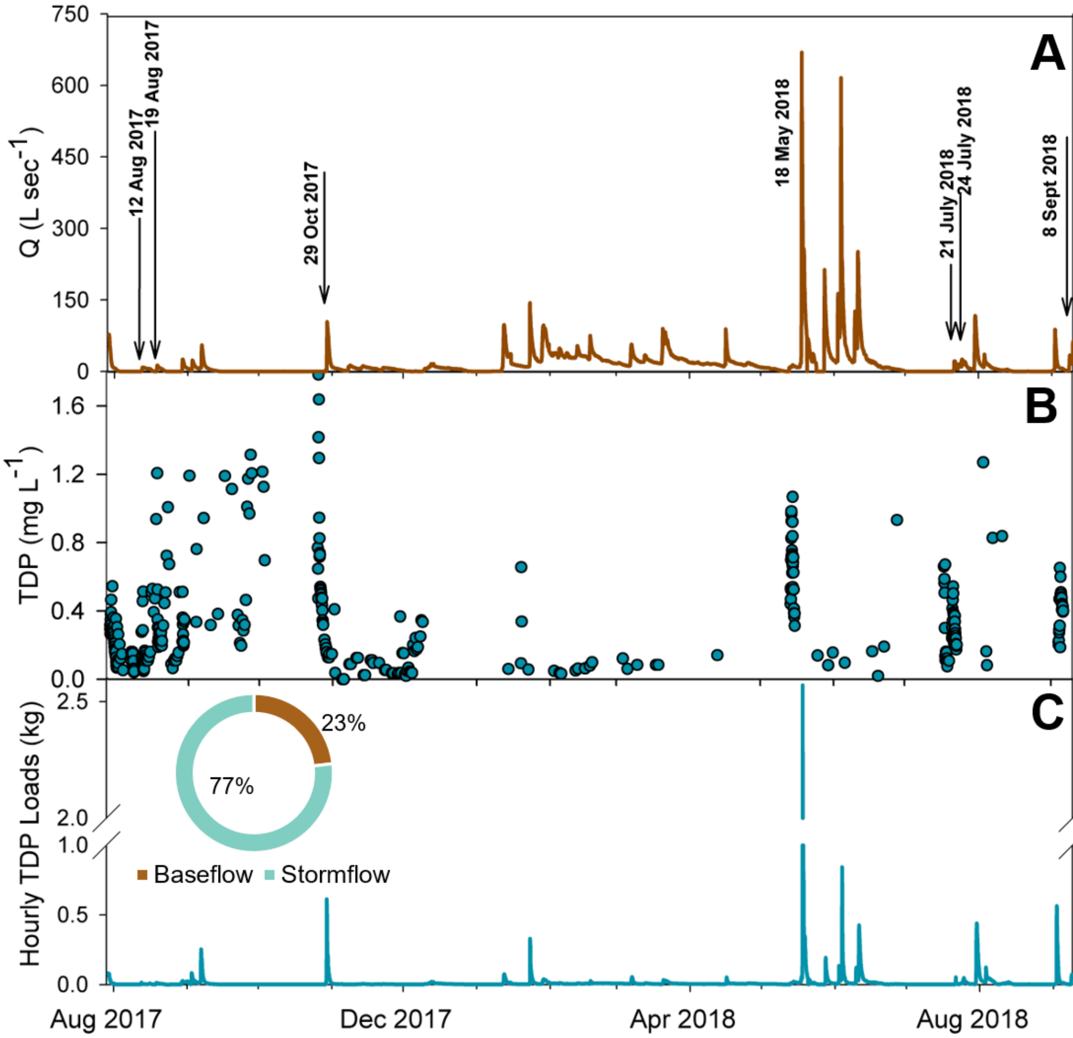

Figure 4.2 (a) Discharge, (b) total dissolved P (TDP), and (c) hourly TDP loads from a 1.5-ha ditch-drained field site at the University of Maryland Eastern Shore farm, as measured during seven storm events between August 2017 and September 2018. The inset graph (c) shows the percentage of TDP loads attributed to baseflow or stormflow over the entire study period.

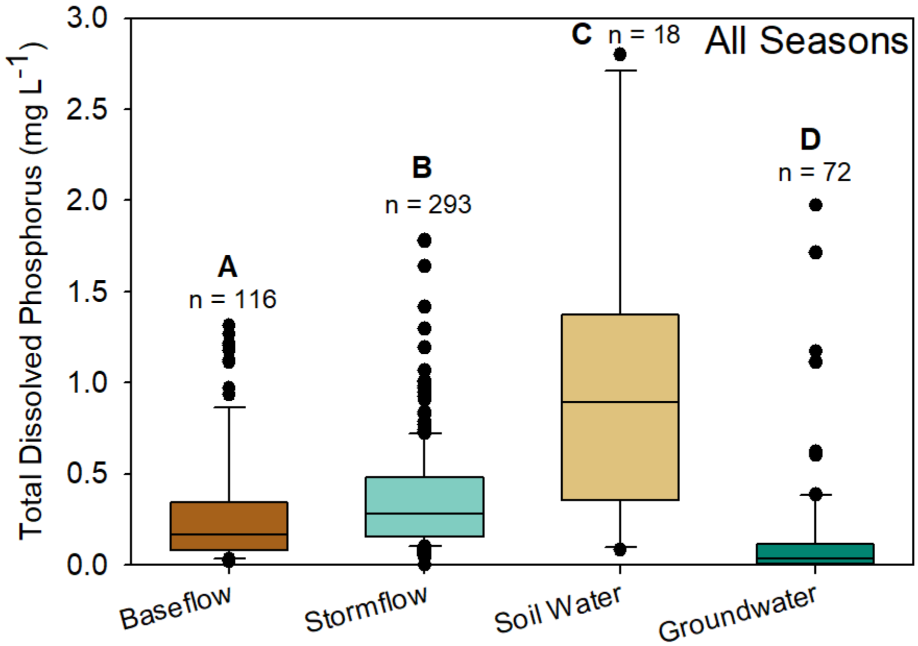

Figure 4.3 Boxplots showing baseflow, stormflow, soil water, and groundwater total dissolved P concentrations from samples collected from the 1.5-ha study field at the University of Maryland Eastern Shore farm. Box plots with different letters are significantly different ($p \leq .05$) according to Kruskal–Wallis analysis followed by Dunn's multiple comparison post hoc test.

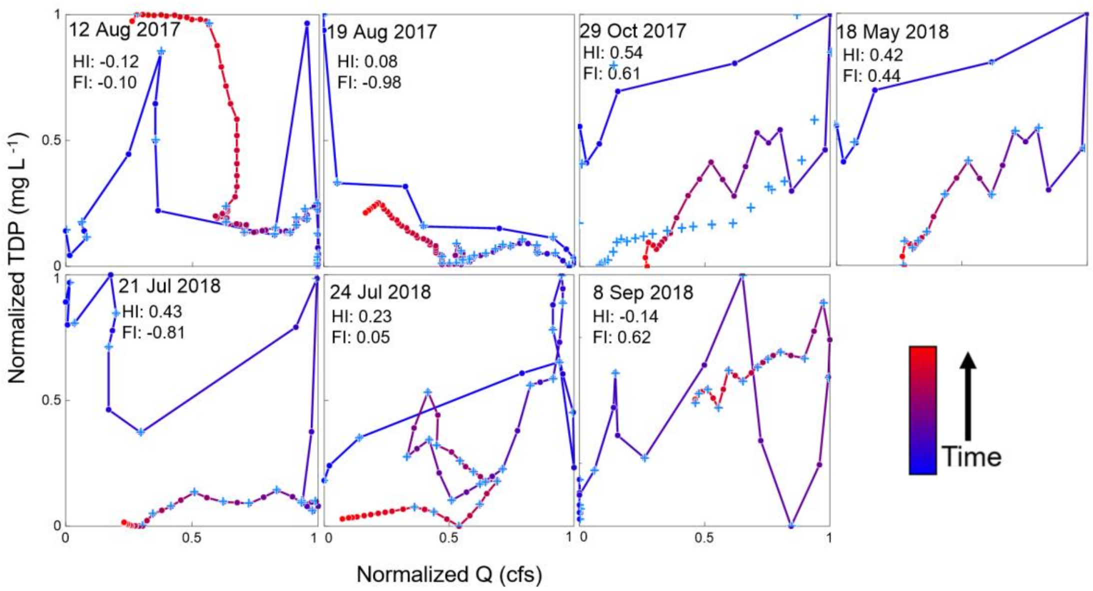

Figure 4.4 Hysteresis loops of normalized total dissolved P (TDP) vs. normalized discharge (Q) and hysteresis and flushing indices (HI and FI) for seven storm events monitored in a 1.5-ha study field at the University of Maryland Eastern Shore farm. Dark blue points indicate the beginning of the storm event; red points indicate the end of the storm. Light blue plus signs (+) indicate measured TDP concentrations.

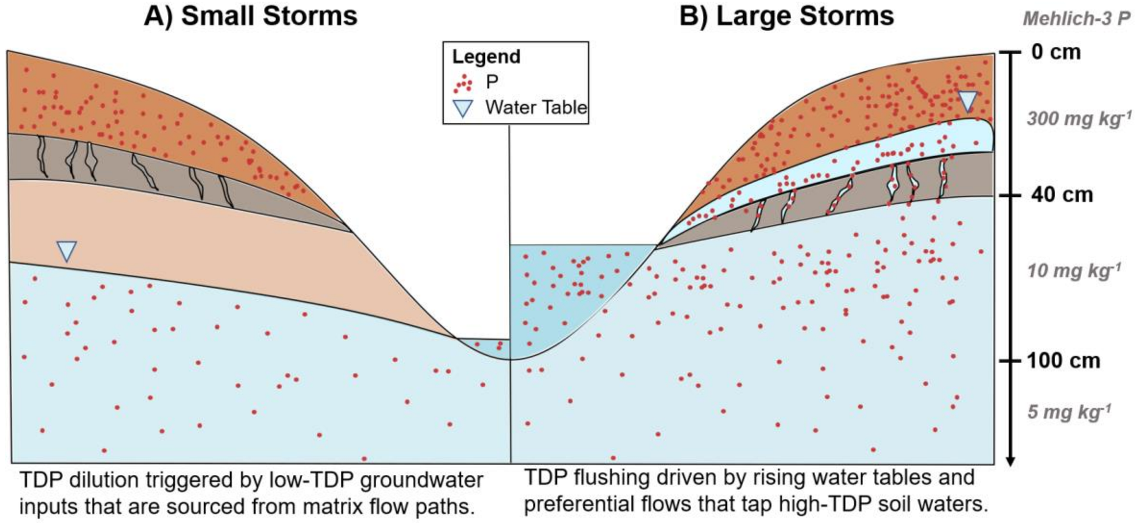

Figure 4.5 Conceptual model of total dissolved P (TDP) sources and flowpaths in an open drained field based on results from seven storm events monitored in a 1.5-ha field at the University of Maryland Eastern Shore farm. (a) During low flow events (<6.4 L s^{-1}), TDP in the ditch is diluted by low-TDP groundwater moving through matrix flow paths. (b) During high flow events (>6.4 L s^{-1}), high TDP concentrations from the high water table interacting with high-TDP soil waters are transported to the ditch through preferential flow paths.

Table 4.1 Discharge characteristics, hysteresis and flushing indices, flow-weighted total dissolved P (TDP) concentrations, TDP loads, and the proportion that each storm contributed to monthly TDP load for seven sampled storm events monitored in a 1.5-ha study field at the University of Maryland Eastern Shore.

Storm	**Qbase**	**Qmax**	**Qmean**	**Flow**	**TDP load**	**Flow-weighted mean TDP**	**HI**	**FI**
	-------------$L\ s^{-1}$-------------			L	kg	$mg\ L^{-1}$	unitless	
8/12/2017 [a]	0.00	8.64	6.55	1461386	0.18	0.13	-0.12	-0.10
8/19/2017	0.00	12.89	4.55	1951136	0.54	0.28	0.08	-0.98
10/29/2017 [a]	3.38	104.36	13.49	9369921	7.24	0.77	0.54	0.61
5/18/2018 [a]	21.81	669.19	115.17	56388191	25.25	0.45	0.42	0.44
7/21/2018 [a]	0.18	21.85	10.39	1683230	0.34	0.20	0.43	-0.81
7/24/2018	5.17	25.53	11.47	4291089	1.23	0.29	0.23	0.05
9/8/2018	0.94	34.30	26.84	10724328	2.37	0.22	-0.14	0.62

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Chapter 5

RESOLVING THE SEASONAL ORIGINS OF DITCH DRAINAGE TO SHED LIGHT ON SUBSURFACE PHOSPHORUS TRANSPORT

5.1 Introduction

Excess phosphorus (P) loading to water bodies can cause eutrophication and result in hypoxia (Bricker et al., 2008; Carpenter et al., 1998). Phosphorus loss from agricultural runoff is a major concern, especially on the Delmarva Peninsula, which is and area of high-intensity broiler and agronomic row crop production (Vadas and Sims, 1998; Boesch et al., 2001). Poultry litter (manure and bedding) was historically applied at N-based rates to many agricultural soils in the region, resulting in soil test P concentrations above the agronomic optimum (>100 mg kg^{-1} Mehlich-3 P; Feyereisen et al., 2010; Toor and Sims, 2015; Sims et al., 2002; Mehlich, 1984). In addition, artificial drainage, most commonly open-ditch drainage, is used to lower high water tables and increase crop productivity in poorly drained settings on the Delmarva Peninsula (Ritter, 2010; Vaughan et al., 2007). In fields with elevated levels of soil P, the presence of a drainage ditch steepens the hydraulic gradient in the vicinity of the ditch, promoting shallow groundwater movement and subsurface P loss (Skaggs et al., 2004). Preferential flow pathways within fine-textured soils have also been found in some Delmarva fields (Kleinman et al., 2015; Robinson et al., 2020), which accelerates water and P transport through the soil to the drainage ditch. Phosphorus within a drainage ditch can be stored or transported through the ditch network and delivered to surface waters that ultimately drain to estuaries Chesapeake and Delaware

Bays, exacerbating the eutrophication of these systems (Sallade and Sims, 1997a; Vadas and Sims, 1998; Needelman et al., 2007).

Previously, researcher found that subsurface transport, not overland flow (i.e., surface runoff), is the primary route of P loss from flat agro-ecosystems, like those commonly found in poorly drained areas of the Delmarva Peninsula (Sims et al., 1998; Kleinman et al., 2007; Shober et al., 2017). In these flat, drained landscapes, vertical and lateral preferential flow (Kleinman et al., 2015; Toor & Sims, 2015; Robinson et al., 2021) and rising water tables during storm or irrigation events allow water to interact with high P soils near the soil surface (Vadas et al., 2007), contributing water and dissolved P to drainage ditches. Even so, a refined understanding of the processes that mobilize and transport contemporary (i.e., recently applied) and "legacy" P sources is needed in order to effectively manage subsurface P losses in artificially drained agricultural soils that are prone to preferential flow.

Several hydrologic tools that use stable water isotopes and geochemical tracers can be applied to flat, agroecosystems to better characterize subsurface pathways of P loss; these tools include hydrograph separation, concentration-discharge (C-Q) relationships (See Chapter 1.2 for more information), and the seasonal origin index (SOI). The SOI is a unitless index that has been used to quantify and compare the relative proportions of winter and summer precipitation in tree xylem water (Allen et al., 2019a) and stream water (Allen et al., 2019b). Since its development in 2019, the SOI has been used to explain water acquisition by trees (Zhang et al., 2021; Goldsmith et al., 2022) and to ascertain the relative importance of winter versus summer precipitation in surface water and groundwater (Xiao et al., 2022).

Following the application of the SOI to tree xylem (Allen et al., 2019a), Allen et al. (2019b) then applied the SOI to 12 streams in Switzerland to determine if summer or winter precipitation was overrepresented in the 12 study streams after accounting for evapotranspiration. Although the SOI is a relatively new concept that has not be applied in artificially drained agroecosystems, this index has the potential to shed important light on the storage, mixing, and transport of subsurface waters that carry dissolved P from fields to ditches. In turn, such knowledge can be used to inform and enhance the nutrient management of these fields.

In this study, we applied the SOI to an open agricultural drainage ditch on the Delmarva Peninsula. Our objectives were to 1) use the SOI to compare the $\delta^{18}O$ values in precipitation and ditch flow to determine if winter or summer precipitation was overrepresented in the ditch flow and 2) estimate the relative importance of matrix and preferential flow for DP discharge to a drainage ditch.

5.2 Materials and Methods

5.2.1 Site Characterization

A detailed overview of the site characterization can be found in section 2.2.1. In brief, the study site was a 1.5-ha agricultural field located at the University of Maryland Eastern Shore Research and Teaching Farm in Princess Anne, Maryland. The study site is located in the Manokin River watershed, which drains to the Chesapeake Bay. The study field is flat, with slopes generally less than 1.5%. The field is bordered on all sides by open ditch drains. The dominant soil in the study field is mapped as poorly drained Quindocqua series (fine-loamy, mixed, active, mesic Typic Endoaquults; Soil Survey Staff, 2019). Historical application of poultry litter at

N-based rates resulted in Mehlich-3 P concentration of 425 mg kg^{-1}, which is ten-fold the Maryland critical agronomic level of 42.5 mg kg^{-1}; Mehlich, 1984; Maryland Department of Agriculture, 2022). Notably, previous researchers have reported the presence of preferential flow pathways in these fine-textured soils (Kleinman et al., 2015; Robinson et al., 2020).

5.2.2 Field Sampling and Analysis

For more details on field sampling and lab analysis see section 2.2.2. Briefly, discharge was measured every 5 min using two H-flumes that were installed at opposing ends of the ditch. Sampling of precipitation and drainage water was conducted over a 14-mo period (July 2017 through September 2018). Four automatic samplers (900Max, American Sigma) collected drainage water every 12-to-72-h, and additionally, every 1-to-2-h prior to and during storm events (Mosesso et al., 2021). Mineral oil was added to the sample bottles to prevent evaporation. Precipitation amounts were measured every 5-min using a tipping bucket rain gauge that was part of a weather station located 0.35 km northwest of the study ditch. The tipping bucket rain gauge was heated in the winter months. At a location just adjacent to the weather station, storm composite precipitation samples were collected in a 1-L bottle with mineral oil, while an automatic sampler collected precipitation every 1-to-2-h during storm events.

All water samples were analyzed for stable water isotopes and concentrations of total dissolved phosphorus (TDP). For the isotope analyses, mineral oil was first removed from drainage water and precipitation subsamples; water subsamples were stored in 15-mL plastic vials and sealed with Parafilm until analysis for $\delta^{2}H$ and $\delta^{18}O$ by cavity ring-down spectroscopy using an isotopic water analyzer (L2140-i, Picarro, and 912-0032, Los Gatos Research). Drainage water and precipitation subsamples for nutrient analysis were filtered (0.45-μm Supor filter with hydrophilic polyethersulfone membrane) and then analyzed for TDP using inductively coupled plasma–mass spectroscopy (iCAP-RQ, Thermo-Fisher) or inductively coupled plasma–optical emission spectroscopy (720-OES, Agilent Technologies).

5.2.3 Data Analysis

Capturing the seasonal isotope cycle of precipitation is crucial to accurately estimating the SOI for a given location. The frequency and duration of precipitation sampling at our study site did not allow us to adequately represent the seasonality of precipitation isotopes. As such, we used the Online Isotopes in Precipitation Calculator (OIPC; Bowen et al., 2005) to calculate the monthly volume-weighted mean $\delta^{18}O$ values to determine the annual volume-weighted mean $\delta^{18}O$ (δ_P) for our study site. The OIPC has been previously used by researchers to compare measured and modeled monthly $\delta^{18}O$ precipitation values (Henderson and Shuman, 2009; Sargeant and Singer, 2016). For comparison, we plot our measured monthly volume-weighted mean $\delta^{18}O$ values in precipitation against modeled monthly volume-weighted mean $\delta^{18}O$ values in precipitation that were generated by the OIPC (Figure 5.1).

We calculated the annual SOI of flow-weighted mean ditch flow ($SOI_{\bar{Q}}$) using the $\delta^{18}O$ values of typical midwinter precipitation (δ_{PW}), typical midsummer precipitation (δ_{PS}), and volume-weighted mean annual precipitation (δ_P) and annual volume weighted-mean streamflow (δ_Q) using the equation 1.

$$SOI_{\overline{Q}} = \begin{cases} \frac{\delta_{\overline{Q}} - \delta_{\overline{P}}}{\delta_{Ps} - \delta_{\overline{P}}}, if\ \delta_{\overline{Q}} > \delta_{\overline{P}} \\ \frac{\delta_{\overline{Q}} - \delta_{\overline{P}}}{\delta_{\overline{P}} - \delta_{Pw}}, if\ \delta_{\overline{Q}} < \delta_{\overline{P}} \end{cases} \quad \text{eqn. 1}$$

The SOI uses the strength of the seasonal isotope cycle in precipitation to represent isotopic differences between annual average discharge and annual average precipitation on a unitless scale from -1 to 1 and differs from a two-endmember mixing model as the SOI accounts for variations in precipitation volume throughout the year (Allen et al., 2019a). An SOI value of -1 indicates that water samples are entirely comprised of winter precipitation, while SOI values near 1 suggest water samples consist wholly of summer precipitation; SOI values near zero generally indicate an even mixture of winter vs. summer water in drainage.

We also calculated monthly SOI_Q values by inputting monthly $\delta^{18}O$ volume weighted-mean streamflow values to better understand water and solute storage, mixing, and transport within our study field and drainage ditch on shorter time scales. Then, we tested daily winter and summer SOI_Q values and daily "low TDP" and "high TDP" SOI_Q values for normality using a Shapiro-Wilk test. Because the data were not normally distributed, we ran a Mann-Whitney U test in the R programming language (version 3.6.1) to compare between summer and winter and "low" and "high" TDP concentration classified ditch SOI values.

Lastly, we expanded the SOI and applied this tool in a new way to estimate the relative amounts of matrix versus preferential P pathways contributing to the drainage water. We assumed that an SOI value close to zero indicated waters that were well-mixed, as would be anticipated in groundwater aquifers where matrix flows prevail. The relative importance of preferential flow in transporting water and TDP to the ditch was presumed to increase when ditch water samples exhibited little to no isotopic offset from the precipitation that generated the ditch flow. Accordingly, as SOI values approached +1 (more summerlike water) in the summer or negative (more winterlike water) in the winter, preferential flow was assumed to increase in significance.

5.3 Results and Discussion

5.3.1 Resolving the seasonal origins of ditch water using water isotopes

The annual $SOI_{\bar{Q}}$ (-0.036) was very close to zero, meaning that the ditch water contained a roughly equal proportions of summer and winter precipitation. Winter and summer SOI_Q values were significantly different with a p-value = 2.2e-16 (Figure 5.3). Monthly SOI_Q values ranged -0.89 to 0.48, indicating periodic overrepresentations of summer and winter precipitation relative to the annual $SOI_{\bar{Q}}$ (Figure 5.2). Drainage water collected during the spring and summer months (April through September) had SOI values that were generally positive, ranging from 0.28 in April to 0.15 in August, suggesting an overrepresentation of summer precipitation. In the fall and winter months (October through March), SOI values were negative (-0.89 to -0.25, respectively), suggesting an overrepresentation of winter precipitation. However, December exhibited an SOI value that was slightly positive. As our drainage water SOI values were isotopically similar the seasonal of phase of precipitation at the time of drainage water sampling (Figure 5.1; Figure 5.2), there is evidence that a fraction of winter and summer precipitation moved rapidly to the ditch, likely through a mix of matrix and preferential flow pathways.

Allen et al. (2019b) found that stream samples collected from several of their catchments showed strong summer or winter overrepresentation (a stronger seasonal pattern), indicative of various transport behaviors, while other catchments had stream samples showing a seasonal mix. However, all catchments had similar $SOI_{\bar{Q}}$, around zero, suggesting that temporal transport behaviors are masked at the annual timescale. In line with Allen et al. (2019) and Xiao et al. (2022), our study drainage ditch exhibited somewhat of a seasonal pattern and had an annual $SOI_{\bar{Q}}$ value close to zero.

5.3.2 Inferring dissolved P transport mechanisms from the seasonal origins of ditch water

Relating the daily SOI to dissolved P concentrations in ditch water has the potential to offer important insight into the processes that affect dissolved P transport. Ditch water sampled during spring and summer months had higher daily TDP concentrations than fall and winter samples (mean = 0.38 and 0.13 mg L^{-1}, respectively). Increased TDP concentrations in summer samples may have been due to low antecedent soil moisture before storm events, resulting in strong P flushing responses (Knapp et al., 2020; Rose and Karwan, 2021).

We saw no clear annual trend between monthly flow-weighted TDP patterns and respective monthly SOI_Q values; however, months with positive SOI (Apr through Sept) had a slightly higher monthly flow-weighted TDP average (0.32 mg L^{-1}) than negative SOI months (0.32 mg L^{-1}). May and October had the highest monthly flow-weighted TDP concentrations, which can be explained by large storm events that occurred in October 2017 and May 2018 (Q_{max} of 104.36 and 669.19 L s^{-1}, respectively). During these events, the connectivity of P hotspots in the topsoil to the ditch was likely increased due to a raised water table that resulted in P transport through preferential flow pathways (Mosesso et al., 2021).

As previously inferred from Figure 5.2, preferential flow played a role in rapid water transport to the drainage ditch throughout the study period, especially with samples with SOI values that showed little to no isotopic offset from the precipitation that generated the ditch flow. Preferential flow transport was likely equally important during winter and summer months as the average daily SOI values during spring/summer and fall/winter months, were 0.22 and -0.20, respectively (Figure 5.3). However, transport of TDP through preferential flow pathways was higher during spring and summer months than during winter months (Figure 5.3). Interestingly, some samples with SOI values closer to 1 (indicating a greater propensity for preferential flow during summer months) did not have the highest sample TDP concentrations. In fact, a cluster of samples with high TDP concentrations (1.0 to 1.3 mg L^{-1}) had SOI values ranging from 0.11 to 0.35, suggesting that the relative importance of matrix flow transport for these samples was greater than preferential flow.

The SOI values of water samples classified as “low DP” (below the mean daily TDP concentration of 0.266 mg L^{-1}) formed a bell curve with the highest frequencies plotting at zero and 0.20 (Figure 5.4b). “High DP” samples also formed a bell curve around 0.20 and 0.40 with a few samples with SOI values ranging from -1.0 to -0.5 (Figure 5.4c). The SOI relative frequencies suggest that matrix flow had a greater relative importance in transporting “low DP” samples, while preferential flow played a larger role in transporting “high DP” samples into the drainage ditch.

5.4 Conclusions and Implications

Our results showed that the relative importance of preferential flow was the same during periods of low soil moisture (summer months) and high soil moisture conditions (winter months), suggesting there is not an increase in preferential pathways within the argillic horizon during the summer months. In addition, the study field was conventionally tilled annually, thus, deeper (< 15 cm) vertical preferential flow pathways remained and played a role in water and TDP transport. Results from this study support the findings in Mosesso et al. (2021) of the importance of preferential flow in TDP transport and loss. However, our study period was relatively short (14-mo); increasing the water quality monitoring period of this study may have allowed us to better understand annual SOI and TDP patterns, especially in months with SOI anomalies (Oct). Moreover, the addition of soil water (bulk and mobile) and groundwater would have added greater insight into the relationships between the SOIs of source waters and ditch waters. In future work, we will evaluate nitrate-N concentrations in ditch water to determine if relative importance of matrix and preferential flows on nitrate-N transport. Given the elevated nitrate-N concentrations in shallow groundwater, we predict that the highest nitrate-N concentrations would cluster around SOI values of zero.

As tillage would not break up deeper vertical and lateral preferential flow pathways to reduce TDP transport, we suggest management strategies that focus capturing or mitigating P loads during summer months as TDP loads were highest during the summer months (e.g., Fe-based P removal structures). Ultimately, we recommend nutrient management strategies (e.g., P application that does not exceed a three-year crop removal rate) that draw down P concentrations within P enriched soils with artificial drainage to mitigate TDP losses from drainage ditches to surface waters.

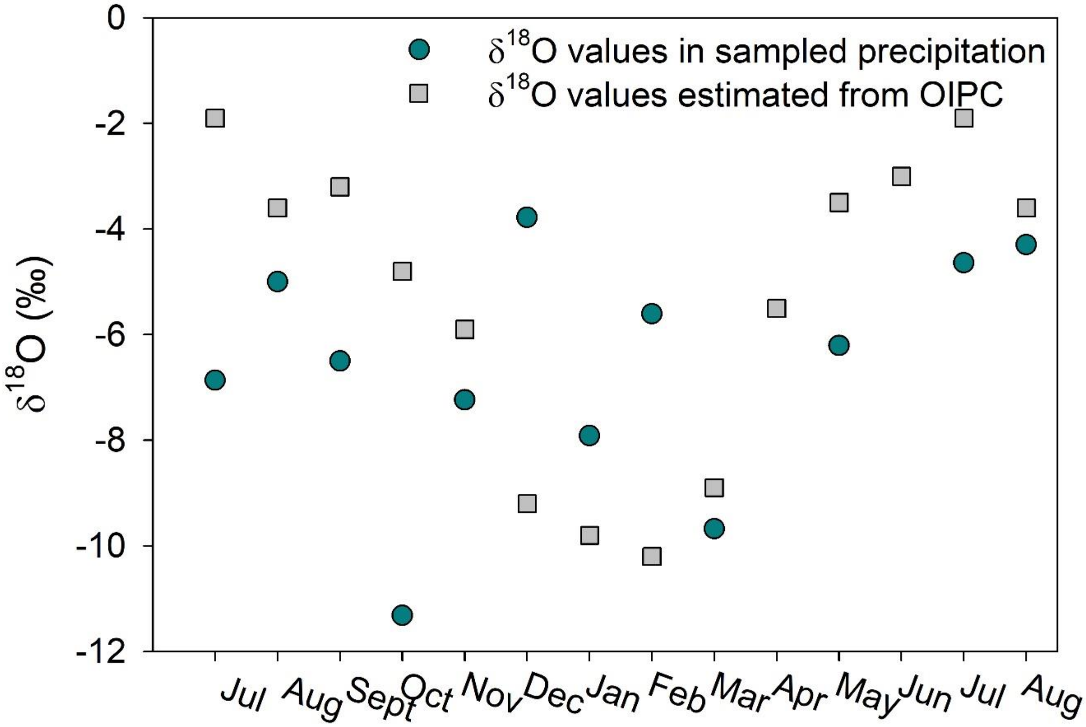

Figure 5.1. Comparison of monthly volume-weighted mean $\delta^{18}O$ values in precipitation sampled at the UMES field site against monthly volume-weighted mean $\delta^{18}O$ values in precipitation that were estimated using the Online Isotopes in Precipitation Calculator (OIPC, waterisotopes.org).

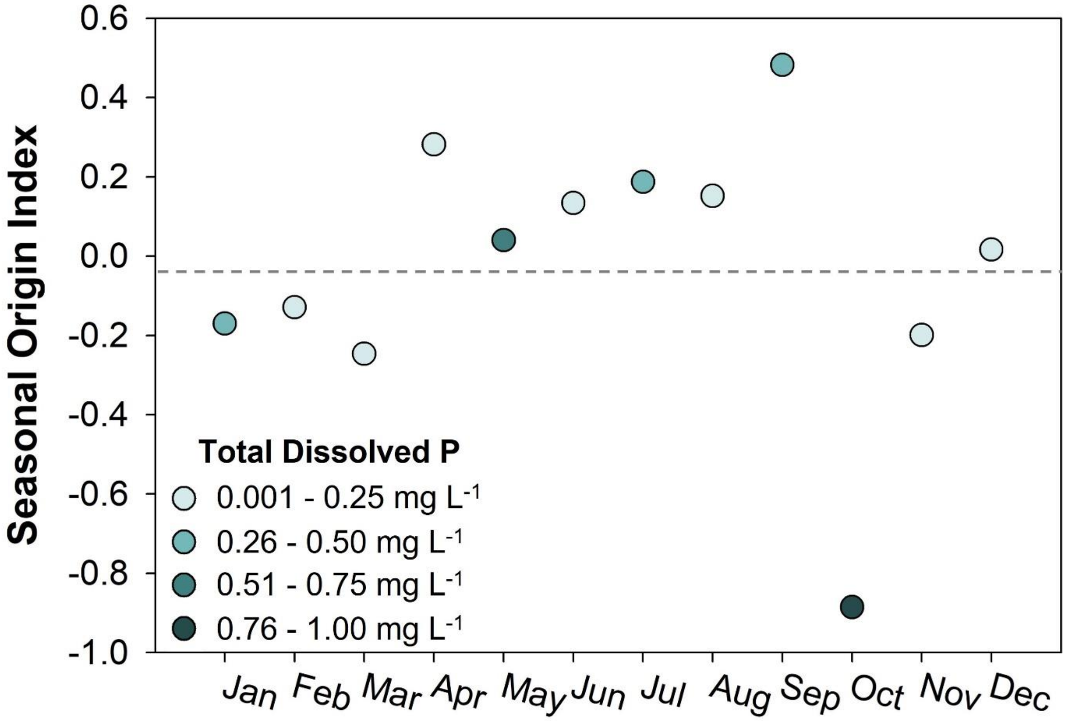

Figure 5.2 The monthly seasonal origin index values of flow-weighted mean ditch flow and corresponding monthly flow-weighted mean total dissolved P concentrations. The dotted line is the annual SOI of weighted-mean ditch water value.

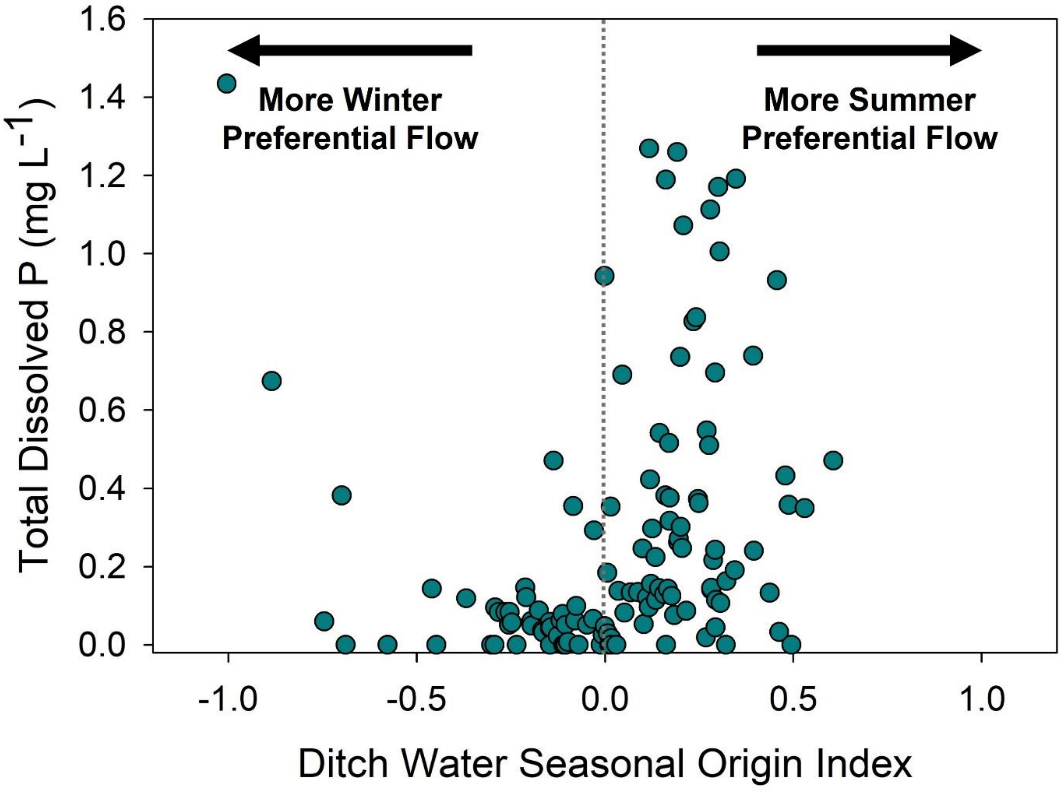

Figure 5.3 The seasonal origin index for daily ditch water vs. the respective total dissolved P concentration (mg L^{-1}). As indicated by the leftward arrow, when seasonal origin indices approach -1, there is a greater likelihood of winter preferential flow relative to matrix flow. The rightward arrow suggests that the significance of summer preferential flow increases relative to matrix flow as the seasonal origin index approaches +1.

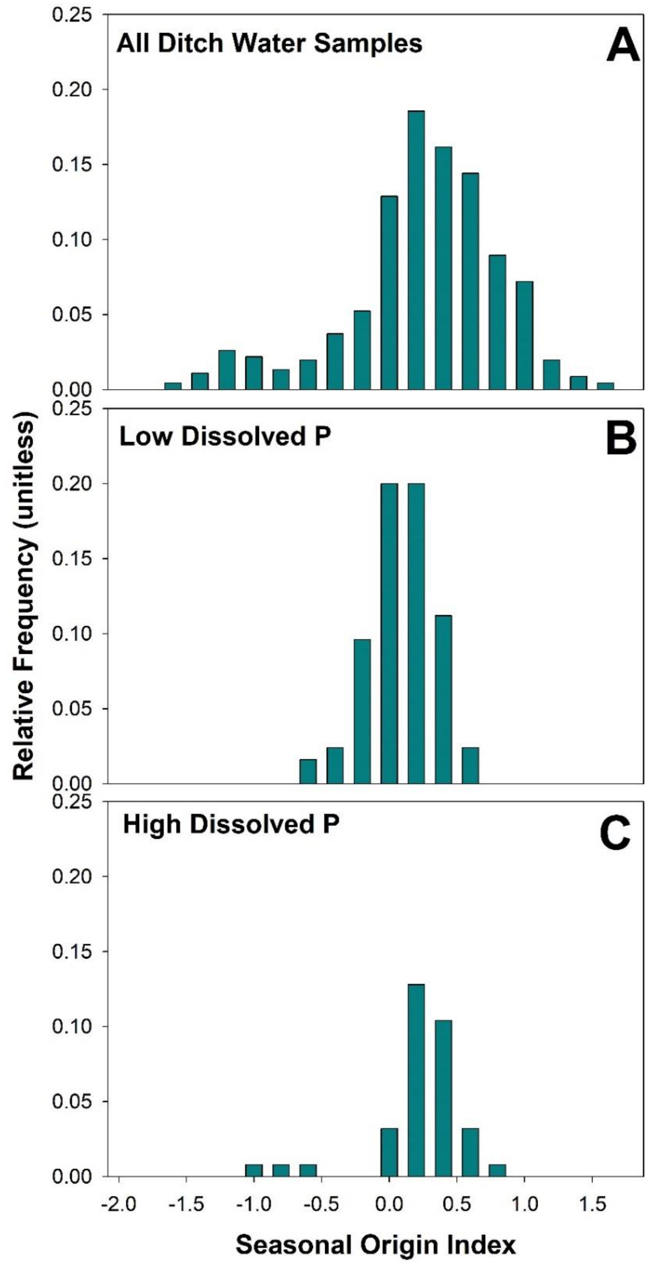

Figure 5.4 Histograms showing the relative frequencies of seasonal origin index values for a) all daily ditch water samples, b) ditch water samples classified as "low" total dissolved P (below mean total dissolved P concentration of 0.266 mg L^{-1} in the study ditch), and c) ditch water samples classified as "high" total dissolved P (above 0.266 mg L^{-1}).

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Appendix A

UNDERSTANDING PHOSPHORUS DYNAMICS IN MANURE AND FERTILIZER IMPACTED DELMARVA SOILS

Table A.1 Common names, formulas, and origin of phosphorus minerals within the standard library and used in linear combination fitting.

Common Name	**Chemical Formula**	**Origin**	**P:Al**	**P:Ca**	**P:Fe**
P Sorbed to Al Hydroxide	$P[Al(OH)_3]$	Synthesized (Shober et al. 2006)	1.5331	--	--
Al Phosphate Semicrystalline (3d)	$AlPO_4 \cdot 2H_2O$	Synthesized (Shober et al. 2006)	0.748	--	--
Al Phosphate Semicrystalline (10d)	$AlPO_4 \cdot 2H_2O$	Synthesized (Shober et al. 2006)	0.627	--	--
Al Phosphate Semicrystalline (30d)	$AlPO_4 \cdot 2H_2O$	Synthesized (Shober et al. 2006)	0.984	--	--
P Sorbed to Boehmite	$P[\gamma\text{-}AlO(OH)]$	Synthesized (Gamble et al., 2020 using method Cornell et al., 2003)	ND	--	--
Wavellite	$Al_3(PO_4)_2(OH, F)_3 \bullet 5H_2O$	Gamble et al., 2020	1.548	--	--

Variscite	$AlPO_4 \cdot 2H_2O$	Purchased from Ward's Natural Science (Rochester, NY)	1.031	--	--
Fe Phosphate (amorphous)	$FePO_4 \cdot 2H_2O$	Synthesized (Shober et al. 2006)	--	--	0.897
Fe Phosphate Semicrystalline (3d)	$FePO_4 \cdot 2H_2O$	Synthesized (Shober et al. 2006)	--	--	1.636
Fe Phosphate Semicrystalline (30d)	$FePO_4 \cdot 2H_2O$	Synthesized (Shober et al. 2006)	--	--	1.337
Phosphosiderite	$FePO_4 \cdot 2H_2O$	Gamble et al. 2020	--	--	ND
Strengite	$FePO_4 \cdot 2H_2O$	Synthesized (Shober et al. 2006)	--	--	1.346
P Sorbed to Ferrihydrite	$P[(Fe^{3+})_2O_3 \bullet 0.5H_2O]$	Synthesized (Gamble et al., 2020 using method Cornell et al., 2003)	--	--	11.51
P Sorbed to Goethite	$P[\alpha\text{-}FeO(OH)]$	Synthesized (Gamble et al., 2020 using method Cornell et al., 2003)	--	--	99.82
Vivanite	$Fe^{2+}{}_3(PO_4)_2 \cdot 8H_2O$	Gamble et al. 2020	--	--	ND
P Sorbed to Hematite	$P[Fe_2O_3]$	Synthesized (Gamble et al., 2020 using method	--	--	ND

		Cornell et al., 2003)			
Monetite	$CaHPO_4$	Purchased from J.T. Baker (Mallinckrodt Baker, Phillipsburg NJ)	--	1.085	--
Brushite	$CaHPO_4 \cdot 2H_2O$	Purchased from Fisher Scientific (Hampton, NH)	--	1.021	--
b-tricalcium phosphate	b-$Ca_3(PO_4)_2$	Synthesized (Shober et al. 2006)	--	1.681	--
Fluorapatite	$Ca_5(PO_4)_3F$	Gamble et al. 2020	--	ND	--
Hydroxyapatite	$Ca_5H(PO4)_3 \cdot 2.5H_2O$	Purchased from Fisher Scientific (Hampton, NH)	--	1.699	--
Phytic Acid	Ca and Na salts	Purchased from Sigma-Aldrich (St. Louis, MO)	0.0119	0.0202	0.0001
Phospholipid	Cl salts	Purchased from Fischer Scientific (Hampton, NH)	--	--	--

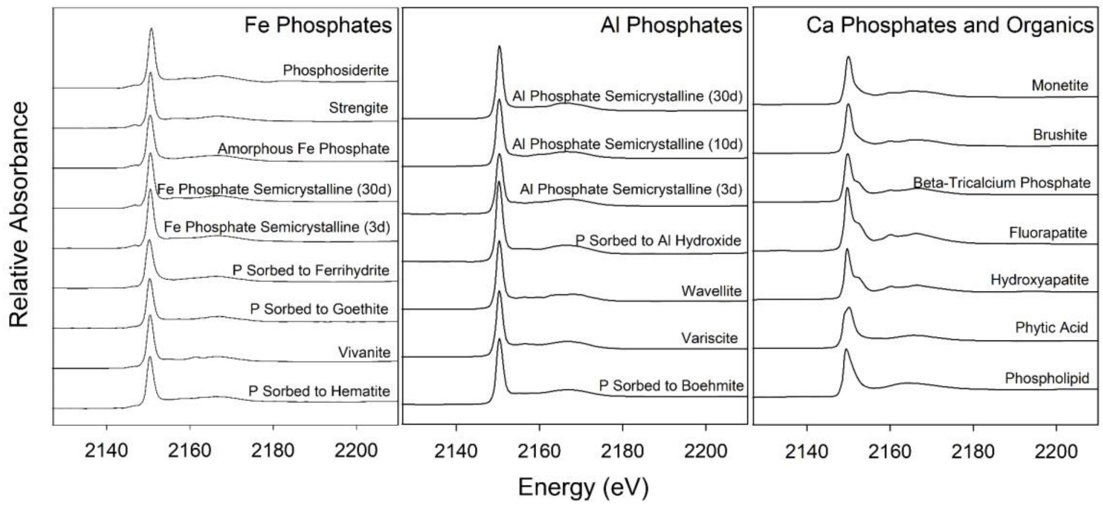

Figure A.1 Phosphorus K-XANES spectra of the 23 phosphate standards used in linear combination fitting.

Table A.2 The details on spectra collection for each sample and standard to include mode, energies, and step sizes.

Sample	Mode	Energy Range	Vortex silica drift detector step size
P sorbed to ferrihydrite, Fe-phosphates (3 & 30 d), amorphous Fe-phosphate, strengite, phytic acid, variscite, wavellite, hydroxyapatite, fluorapatite, Al-phosphates (3, 10, & 30 d), P sorbed to Al hydroxide, beta-tricalcium phosphate, brushite	TEY	2099-2309 eV	2.0 eV for 2099-2134 eV, 0.125 eV for 2134-2179 eV, and 1.0 eV for 2179-2309 eV
Stds boehmite, P sorbed to goethite, P sorbed to hematite, phospholipid, phosphosiderite, vivanite, monetite	TEY	2120-2271 eV	1.0 eV for 2120-2145 eV, 0.12 eV for 2145-2151.5 eV, and 0.05 for 2151.5-2271 eV
Hambrook, Pepperbox, Bojac-Fertilizer, Bojac-Manure, Mullica-Berryland-MD1, Mullica-Berryland-DE, Mullica-Berryland-MD2, and Donlonton	Fluorescence	2109-2286 eV	2.0 eV for 2109-2139 eV, 0.12 eV for 2139-2174 eV, and 0.05 for 2174-2286 eV

Table A.3 The percentage of total extractable inorganic Al, Ca, and Fe solubilized by H_2O, $NaHCO_3$, NaOH, and HCl for all eight soils. Mullica-Berryland fields are abbreviated to "MB-#." Note, data for the Donlonton field was collected in 2005.

Fraction	**Bojac -fert**	**MB-MD1**	**MB-MD2**	**Ham-brook**	**Pepper box**	**Bojac-manure**	**MB-DE**	**Donlo-nton**
	Extractable Al (%)							
H_2O	0.83	1.35	1.56	1.96	1.86	0.92	0.71	0.826
$NaHCO_3$	1.94	6.40	4.97	1.26	5.05	3.01	12.76	1.87
NaOH	76.13	79.36	81.64	60.91	73.92	77.01	71.81	66.94
HCl	21.09	12.89	11.83	35.87	19.17	19.06	14.73	30.36
	Extractable Ca (%)							
H_2O	7.26	8.10	8.16	5.00	6.28	6.19	5.71	10.6
$NaHCO_3$	47.82	39.58	41.73	56.13	53.32	46.71	51.66	60.56
NaOH	4.10	11.06	14.27	7.72	6.78	4.94	3.64	1.79
HCl	40.82	41.27	35.84	31.15	33.61	42.17	38.99	27.04
	Extractable Fe (%)							
H_2O	0.93	0.88	1.08	0.40	1.32	0.96	1.19	1.56
$NaHCO_3$	5.21	15.43	17.61	1.05	15.97	8.27	19.31	10.89
NaOH	20.97	16.35	23.80	1.45	10.55	22.17	14.44	4.30
HCl	72.89	67.34	57.52	97.11	72.16	68.61	65.06	83.24

Appendix B

SOIL HEALTH TRADEOFFS MAY BE MINIMAL WHEN SOILS ARE SEVERELY ENRICHED WITH PHOSPHORUS

Table B.1 Soil series, management history and soil P characteristics by depth of five fields managed under conventional tillage with no cover crops (CONV) and five fields managed under soil health practices (SH; conservation tillage or no-till and winter cover crops) for five or more years in Sussex County, Delaware.

Soil Series	Mgt.	Taxonomy	Depth	M3 P	M3 Fe	M3 Al	PSR
			cm	-------------mg kg $^{-1}$-------			
Evesboro Field 1 Lewes	CONV	Mesic, coated Lamellic Quartzipsamments	0-5	91.0	90.2	720.5	0.10
			5-10	89.6	91.8	755.0	0.10
			10-15	83.4	86.5	796.7	0.09
			15-25	79.0	83.4	870.1	0.08
			25-36	31.3	64.2	850.6	0.03
			36-46	9.4	51.5	781.0	0.01
			91-97	6.9	42.0	567.7	0.01
Woodstown Field 3 Harbeson	CONV	Fine-loamy, mixed, active, mesic Aquic Hapludults	0-5	341.6	8.6	14.4	0.30
			5-10	351.5	8.8	14.4	0.30
			10-15	324.5	7.5	12.4	0.27
			15-25	174.8	3.7	10.2	0.15
			25-36	38.4	1.3	10.0	0.04
			36-46	20.8	0.9	12.2	0.02
			91-97	7.3	0.6	12.6	0.01
Pepperbox-Rosedale-1 Field 5 Millsboro	CONV	Loamy, mixed, semiactive, mesic Aquic Arenic Paleudults and Loamy, siliceous, semiactive, mesic Arenic Hapludults	0-5	122.7	115.7	620.5	0.16
			5-10	123.7	118.2	618.5	0.16
			10-15	122.0	125.7	642.4	0.15
			15-25	110.1	116.6	683.6	0.13
			25-36	66.9	78.7	694.8	0.08
			36-46	33.2	51.3	662.8	0.04
			81-97	3.7	41.4	870.6	0.00

Rosedale Field 8 Laurel	CONV	Loamy, siliceous, semiactive, mesic Arenic Hapludults	0-5	379.8	203.0	678.8	0.43
			5-10	388.1	212.1	703.2	0.42
			10-15	380.2	199.7	688.4	0.42
			15-25	345.2	167.6	700.3	0.38
			25-36	239.6	113.1	747.3	0.26
			36-46	158.9	86.6	706.0	0.19
			91-97	65.7	62.2	742.8	0.07
Rockawalkin Field 10 Gumboro	CONV	Loamy, mixed, semiactive, mesic Aquic Arenic Hapludults	0-5	293.4	145.6	565.6	0.40
			5-10	312.5	154.5	580.8	0.42
			10-15	284.3	155.3	599.8	0.37
			15-25	210.8	124.6	637.1	0.26
			25-36	139.9	81.8	660.6	0.17
			36-46	97.5	62.3	687.4	0.12
			46-56	72.7	61.4	731.0	0.08
Pepperbox-Rosedale-2 Field 9 Gumboro	5+ years SH	Loamy, mixed, semiactive, mesic Aquic Arenic Paleudults and Loamy, siliceous, semiactive, mesic Arenic Hapludults	0-5	328.5	155.5	570.7	0.44
			5-10	349.5	185.6	653.0	0.41
			10-15	337.7	193.8	679.7	0.38
			15-25	314.6	206.4	723.0	0.33
			25-36	249.2	194.5	767.2	0.25
			36-46	96.3	111.5	645.2	0.12
			46-61	40.4	81.5	562.7	0.06
Henlopen Field 7 Laurel	5+ years SH	Sandy, siliceous, mesic Lamellic Paleudults	0-5	331.6	149.3	613.2	0.42
			5-10	384.7	175.2	690.7	0.43
			10-15	431.6	201.9	780.0	0.43
			15-25	472.4	219.8	881.3	0.42
			25-36	338.2	132.0	864.1	0.32
			36-46	254.0	101.2	770.2	0.27
			91-97	68.2	57.2	704.5	0.08
Downer Field 6 Lewes	5+ years SH	Coarse-loamy, siliceous, semiactive, mesic Typic Hapludults	0-5	60.8	70.3	709.0	0.07
			5-10	32.6	64.5	742.0	0.04
			10-15	19.7	64.2	831.1	0.02
			15-25	14.6	62.0	781.6	0.02
			25-36	9.7	61.9	720.4	0.01
			36-46	12.9	62.9	748.4	0.01
			91-97	16.1	52.9	703.0	0.02

Pepperbox-Rosedale-3 Field 4 Millsboro	5+ years SH	Loamy, mixed, semiactive, mesic Aquic Arenic Paleudults and Loamy, siliceous, semiactive, mesic Arenic Hapludults	0-5	294.4	111.8	582.1	0.40
			5-10	316.5	128.6	663.1	0.38
			10-15	279.1	126.7	708.1	0.32
			15-25	259.7	125.8	754.8	0.28
			25-36	139.5	84.5	733.2	0.16
			36-46	72.1	60.9	665.7	0.09
			86-97	23.8	38.5	700.2	0.03
Pepperbox-Rosedale-4 Field 2 Harbeson	15+ years SH	Loamy, mixed, semiactive, mesic Aquic Arenic Paleudults and Loamy, siliceous, semiactive, mesic Arenic Hapludults	0-5	287.4	127.7	640.0	0.36
			5-10	286.9	133.0	660.4	0.34
			10-15	320.2	158.9	803.1	0.32
			15-25	262.5	152.7	816.6	0.26
			25-36	90.7	69.3	771.6	0.10
			36-46	41.8	44.9	741.4	0.05
			86-97	6.9	24.6	739.3	0.01

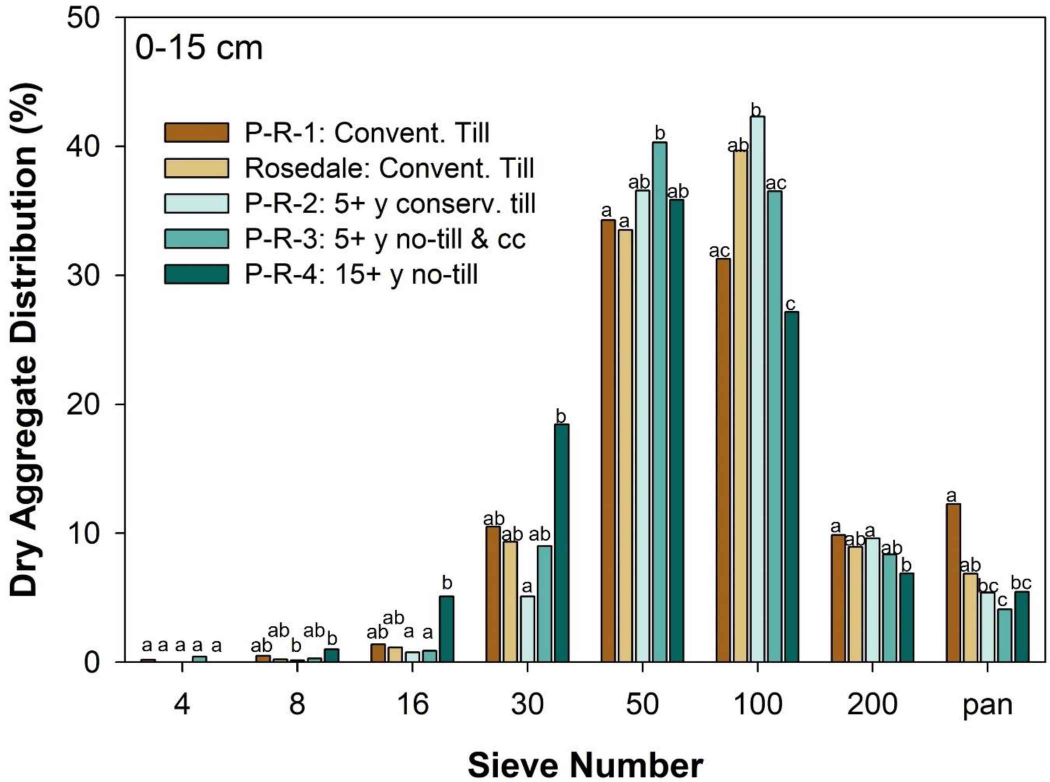

Figure B.1 The average dry aggregate distribution retention % for only fields classified as Pepperbox-Rosedale soil series fields from 0-15 cm depth. Bars with different letters are significantly different ($p \leq 0.05$) according to Kruskal–Wallis analysis followed by Dunn's multiple comparison post hoc test.

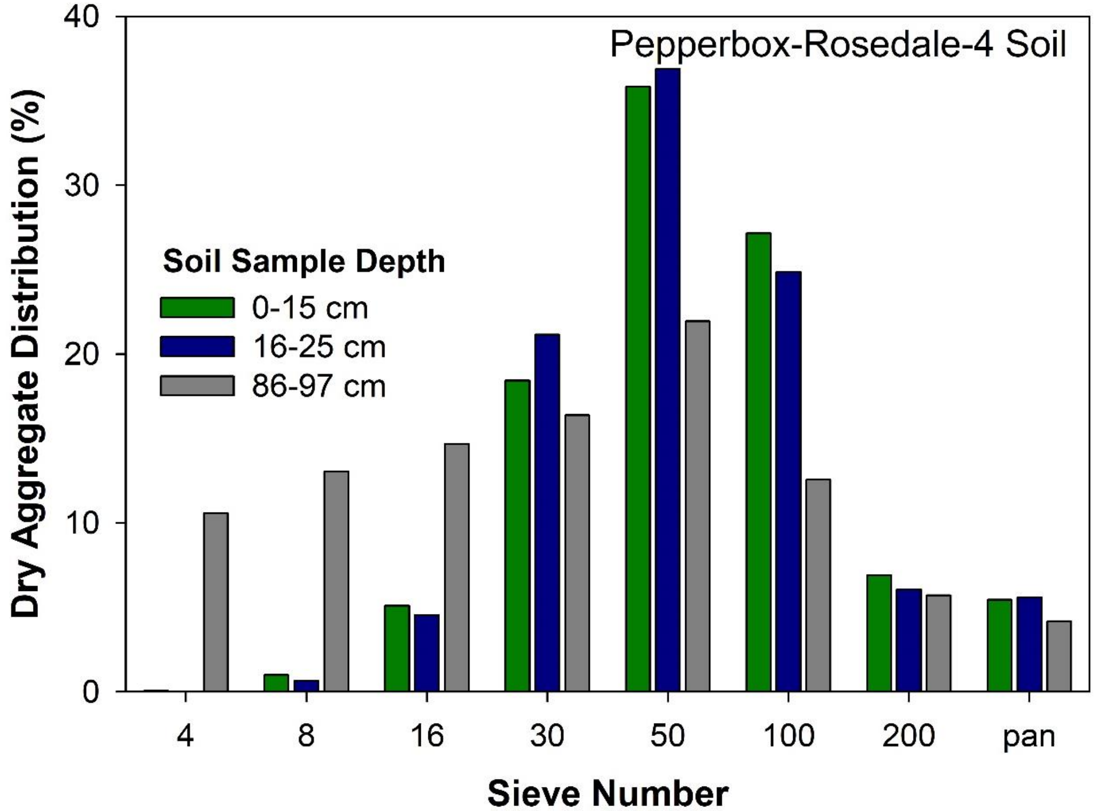

Figure B.2 The average dry aggregate distribution retention % for Pepperbox-Rosedale-4 soils at three sample depths (0-15, 16-25, and 86-97 cm).

Appendix C

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