Biogeochemical Storage and Transformation of Sediments from Geographically Isolated Wetlands in Agriculture Landscapes

by

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Abstract

Geographically Isolated Wetlands (GIWs) provide many beneficial ecosystem services including biogeochemical storage and processing. However, due to the absence of hydrologic connectivity to surface waters, they lack legal protections leading to a knowledge gap of their potential in processing and storing substantial quantities of nutrients and elements alike. The Dougherty plain of Southwest Georgia contains upwards of 11,000 small GIWs. Yet the region is also characteristic of having intensive row-crop agriculture that has the potential to transport materials into nearby GIWs. This study aims to assess nutrient storage in the sediment of GIWs in agriculture wetlands. It was discovered that agriculture GIWs receive two-magnitudes higher sediment per mg cm^{-2} yr^{-1}, stores 25 tons of carbon and 13 tons of phosphorus. Historic phosphorous concentrations peaked in 1970 coinciding with the onset of intensive agriculture practices. A surface sediment survey assessed agriculture wetlands differ in composition having elevated agriculturally associated elements.

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List of Abbreviations

Ag - Agriculture

BPM – Best Management Practices

CRS – Constant Rate of Supply Model

CWA – Clean Water Act

GIW -Geographically Isolated Wetland

LOI – Loss on Ignition

MSR – Mass Sedimentation Rate

OS78 – Agriculture Wetland OS78

OS79 – Agriculture Wetland OS79

OS80 A, B, C – Agriculture Wetland OS80, A, B, C

W37 – Reference Wetland W37

W53 - Reference Wetland W53

USDA – United States Department of Agriculture

USEPA – United States Environmental Protection Agency

WOTUS – Water of the United States

Chapter 1: Geographically Isolated Wetlands in Agriculture Watersheds

1.1 Geographically Isolated Wetlands in an Agricultural Watershed

Geographically isolated wetlands (GIWs) are completely surrounded by uplands and lack a surface connection to other aquatic environments (Tiner 2003a). GIWs provide numerous ecosystem services such as flood mitigation, pollution filtration, habitat for biodiversity, and nutrient cycling and storage (Marton et al., 2015). However, the absence of surface hydrologic connections to other waters of the United States (WOTUS) precludes GIWs from legal protections under the Clean Water Act (USEPA, 2015a). The lack of legal recognition has led to a gap in research of GIWs despite their ability to provide extensive ecosystem services (Marton et al. 2015, Cohen et. al 2016).

The limestone bedrock characteristic of the majority of southeastern United States Coastal Plain leads to the formation of sinkhole wetlands (Tiner, 2003a). Limestone fractures allow acidic water to flow preferentially through the crevices. In time, the carbonic acid slowly dissolves the rock creating sinkholes that can fill with sediment and become basins that hold water (Barrie 2019, Gala & Young, 2015). The newly created aquatic system is suitable for the establishment of wetland flora and fauna.

As GIWs receive runoff from their surrounding uplands, the accumulation of clays and silts transported into the basin leads to the formation of a clay lens. Because clay and silt are *low-permeable sediment,* interactions between the wetland system and the groundwater are restricted (Hendricks & Goodwin, 1952, Hayes et. al, 1983, Gomez et al., 2014). The formation of this semi-closed system allows for the establishment of biota capable of processing and storage of nutrients prior to the flow of water to other aquatic ecosystems or groundwater (Cohen et. al

2016). One setting where mechanisms of nutrient transformation could be magnified in importance is in agricultural landscapes.

Agriculture causes extensive landscape alteration by clearing native vegetation, historical tilling, plowing, and harvesting (Nearing et. al, 2017) leading to elevated rates of soil erosion (Pimentel, 1987). While much research has focused on soil being lost to adjacent waterways (Cooper, 1993, Walker, 2019), less is known of the fate of the sediment after input into GIWs. Various improvements have been made in farming practices to maintain soil health and limit erosion of sediments through precision agriculture techniques, changes in tillage, cover crops and other BMPs (Pierce & Nowak, 1999), but the many GIWs that are scattered throughout agricultural landscapes have previously been overlooked as sentinels for sediment storage and nutrient processing. GIWs in agriculture fields maintain many of the distinct features of wetlands such as hydric soil, wetland vegetation, and growing season inundation; but the surrounding land use alters their nutrient dynamics, sediment inputs, and vegetation making it important to assess their integrity as functioning wetlands. Here, I studied the role of GIWs to serve as areas of biogeochemical storage and transformation within agriculture landscapes by applying paleolimnological techniques.

Paleolimnology is the reconstruction the environmental conditions of an ecosystem by determining the age and composition of sediment accumulated in lakes, reservoirs, or wetlands. Large shifts in sediment nutrient composition can give insight into historical land use changes. In agricultural landscapes, changes can include the onset of intensive agriculture, the installation of groundwater pivot-irrigation systems (Rugel et al, 2012), changes in tillage practices, or large changes in fertilizer usage. A paleolimnological investigation can piece together historical land use changes to understand past conditions that will inform future decisions for best practices to maintain or enhance environmental quality of agricultural landscapes.

1.2 Significance and Rationale

Wetlands have been in a global decline since the mid-1950s (Finlayson and Davidson, 1999). In the United States almost half of the wetlands are found in the southeast, and wetland loss is disproportionately greater in this region due to the conversion of wetlands to agriculture (Hefner & Brown, 1984). In addition to causing wetland loss, intensive agriculture also has the potential to contaminate waterways with non-point source pollution (Ongley, 1996). While multiple forms of pollution are of concern, nutrients (C, N, P) and sediments are among the primary stressors to aquatic systems from agricultural practices.

Inputs of nitrogen and phosphorous into aquatic systems from surrounding agricultural, industrial, or other developed landscapes can create hazardous eutrophication conditions (Wurtsbaugh et al., 2019). The resultant algal blooms can be toxic, promote anoxia, and decrease biodiversity (Huisman et al., 2018). However, it is well established that natural riparian wetlands mitigate deleterious effects of non-point source runoff from agricultural landscapes (Lowrance et al 1984). But less is known about the capacity of GIWs to mitigate non-point source runoff. It is hypothesized that GIWs limit the transport of pollutants and promote nutrient storage in sediments (Cohen et. al 2016). Thus, GIWs potentially mitigate eutrophication and prevent N and P from traveling further downstream and impacting subsequent ecosystems (Saunders & Kalff, 2001). Whereas the movement of nitrogen and phosphorus are typically managed together, the mechanisms governing nutrient storage and processing in wetlands are more complex. The invention of the Haber-Bosch process in the 1930's made industrial nitrogen fixation easier and more affordable. Subsequent nitrogen fertilizer usage has increased exponentially (Paull, 2009).

Excess fertilizer applied to fields is transported to surrounding wetlands during rain events where multiple pathways can occur including biological uptake, biogeochemical processing, or storage. The combined processes of denitrification, nitrogen sedimentation, and plant uptake are generally magnified in wetlands, increasing nutrient removal (Bowden, 1987). Specifically, the high organic matter and frequent inundation promotes denitrification, a microbially mediated conversion of NO_3-N to N_2 gas, removing nitrogen from the landscape (Sirivedhin & Gray, 2006).

Phosphorous fertilizer is also common, but unlike N, its elemental state lacks a gaseous phase making the presence of P in an aquatic ecosystem more permanent. Wetlands foster anoxic conditions allowing the separation of P from elements Fe and Al releasing it to be available for uptake by primary producers. The resuspension of bioavailable P into the water column can result in algal blooms in shallow aquatic systems (Janse 2008). As large masses of algae die, they are a source of labile organic carbon for decomposers to consume and in doing so deplete the water of dissolved oxygen. The resultant anoxia is detrimental to aquatic life such as fish and macroinvertebrates. Eutrophication events can also be caused by agricultural activity transferring large amounts of allochthonous carbon into the water (Heathcote & Downing, 2012).

Carbon dynamics in wetlands are more complex as there are pathways that can both increase and decrease ecosystem services. High levels of carbon accumulate in wetlands as a result of the rate of primary productivity exceeding the rate of decomposition due to anoxic conditions (Brinson et al., 1981) Furthermore, increased allochthonous material from agriculture accelerates sediment accumulation rates leading to higher C burial in agriculture systems (Waters et al., 2019). Globally wetlands have a disproportionate concentration of global organic C and act as carbon sinks when inundated (Mitsch et al., 2003a). However, as climate change continues, wetlands are at risk changing through drying out from increasing temperatures or inundation by way of sea level rise. (Morse et al., 2012 & Burkett & Kusler 2000). Yet, as agricultural wetlands begin to flood in the coastal plain, research suggest that some wetlands retain their carbon storage capacity (Morse et al., 2012). This emphasizes the need to protect GIWs despite a changing climate to prevent them from converting to carbon sources and emitting highly potent greenhouse gas methane.

There has been research on the mass sedimentation rate (MSR) of GIWs; yet research is lacking on the MSR of GIWs directly within agricultural fields. Craft and Casey (2000) also quantified the MSR in the agriculture intensive Dougherty Plain in the Gulf Coastal Plain of southwestern Georgia. MSR was greater over a 100 year time scale (1036 g/m^2/yr), compared to a 30 year time scale. Nutrient storage was quantified for organic C (79 g/m^2/yr.), N (6.0 g/m^2/yr.), and P (0.38 g/ m^2/yr) (Craft & Casey, 2000). In agriculture catchments in the Midwest, nitrogen storage was also greater than in natural catchments (Bernot et al., 2006).

The degree of anthropogenic influence in a watershed directly influences sediment and nutrient accumulation in GIWs (Craft & Casey, 2000). Climatic and human degradation of wetlands leads to diminished in ecological services of GIWs to humans, wildlife, and water. Nevertheless, even degraded GIWs may retain sufficient function to store and process sediments from surrounding watersheds mitigating deleterious effects of non-point source runoff from agriculture.

1.3 Study Site

The Dougherty Plain of southwestern Georgia contains more than 11,000 GIWs with most of them less than 1 hectare (Martin, 2013). The dominant land uses are pine silviculture and intensive irrigated row-crop agriculture. The primary source of water for irrigation is groundwater from the upper Floridian aquifer which extends north from Florida into southwestern Georgia (Miller, 1986, Blood, 1997). Center pivot irrigation systems introduced in the 1970's allow landowners to access groundwater as a readily available and reliable water source for crops during frequent periods of rainfall deficit (Bartels, et al 2013, New & Fipps, 2000, Harrison and Hook, 2005). Row-crops generally include peanuts, cotton, soybeans, and corn.

This project examined GIWs on working private farms (ag wetlands) with those found in forested areas (reference wetlands) (Figure 1). The two reference wetlands (W53 and W37) (Table 1) are located at the Jones Center at Ichauway: an ecological research center dominated by mature second growth long-leaf pine forest, with scattered wildlife food plots, and 1,000 acres of wetlands. The 12,200-ha forest is situated on the west bank of the Flint River south of Newton, Georgia. The land is managed for wildlife and conservation using biennial, low intensity prescribed burning. The reference GIWs are freshwater marshes with dominant herbaceous vegetation composed of sedges and other hydrophytes. W53 is large (3.17 ha) and surrounded by forest while W37 is a smaller (0.89 ha wetland with a county road on the southwestern edge (Figure 2). The agricultural GIWs are located are embedded and adjacent to agriculture fields and receive run-off of sediment and nutrients (C, N, P). The embedded agriculture GIWs receive 100 percent agriculture runoff making these systems unique when compared to other systems receiving materials from a variety of land uses. Agriculture wetland OS79 is 'embedded', i.e., entirely within an 11.81 ha field. 'Adjacent' agricultural wetlands lie off the edges of fields having catchment with both agriculture and forest. OS78 is an adjacent wetland that is large (4.22 ha) and deep (2 m). OS80 is an adjacent wetland that is subdivided into three basins to allow for the pivot-irrigation system to travel through the wetland on constructed berms. This subdivision creates a complex alteration that is of interest to understand hydrologic connectivity and nutrient transport.

Among differences in land use, the two wetland types vary in hydroperiods. Reference wetlands receive solely rainfall inputs while agriculture sites have irregular hydroperiods from agriculture practices (Tyson & Harrison, 1993). Agriculture wetlands have longer hydroperiods due to soil compaction (less seepage to groundwater), and lack of dense wetland vegetation (due to historical tillage). By supplementing soil moisture, irrigation allows agriculture wetlands to fill in response to less rainfall and helps maintain a positive hydraulic gradient from upland catchment to wetland basin. Along with varying hydrology, the reference and agriculture wetlands differ in macrophyte assemblages (Stuber, 2016) with the agriculture wetlands having a more open-water compared to hydrophyte-dominated reference marshes. The two wetland types provide a comparison to investigate the influence of agricultural land use on sediment dynamics of GIWs using paleolimnological reconstructions, nutrient storage, and nutrient distribution.

1.4 Study goals

GIWs that are within agricultural fields are poorly understood and while functionally degraded it is important to document quality and quantity of ecosystems services they provide. Without this understanding, GIWs are susceptible to draining, filling, or additional degradation (Moser et. al, 1996, Mitsch & Hernandez 2013). The aim of this project is to reconstruct nutrient deposition histories and to quantify nutrient storage in reference and ag-wetlands (described above). Paleolimnological analyses of sediment cores were used to understand land-use history, changes in agriculture practices, and estimate the storage of nutrients (Cohen, 2003). Sediment cores collected from the center of a wetland provided a reconstruction of historical nutrient runoff. Surface sediment cores also aided in identifying sediment spatial distribution within each wetland. Investigation of the paleo-record of sedimentary C, N and P as well as numerous non-reactive elements such as Mg, Ca, K, Pb, Fe among others, were used to identify changes in land use surrounding the system. Radio isotopic dating of the sediment using isotope ^{210}Pb provided a Mass Sedimentation Rate (MSR) to quantify sediment transport into wetlands through time (Oldfield & Appleby, 1984). Lead-210 dating concentrations provided dates of each section of sediment that were aligned with nutrient concentrations downcore to create nutrient profiles dating back to the late 1800's. Nutrient storage of the entire wetland was estimated once a sediment focusing factor was established using the MSR and then multiplied by nutrient concentrations and the wetland area to estimate nutrient storage capacity (e.g., Hobbs et al., 2013, Waters et al., 2019). Nitrogen and phosphorous storage capacities were then estimated.

The aims of this study are to 1) reconstruct land-use histories and agriculture practice changes from nutrient input histories reconstructed from sediment cores collected from each wetland, 2) quantify nutrient storage in whole-wetland systems using historical nutrient concentrations and mass sedimentation rates through time, 3) assess the spatial distribution of nutrients throughout the wetland using surface sediment cores to document sedimentary nutrient distribution within each system, and 5) to identify storage trends and mechanisms within agriculture wetlands and communicate findings with various stakeholders and landowners. It is hoped that this work can be used to develop management practices and incentives that mitigate nutrient runoff into downstream systems and enhance ecological services provided by GIWs in agricultural settings.

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Chapter 2: Temporal change of nutrient deposition and storage in a geographically isolated wetland located in an intensely agricultural landscape

2.1 Introduction:

2.1.1 Geographically Isolated Wetlands in an Agricultural Watershed

Wetlands completely surrounded by uplands and lacking a surface connection to other aquatic environments are called Geographically Isolated Wetlands (GIWs) (Tiner 2003a). GIWs provide numerous ecosystem services such as flood mitigation, pollution filtration, habitat for biodiversity, and nutrient cycling and storage (Marton et al., 2015). However, the absence of hydrologic connections to other Waters of the United States (WOTUS) precludes GIWs from legal protections under the Clean Water Act (USEPA, 2015a), which has led to a gap in recognition of GIWs despite their extensive benefits to watershed landscapes where they exist (Marton et al. 2015, Cohen et. al 2016).

As GIWs receive runoff from their surrounding uplands, the accumulation of clays and silts transported into their basins leads to the formation of an impermeable sediment lens. Because clay and silt are *low-permeable sediment,* interactions between the wetland system and the groundwater are restricted (Hendricks & Goodwin, 1952, Hayes et. al, 1983, Gomez et al., 2014). The formation of this semi-closed system allows for the establishment of processes capable of biogeochemical transformation and storage of nutrients prior to the flow of water to other aquatic ecosystems or groundwater (Cohen et. al 2016). One setting where mechanisms of nutrient transformation could be magnified in importance is in agricultural landscapes.

Agriculture causes extensive landscape alteration by clearing native vegetation, historical tilling, plowing, and harvesting (Nearing et. al, 2017) leading to elevated rates of soil erosion (Pimentel, 1987). While much research has focused on soil being lost to adjacent waterways (Cooper, 1993, Walker, 2019), less is known of the fate of the sediment and associated nutrients after input into GIWs. Various improvements have been made in farming practices to maintain soil health and limit erosion of sediments to adjacent waterways through precision agriculture techniques, changes in tillage, cover crops and other BMPs (Pierce & Nowak, 1999), but the many GIWs that are scattered throughout agricultural landscapes have previously been overlooked as sentinels for sediment storage and nutrient processing. GIWs in agriculture fields maintain many of the distinct features of wetlands such as hydric soil, wetland vegetation, and growing season inundation; but the surrounding land use alters their nutrient dynamics, sediment inputs, and vegetation making it important to assess their integrity as functioning wetlands.

A dominant ecosystem service that wetlands provide is nutrient transformation and deposition. Geographically Isolated Wetlands in agriculture catchments receive high loads of materials from frequent land disturbances specifically C, N, P and, sediment. One wetland sediment study measuring wetland nutrient storage ecosystem services puts a monetary value of sediment damages in a group of three small watersheds (each $< 4km^2$) to be over 180,000 US$ annually (Rogers et al., 2022). Excess nutrients cause eutrophication s in downstream waterways (Wurtsbaugh et al., 2019). However, it is well established that natural riparian wetlands mitigate deleterious effects of non-point source runoff from agricultural landscapes through nutrient transformations (Lowrance et al 1984). With the invention of the Haber-Bosch process, use of industrial nitrogen increased exponentially (Paull, 2009). Yet, the elevated organic matter and frequent inundation of GIWs promotes a suitable environment for denitrification to occur (Sirivedhin & Gray, 2006). GIWs also have the potential to limit the transport of pollutants and promote nutrient storage in sediments (Cohen et. al 2016). Wetlands globally accumulate high levels of carbon because anoxic conditions decrease the rate of decomposition (Brinson et al., 1981). Furthermore, agriculture accelerates input of allochthonous material leading to higher C burial in aquatic systems (Waters et al., 2019). Burial of C in sediment reduces transport of C downstream and reduces the emittance of CO_2 or methane to the atmosphere (Nahlik et al., 2016). Phosphorous exhibits increased storage since it lacks a gaseous phase making the presence of P in an aquatic ecosystem elevated and more permanent. The fate of excess nutrients can also include biological uptake of P and N for the growth of primary producers such as plants and algae. Of particular interest is the dissolution of P binding to Al or Fe due to the anoxic conditions in wetland sediments causing eutrophication upon resuspension. One method capable of reconstructing and quantifying sediment dynamics through time is the application of paleolimnological techniques to sediment cores collected from GIWs.

Paleolimnology is the reconstruction of environmental conditions of an aquatic ecosystem and surrounding landscape by determining the age and composition of sediment accumulated in lakes, reservoirs, or wetlands. Large shifts in sediment nutrient composition can give insight into historical land use changes as well as depositional mechanisms that can be considered long term nutrient removal from ecosystems (Clemmensen et al. 2013, Brenner et al., 2006). Radio chronometric dating techniques such as the analysis of excess ^{210}Pb and the constant rate of supply (CRS) model can provide dates and sedimentation rates for sediment core sections over the last ~150 years (Appleby 2001). In agricultural landscapes, changes in the measured concentrations of C, N, and P can be used to reconstruct the onset of intensive agriculture, the installation of groundwater pivot-irrigation systems, changes in tillage practices, or large changes in fertilizer usage (Schelske et al. 2005, Waters et al. 2009). A paleolimnological investigation can piece together historical land use changes to understand past conditions that will inform future decisions for best practices to maintain or enhance environmental quality of agricultural landscapes.

Paleolimnological investigations of GIWs have been limited to forested landscapes with only a few studies on GIWs in agricultural settings with most studies concluding that anthropogenic influence in a watershed directly influences sediment and nutrient accumulation in GIWs (Craft and Casey 2000). In agriculture catchments in the Midwest, nitrogen storage was 10 times greater than in natural catchments (Bernot et al., 2006). Climatic and human degradation of wetlands leads to diminished ecological services of GIWs to humans, wildlife, and water. Nevertheless, even degraded GIWs may retain sufficient function to store and process sediments from surrounding watersheds mitigating deleterious effects of non-point source runoff from agriculture.

Here, I applied paleolimnological techniques to sediment cores collected from a GIW located within a completely agricultural watershed and a “reference” GIW collected from a completely forested watershed. Both GIWs were in the Dougherty Plain of southwestern Georgia, USA. Paleolimnological measurements of organic C, total N, total P and photosynthetic pigments were analyzed on each sediment core, which were dated using excess ^{210}Pb analysis and the CRS model. The research objectives of this study were 1) to reconstruct the impacts of land-use histories and agriculture practice changes from nutrient input and depositional histories reconstructed from sediment cores collected from each wetland, and 2) to quantify nutrient storage in whole-wetland systems using historical nutrient concentrations and mass sedimentation rates through time. This work can be used to develop management practices and incentives that mitigate nutrient runoff into downstream systems and enhance ecological services provided by GIWs in agricultural settings.

2.2 Methods

2.2.1 Study Site

The Dougherty Plain of southwest Georgia contains more than 11,000 GIWs with most of them less than 1 hectare (Martin, 2010). The dominant land uses are pine silviculture and intensive irrigated row-crop agriculture. The primary source of water for irrigation is groundwater from the upper Floridan aquifer which extends north from Florida into southwestern Georgia (Miller, 1986, Blood, 1997). Center pivot irrigation systems, introduced in the 1970's, allow landowners to access groundwater as a readily available and reliable water source for crops during frequent periods of rainfall deficit (Rugel et al., 2012, Bartels, et al 2013, New & Fipps, 2000, Harrison and Hook, 2005). Row-crops generally include peanuts, cotton, soybeans, and corn.

This project examined a GIW on a working private farm (ag wetland) with a reference wetland located in a nearby forested area. The reference wetland (W53) is located at the Jones Center at Ichauway: an ecological research center dominated by mature second growth long-leaf pine forest, with scattered wildlife food plots, and 1,000 acres of wetlands. The 12,200ha forest is situated on the west bank of the Flint River south of Newton, Georgia. The land is managed for wildlife and conservation using biennial, low-intensity prescribed burning. The reference GIWs are freshwater marshes with dominant herbaceous vegetation composed of sedges and other hydrophytes. W53 is large (3.17 ha) and surrounded by forest. The agricultural GIW OS79 is embedded in an 11.81 ha agriculture field and receives run-off of sediment and nutrients (C, N, P) from solely agricultural practices. OS79 receives 100 percent agriculture runoff making it unique when compared to other wetlands receiving materials from a variety of land uses.

2.2.2 Field work:

Paleolimnological techniques were implemented to gather sediment samples from within wetland sites. Clear polycarbonate core barrels were inserted into wetland sediments using manual percussion, removed, and capped to be transported to the lab. Core sites were selected in undisturbed areas with cores collected from the center of each wetland where it is assumed that sediment accumulation and storage is highest. GPS coordinates of core locations were recorded using a handheld Garmin GPS device. Once wetland sediment was retrieved from the site, each core was sectioned into 1-2cm increments to be analyzed as independent samples. The choice to section sediment into small intervals allowed for necessary resolution essential for observation of systems with low sedimentation rates and to accomplish the research objectives. Samples were then refrigerated and kept in the dark.

2.2.3 Lab work:

Archive and Loss-On-Ignition

A wet aliquot was removed from each sediment section and used for gravimetric analysis (Heiri et al., 2001). A known volume of sediment was weighed and dried in an oven at 50° C. The dried sediment was reweighed, and bulk density was measured as g dry cm^{-3} wet. Organic matter was calculated as loss-on-ignition where dried sediments were placed in a muffle furnace at 500° C for 3 hrs. and expressed as a percentage. The remaining wet sediment was freeze-dried and ground using a mortar and pestle.

Elemental analysis

To measure element concentrations, an ICP method was used at Waters Agricultural Lab, Camilla GA. Homogenized ground dry sediment was analyzed for phosphorus and other elements including heavy metals following acid digestion in a heated block and measured using ICP-ARL following standard Environmental Protection Agency methods (US EPA, 2015).

Carbon and Nitrogen analysis

Carbon and nitrogen were measured using a Costech Carbon and Nitrogen elemental combustion system with attached auto sampler to measure inorganic and organic carbon (C) and nitrogen (N) percentages. For organic carbon, samples were acidified for 24 hours in HCl vapors to remove inorganic C prior to analysis.

^{210}Pb Dating: Mass Sedimentation Rate and Nutrient Storage

To measure rates of sedimentation and to determine dates for each core section, a Geranium Well Detector was used to measure excess ^{210}Pb in mg cm^{-2} yr^{-1}. Sediments were weighed into plastic tubes and sealed with an epoxy for a minimum of 19 days to allow for secular equilibrium between atmospheric gases ^{226}Ra and ^{210}Pb. Supported ^{210}Pb was determined from the measurement of radioisotopes (^{226}Ra $\rightarrow$ 222Rn $\rightarrow$ ^{218}Po $\rightarrow$ ^{214}Pb $\rightarrow$ ^{214}Bi $\rightarrow$ ^{214}Po) which precede ^{210}Pb in the decay sequence. Supported ^{210}Pb was subtracted from measured total ^{210}Pb to determine excess ^{210}Pb used in the Constant State of Supply (CRS) model (Appleby and Oldfield, 1983). The CRS model assumes ^{210}Pb fallout from the atmosphere is constant allowing fluxes in excess ^{210}Pb to be a result of changes in sedimentation rate. Calculated dates for sediment sections were matched with known dates of land-use conversion to agriculture and changes in agricultural practices including installation of pivot irrigation (~1970 CE) (Rugel et al., 2012 Martin, 2013), implementation of precision agriculture (Pierce & Nowak, 1999), and any known fertilization practices (~1990 CE) (Cao et al., 2018).

Nutrient concentrations (C, N, P) were multiplied by the sedimentation rate to determine nutrient storage over time in each wetland system (Figure 3). A sediment focusing factor for the agricultural wetland was determined to be 1.06 by comparing excess ^{210}Pb in the surface sample of the core with known ^{210}Pb fallout for the geographic area (Waters et al. 2019, Hobbs et al. 2013). Each respective nutrient concentration was multiplied by MSR and the focusing factor to calculate nutrient storage in g m^{-2} yr^{-1}. To get a nutrient storage estimation for the whole wetland, the nutrient storage value was multiplied by the wetland area (calculated using standard wetland delineation parameters) to provide cumulative nutrient storage (g yr^{-1}) per wetland in the ~150 yr. sediment history. Cumulative nutrient storage calculations were calculated for C, N and P. Units were also converted to pounds and tons to communicate in preferred units to farmers and stakeholders alike. Using methods from Rogers et al., (2022), a monetary value was placed on nutrient storage in the agriculture wetland. The 2019 societal cost of C, N and P were multiplied by cumulative nutrient storage and aggregated to reach a total value of nutrient storage in the system in US$.

Photosynthetic pigments

Photosynthetic pigments were run as a proxy for primary producer abundance and to identify historical algal community composition. High-Pressure Liquid Chromatography (HPLC) was used to measure pigment concentrations. Methods followed Leavitt and Hodgson (2002) and Waters et al. (2015). Pigments measured include Alloxanthin (*cryptophyta*), Diatoxanthin (*Bacillariophyta* (diatoms)), Lutein and Zeaxanthin (*Chlorophyta + Cyanobacteria)*, Canthaxanthin (Cyanobacteria (attached, colonial), Chlorophyll a (total primary producer abundance), Chlorophyll b (*Chlorophyta*, macrophytes), Pheophytin a (total primary producer abundance), and pyroxanthin.

2.3 Results

2.3.1 Sedimentation rate and historical periods

Physical appearance of the reference wetland core was dark in color indicating organic matter (Figure 4) compared to the pale grey color of the agriculture wetland core (Figure 5).

The MSR acquired using excess ^{210}Pb and the CRS model provides a sediment history for both the reference wetland and the agriculture wetland. The datable sediment of the reference wetland extended to 8cm in depth and is representative of a 125-year history. The most recent attainable date at depth of 1 cm is 2015 ± yrs. and dates to 1890 ± 14 yrs. at a depth of 8cm (Figure 6). Sedimentation rates were low throughout the period of record with average sedimentation rates of 22 ± 12 mg cm $^{-2}$ yr^{-1}. The maximum for the reference wetland reached 40 mg cm $^{-2}$ yr $^{-1}$at the top of the core (year 2015).

Conversely, the agriculture wetland provided a different profile when dated using ^{210}Pb. Agriculture wetland OS79 had a 136-year history extending from 37 cm to the surface of the core that showed great fluctuations moving up core. From years 1886-1948, MSR was low at a background level averaging 114 ± 60 mg cm $^{-2}$ yr $^{-1}$ (Figure 7). In 1954, the MSR spiked to 1083 mg cm $^{-2}$ yr^{-1}.: an order of magnitude greater. Then MSR decreased to 346 ± 338 mg cm $^{-2}$ yr^{-1} until 1969 when MSR reached its greatest 1946 ± 257 mg cm $^{-2}$ yr $^{-1}$. Sedimentation flux during this period, represented approximately 3 cm per year: 29cm, 28cm and 27cm with MSR's of 2227, 1723 and 1888 mg cm $^{-2}$ yr^{-1}. Respectively identifying a period of consistently higher sedimentation rates. Radiometric dating using ^{210}Pb over a centenary time scale creates lessens the degree of precision in dates (appendix a). The 1969 event has an associated error of ± 15 years and will be henceforth referred to the early 1970s MSR event. This massive sedimentation event around the 1970s was two magnitudes higher than the maximum of the reference wetland

(40 mg cm $^{-2}$ yr-1). Following the spike in MSR in early 1970s, rates dropped to an average of 577± 326 mg cm $^{-2}$ yr $^{-1}$ before peaking again in 1977 (990 mg cm $^{-2}$ yr $^{-1}$) and further increasing the subsequent year (1157 mg cm $^{-2}$ yr^{-1}). From 1979-2006, the MSR remained consistently low with an average of 425 ± 118 mg cm $^{-2}$ yr $^{-1}$. In 2008, the MSR increased to 1202 mg cm $^{-2}$ yr^{-1}. Following the year 2008, MSR decreased but remained higher than the baseline (809 mg cm $^{-2}$ yr^{-1}). 2011-2000 had an average MSR of 590 ± 117 mg cm $^{-2}$ yr^{-1}.

To compare sedimentation dynamics with known changes in agricultural history, the agricultural wetland core was divided into three historic eras to identify specific trends within each time period. The dates were chosen based upon large trends in the MSR, known changes in agricultural practices and historic aerial photography (United States, United States Agricultural Stabilization and Conservation Service). For the agriculture wetland, time periods were created to better link each sediment profile with known agricultural periods: the historical agriculture era, the intensive agriculture era, and the modern agriculture era. The historic agriculture era is defined by the start of the bottom of the core (61cm) to the year 1948 (33 cm) where historic aerial photography prior to date shows low intensity row crop agriculture (United States, United States Agricultural Stabilization and Conservation Service) and MSR was low (Craft & Casey, 2000). The intensive agriculture era is defined by years 1954-1993 (32-15cm) where MSR dramatically increases and shows its all-time high within this period, and the land appears to receive substantial land transformations to adjust for the preparation of intensive agriculture. Any remnant forestry was cleared as the land use transitioned from historic low-intensity row-crop agriculture to present-day intensive ground-water irrigation agriculture (Martin et al., 2013). The modern-day agriculture era is defined by a decrease in MSR and the first historical aerial photograph to identify a center-pivot irrigation system at the start of the era and continues to modern day 2020 (14-0 cm) (United States, United States Agricultural Stabilization and Conservation Service).

2.3.2 Organic matter and Nutrients

Throughout most of the sediment record, percent organic matter of the agriculture wetland historically is 11.3%± 2.49; however, the very bottom of the core from 55-61cm has higher percent OM (14.9% ± 1.45) (Figure 8). Greater OM concentration is apparent in the dark brown appearance of the sediment compared to the remainder of the core which shifts to a pale grey color (Image 4). During the Intensive Agriculture era from 1954-1993 (32cm-15cm), percent organic matter was 10.56 ± 1.12 and bulk density was 0.99±0.18 g dry cm^{-3} wet. The modern agriculture era from 1996 to present day (14cm-0cm) has an average percent organic of 10.93%±0.37 and a bulk density measurement of 0.97±0.20 g dry cm^{-3} wet.

Organic C concentration is high at the bottom of the core (5.3%±0.67) from 61cm to 55 cm, followed by a decrease to 3.66%±1.38 from 55cm to 33cm moving up the core. Organic Carbon values for the intensive agriculture era are lower than the historic agriculture era (1.82±0.19). Modern era percent organic carbon values were 2.10 ± 0.20, lower than the historic era but higher than the intensive agriculture era. Percent N is consistent with the trend having high N concentration at the bottom (0.31%±0.03) that decreases to 0.17%±0.1 during the historic era. Total Nitrogen concentration for intensive agriculture era (0.09±0.02) is near undetectable levels for our analysis. Percent total nitrogen values increase in the modern era averaging 0.14±0.03. Phosphorous concentrations in the historic era on average are 0.68±0.07 mg g^{-1}. Phosphorous then increases by 60% to 1.1±0.24 mg g^{-1} in the intensive agriculture era. Phosphorus then decreases in the modern agriculture era by decreasing to 0.95±0.05 mg g^{-1}.

The historic era has an average C/N of 18.22±2.72 molar. The C/N decreases slightly to 16.9±3.5 in the intensive agriculture era and continues to decrease to 13.5±0.91 in the modern agricultural era. The nitrogen to phosphorous ratio is historically high (0.67±0.3 molar ratio) and decreases to 0.22 ±0.06before recovering to 0.33±0.03 in the modern era. The N/P ratio in the historic era has an average of 5.5±3.27 which decreases during the intensive agriculture era to 1.95±0.42 and then increases to a steady 3.35±0.64 during the modern agriculture era.

2.3.3 Additional Elements

In addition to C, N, and P, other elements were measured that historically have been associated with agricultural practices (K, Mg, Ca, and S) as well as elements that bind with P such as Fe and Al (Figure 9). Iron concentrations in the historic era average 12.49±4.91 mg g^{-1} and increased to 28.4±4.0 mg g^{-1} in the intense ag era. Fe concentrations decreased during the modern era (24.3 ±0.89 mg g^{-1}). Aluminum also had its maximum during the intensive agriculture era when increased from 24.0±1.2 mg g^{-1} to 30.4±1.9 mg g^{-1}. Aluminum returned to historic levels during the modern era (24.6±1.9 mg g^{-1}).

In the historic era, K averaged 0.45±0.08 mg g^{-1} and slightly increased during the intensive agriculture era to 0.66±0.08 mg g^{-1} and remained at this level for the modern agriculture era (0.62±0.08 mg g^{-1}). Magnesium values were relatively consistent starting at 0.68±0.10 mg g^{-1} in the historic era then increasing 0.84±0.05 mg g^{-1} during the intensive era and returned to 0.69±0.05 mg g^{-1} in the modern era. Calcium remained constant through the core period but with a slight increase through the eras (2.44±0.23 mg g^{-1} to 2.65±0.23 mg g^{-1} to 2.75±0.16 mg g^{-1}). Sulfur concentrations during the historic era were 0.35±0.11 mg g^{-1} on average and decreased slightly in the intensive agriculture era (0.25±0.05 mg g^{-1}) then returning to 0.34±0.05 mg g^{-1} during the modern era.

2.3.4 Photosynthetic Pigments

For the agriculture wetland, photosynthetic pigments followed a similar pattern during the historic era and intensive agriculture era (Figure 10). Pigment concentrations during the modern era showed variability in concentration with general increasing trend for most pigments. Alloxanthin, a pigment diagnostic for cryptophytes, almost doubled from 1.67 ± 1.43 nmol pigment g^{-1} organic matter (org) to 3.02±3.01 nmol g^{-1} org from the historic era (bottom of the core – 1948) to the intensive agriculture era (1954-1993) where it exhibited peak concentration coinciding with the early 1970s MSR event at 13.0 nmol g^{-1} org; 7 times higher than the baseline value. Alloxanthin then fell to 2.6±1.7 nmol g^{-1} org in the modern era. Diatoxanthin, indicative of diatom presence, follows a similar trend with a very low initial concentrations 1.11±1.17 nmol pigment g^{-1} org matter that increase to 2.93±3.98 with the early 1970s event reaching 16.0 nmol g^{-1} org before decreasing to 0.59±0.43 nmol g^{-1} org. Lutein+zeaxanthin has a historic average concentration of 0.65 ± 0.87 nmol pigment g^{-1} organic matter with very little pigment appearing in the bottom of the core. Lutein+zeaxanthin, a mixture of green algae and cyanobacteria pigments, follows a similar trend as the previous pigments with a sharp increase to 1.7±2.1 nmol g^{-1} org in the 1970s and a maximum concentration of 8.5 nmol g^{-1} org near the early 1970s event, then remained high (2.3 ± 1.6 nmol g^{-1} org) through the modern era. Chlorophyll-b, an additional marker for green algae, is 0.35±0.47 nmol pigment g^{-1} organic matter in the bottom of the core and increases 5-fold to 1.72 ±1.36 nmol pigment g^{-1} org and continues to increase to 8.1±8.2 nmol pigment g^{-1} org during the modern agriculture era. Chlorophyll-a, a marker for total primary producer abundance, has a baseline historic value of 0.14±0.14 nmol pigment g^{-1} org; increases to 0.48±0.37 nmol pigment g^{-1} org with a high modern concentration of 7.6 ±10.0 nmol pigment g^{-1} org. Historically, pheophytin-a (total abundance and a marker for degradation) is 3.27±4.58 nmol pigment g^{-1}org with almost a four-fold increase to 12.0±8.8 nmol pigment g^{-1} org and a two-fold increase to 26.4 ± 12.8 nmol pigment g^{-1} org in the modern agriculture era. The degradation ratio (chlorophyll-a/pheophytin-a) is low for the historic, intensive, and modern agriculture eras (0.07±0.03 and 0.04±0.01, respectively).

2.3.5. Reference Forested Wetland Results

The reference core was broken down into two sections for further elemental analysis: the bottom undated portion of the core from 50cm-6 cm and the top of the core (5cm – 0cm) dating from 2015-1996 CE. The forested wetland had an average percent organic matter of 9.3 ±12.3% with bottom of the core having a LOI of 5.0±2.9% that increases by a factor of 8 to 38.5±12.1% in the top 5 cm (Figure 11). The average bulk density was 1.1±0.5 g dry cm^{-3} wet. Organic carbon concentration also had a low baseline (1.9±1.3%) and increased at the top of the core (16.9 ± 4.7%) with an average of 3.8±5.4%. Total nitrogen was low at the bottom of the core (0.17±0.13%) and increased to 1.2±0.3% at the top 5 cm with an average of the whole core as 0.3±0.4%. Phosphorous concentrations averaged 0.3±0.3 mg g-1 with the bottom 45 cm having a concentration of 0.22±0.15 mg g-1and the top having a concentration of 0.88±0.13 mg g^{-1}. The carbon: nitrogen ratio in the reference forested wetland on average was 14.2±2.2 with the top of the core (16.8 ± 2.1) higher than the bottom of the core (13.8±1.9). The N/P was 2.0 ± 0.6 for the whole core, 1.8±0.4 for the bottom 45 cm of the core and 2.9±0.4 for the top of the core. Elemental concentrations of the reference wetland were consistent with an elevated concentration in the top of the core (Figure 12). Photosynthetic pigments in the forested wetland were not as diverse as the agriculture wetlands (Figure 13). Alloxanthin had an average concentration of 0.4±1.1 nmol pigment g^{-1} organic matter while there was no diatoxanthin present, lutein+zeaxanthin averaged 2.3±8.4 nmol pigment g-1 organic matter. Canthaxanthin was 0.3±1.0 nmol pigment g^{-1} organic matter, Chlorophyll a and Chlorophyll b were 1.9±8.9 nmol pigment g-1 organic matter 2.4±9.0 nmol pigment g-1 organic matter. Pheophytin-a is 12.1±24.2 nmol pigment g-1 organic matter.

2.3.6 Sediment Storage

Sediment storage in the entire agricultural wetland OS79 (0.5 ha) was calculated for the 136-year dated sediment history for each nutrient (Table 2) (Figure 3). Briefly, nutrient concentrations were multiplied by the sedimentation rate and a local focusing factor for each core section to give mg nutrient per cm^{-2} $year^{-1}$. The focusing factor was generated by normalizing the excess ^{210}Pb values of the top sample of the core with expected values from the literature following Waters et al. (2019). Cumulative storage per wetland was then calculated using the wetland area in hectares and the depth of the dated portion of the core. Various units are presented to communicate the generated values to multiple stakeholders (i.e., scientists, landowners, common citizen) in understanding the magnitude of nutrient storage (Table 2). Sediment storage is substantially higher for both carbon and phosphorous. Carbon stored in the wetland was calculated to be greater than 20,000 kg and phosphorous greater than 10,000 kg. Nitrogen storage, conversely, was low (1406 kg) for the entire 136-year history. In the 3.17ha reference wetland for the 125-year history of the system, carbon storage was 9135 kg, nitrogen storage was 606 kg and nitrogen storage was 159 kg; all values lower than storage of nutrients in the agriculture wetland.

2.4 Discussion

Results from the sediment record of agricultural wetland OS79 show periods of high sediment deposition, more graduate changes in phosphorus loading, and substantial nutrient storage capacity. The MSR of the agriculture wetland is 2 magnitudes higher than the reference wetland reaching a maximum of 2227 mg cm^{-2} yr^{-1} with the year 1969 accumulating 3 cm of sediment in the small 0.5-hectare wetland. Phosphorous was transported into the system historically yet spiked in the 1970s aligning with the introduction of center-pivot irrigation installation in the region (Rugel et al 2012) creating a driver for sediment transport carrying reactive nutrients such as P. The phosphorous then decreased around 1996 as MSR declined showing the driver of P delivery rather than P use in the system. Once intensive agriculture was established in the area, the dominant driving force of massive sediment influx was removed allowing sedimentation rates to return to baseline levels yet slightly elevated as a result of routine intensive agriculture. This decrease could also suggest successful agricultural best management practices being implemented in the last few decades such as erosion controls, cropping practices and increased efficiencies in general (Pierce & Nowak, 1999). Finally, with high sediment transport, there was high nutrient storage capacity for Carbon and Phosphorous and postulated denitrification of N.

2.4.2.1 Historical Agricultural Era (1886-1948)

The high percent organic matter in the bottom of the agricultural wetland core suggests that prior to agriculture, surrounding land use did not result in extensive sediment transport (Martin et al 2013, Craft & Casey 2000). Although the dates for the sediment core do not extend beyond 37cm, the high organic matter deposition indicates a natural wetland system typical of high organic matter or peat-like material (Maltby, 2009. Mitsch et al., 2013). When compared to the reference wetland percent organic matter, the bottom portion of OS79 exhibits similar LOI values to the natural reference wetland studied (Bottom of OS79 ~ 15% and top of W37 ~ 22%). Percent nitrogen and percent carbon were also greater during this period and showed similar decreases as the percent organic matter 60-50 cm in depth.

The Southeastern United States has a long history of agriculture presence. Beginning in the colonial era, the British utilized the extended growing season of the south to grow crops (Bonner 2009). However, historical agriculture practices were inefficient and often detrimental to soil integrity, leading to erosion and soil degradation (Bonner 2009). Historic sedimentation rates in the agriculture wetland were least at the bottom of the core (114 ± 60 mg cm -2 yr -1) indicative of minimal disturbance; However, these estimates are still higher than the maximum MSR of the reference wetland (maximum MSR of W53 = 45 mg cm -2 yr -1). Nutrient concentrations during the historic agriculture time period (1886-1954) showed a decreasing trend for percent C and N that coincided with an increase in C/N values. An increase in C/N indicates an influx of more terrigenous material which could indicate the clearing of land for agriculture or the input of crop residue from tillage practices (Nicolardot et al., 2001).

Most element concentrations during the historical agriculture era were also consistent through time. However, iron gradually increased from 5mg/g to 20mg g^{-1}. Calcium showed fluctuations that may be attributed to historical liming of the field where dolomite or limestone are added to buffer the pH of the soil, a common agricultural amendment in the region (Goulding, 2016). Furthermore, calcium is naturally present in the geography because of the karst bedrock.

Photosynthetic pigment concentrations of are low or absent during the historic agriculture period. Alloxanthin, diatoxanthin and pheophytin-a do have measurable concentrations that increased during the 1930's. Lutein+zeaxanthin shows a unique profile that exhibits a spike in pigment concentration at 39 cm which is premature to pheophytin-a's pulse at 36cm. Pigment peaks during the historical agriculture era do not correspond to nutrient pulses suggesting that these increases in primary producers were detectable but not at levels suggesting eutrophication. However, other paleolimnological investigations have shown increases in primary producers in response to elevated nutrient inputs during periods of disturbance (Waters et al. 2015, 2009). In wetland OS79, the early 1970s was a period of very high sedimentation rate that aligned with a spike in pigment concentrations indicating a notable increase in primary producer abundance.

2.4.1.2 Intensive Agriculture Era (1954-1993)

In the intensive agriculture era, increased sediment delivery in early 1970s to the wetland a period of disturbance to the wetland and surrounding landscape. Sediment inputs are two magnitudes greater than the MSR of the reference wetland and rival that of any other high sedimentation rates from other aquatic systems (Sadler, 1981, Craft & Casey, 2000, Waters et al., 2019). Craft & Casey (2000) reported sedimentation rates from wetlands in the same geographic region as having an average 100-year MSR of just half of our maximum. Other studies having similar sedimentation rates include a Bottomland hardwood wetland in eastern Arkansas (> 1cm yr^{-1}) (Kleiss, 1996), a Missouri Small Riparian Wetland (< 1cm/yr) (Heimann et al., 2000) and in agricultural watersheds of Maryland (1.6 cm/yr) (Costa 1975). However, none of these systems approached 3cm yr^{-1} sedimentation rate observed in the agriculture wetland from this study. The MSR in the intensive agriculture era is a magnitude higher than the previous era and rivals that of hypereutrophic lakes (Schelske et al. 2005, Waters et al. 2019). The date of this even also coincides with the adoption of pivot agriculture irrigation in the area (Pierce et al., 1984, Rugel et al., 2012) as well as evidence of deforestation from aerial photographs (United States

Agricultural Stabilization and Conservation Service, 1968). Although the slopes of this watershed are relatively steep allowing for surface runoff and downslope sediment movement, the watershed itself is small, highlighting the potential for high erosion rates with historical intensive agricultural practices.

In addition to increased sedimentation, P concentrations increased in the 1970's also coinciding with the adoption of irrigation. The abundance of groundwater and minimal regulation on its use, allowed for intensification of agriculture during the extended growing season characteristic of the region. In addition to P, Fe and Ca show similar stratigraphies during this period. The elemental inputs do not directly follow the spikes in MSR suggesting that the episodic processes causing the erosion events were independent of the chronic and constant input of elements linked to agricultural practices in the area.

The influx of sediment and nutrients did impact the primary producer community of the wetland. We can deduce that the spikes in pigments are not a result of fluxes of nutrients (C, N or P) because carbon and nitrogen stay very consistent during this period and P does not increase until after the pulse in primary productivity. Therefore, the driver of the algal increase appears to be linked to erosional disturbance rather than nutrient input. Pigments for alloxanthin (cryptophytes), diatoxanthin (diatoms) and lutein+zeaxanthin (green+cyanobacteria) collectively increased in the intensive agriculture period. However, canthanxathin, the only pigment specifically for cyanobacteria measured in the study, did not show an increase (Leavitt and Hodgson 2001). As a result, it is inferred that the primary producer community increased but did not for harmful algal bloom conditions. The increase in aquatic primary producers is also supported by a decrease in C/N during the same period (Meyers and Teranes 2002). While direct nutrient inputs are usually linked to primary producer increases, other studies have shown that water level changes and sediment disturbances can also cause primary producer abundance to increase (Waters et al. 2015, Waters et al. 2009).

2.4.1.3 Modern Agriculture Era (1993 – 2020)

The modern-day intensive agriculture period from 1993-2020 shows reduction in sediment and nutrient delivery, but also shows increases in primary producer abundance and cyanobacteria. The MSR decreases substantially in this era with only one episodic event of erosion. This event occurred around 2008 as identified by the CRS model which followed a significant drought in the area (appendix b). While all the spikes in MSR throughout the core do not coincide with drought events, intense rainfall following periods of drought could be a mechanism of episodic erosion in future investigations. In addition to lower MSR, P influx also diminishes. Phosphorous concentrations show a decrease from 1.10± 0.24 mg g^{-1} in the intense era to an average of 0.95±0.05 mg g^{-1}in the modern period (Figure 14). The decrease in P beginning in 1993 coincides with multiple changes in agricultural practices that could reduce nutrient delivery. The implementation of precision agriculture techniques and incentives such reduction of tillage during the Food Security act of 1985 (Uri, 2000), cover crop use (Pierce & Nowak, 1999) among other financial and technological aid to improve crop efficiency and reduce soil erosion and degradation were widely adopted in the region during this period. Furthermore, precision agriculture techniques have continued to reduce excess fertilizer application through advancing science, technology, and education (Comi 2020). Despite the decrease in P deposition, pigment concentrations conversely are high. Some of these increases could be better degradation, but even the reduced delivery of nutrients and constant irrigation from the pivot systems would provide favorable conditions for algal and cyanobacteria growth. Of particular interest is the increase in they cyanobacteria pigment, canthaxanthin, which began to be detected during this period. While relative nutrient delivery decreased during this period, the reduction in erosion would also decrease turbidity and light limitation thus favoring some primary producers. Collectively, sediments in the modern agriculture era show less influence of intensive agriculture effects despite known intensive agriculture practiced in this field.

2.4.2 Storage

Nutrient storage values were minimal in the reference wetland for C, N, and P due to the low MSR of only 45 mg cm -2 yr -1 creating little capacity for nutrients to accumulate in the sediment overtime. In the agriculture wetland, however, nutrient storage in the small half hectare wetland is substantial for C, N and P. The storage values of 25 tons of carbon and 13 tons of phosphorus suggest the extensive ecosystem services provided by GIWs and merit further study to determine economic value of nutrient storage. Once these nutrients enter the GIWs, they are likely sequestered from other aquatic systems due to the lack of connection to surface waters. Therefore, this storage prevents further transport to downstream waters such as lakes and streams effectively reducing the risk of harmful eutrophication from excess nutrients (Cohen et al., 2016, Ardon et al., 2010). In a karst topography, water is often recharged into local aquifers; yet storage of excess nutrients in sediment may reduce the likelihood of contamination of some nutrients (phosphorous) (Ballantine et al., 2009) to groundwater while permitting some leaching of nitrogen to reach aquifers (Beck et al., 1985, Hubbard & Sheridan, 1989). Conversely, fertilizer costs have continued to increase, which increases economic burden on farmers (Quinn, 2020). This study identifies a new method to quantify nutrient transport that could initiate conservation conversations with farmers to further progress precision agriculture techniques, limit excess fertilizer application and reduce erosion from agriculture lands and highlights the success of investments in conservation practices under precision agriculture.

Vitousek et al. (1997) and Galloway and Cowling (2002) identified a growing use of nitrogen fertilizers globally, and it is well assumed that most farmers apply nitrogen fertilizer to their lands; however.   Nitrogen levels in the sediment of OS79 are very low compared to the C and P storage values. Low nitrogen storage in this system suggests denitrification could be occurring thus also removing N from surrounding ecosystems. GIWs maintain the proper conditions for denitrification to occur anoxia (typical of wetlands), warm temperatures (from shallow water levels), and labile organic carbon for heterotrophic microbes (Knowles, 1982). I did not directly measure denitrification in this study, but future studies of GIWs should include the measurement of denitrification processes.

High organic carbon storage is expected because it is likely that a high proportion of the allochthonous material entering the system is from crop fragments (C/N ~20). Although there is evidence of autochthonous carbon fixation from pigment data and observed algal mats in the system, C/N values indicate that the majority of the carbon in the wetland is transported from the 100% agriculture surrounding watershed especially in times of harvest and removal of leftover crop litter. High carbon storage creates potential application for the global carbon models. Although wetlands nationwide are known to have high carbon content (Nahlik et al., 2016), GIWs in general are overlooked from being included in the carbon budget the way that soils are credited as sinks (Najjar et al., 2018, Friedlingstein et al, 2020). Despite showing evidence of degradation, this study shows that agricultural wetlands have the potential to store substantial carbon and nutrient, thus retaining important functions. Future precision agriculture programs should recognize this potential and provide incentives for landowners to manage for and enhance critical wetland functions. Doing so would provide valuable ecosystem services in the form of biogeochemical processing and storage of excess nutrients and improve the environmental quality of rural communities.

Our nutrient storage data supports the notion that GIWs support biogeochemical processing and transformation; yet further calculations can be done to put a monetary value to this ecosystem service. A current estimate of the social cost of Carbon is 31 US$ per ton of carbon scaled to 114 US$ when considering the mass of C in CO_2 making the cost of this wetland's storage to be about $2850 comparable to Rogers et al.'s study (2022) (Table 3). The value for nitrogen in this site is 2620 US$ according to nitrogen's societal cost estimate (Keeler et al., 2016). P value is based on cost of removal making the rate 2381 US$ per ton with our wetland costing almost 40,000 US$. This estimate is based on removal of excess P from a system; however, it can also be viewed as a lost cost to farmers. Phosphorous fertilizer is expensive, and costs have only increased in recent years. The calculated MSR demonstrates that landowners are losing sediment to GIWs through erosion and with that they are losing reactive nutrients- P specifically. These economic values calculated are for the entire 136 history of the system but the aggregate value of C, N, and P storage capacity that this wetland is providing is about 46,000 US$ (Table 3).

2.5.1 Conclusion

This study examined the sedimentation and storage of nutrients in agriculturally influenced geographically isolated wetlands and documented the value paleolimnological investigations in natural and agricultural systems alike. Martin (2010) calculated that in the Dougherty plain alone there are upwards of 11,000 small GIWs. The results from my study show large amounts of sediment and nutrients entering and being stored in this GIW suggesting substantial benefits to regional or larger scales. Phosphorous showed a pulsed inputs independent of MSR and declining inputs under modern agricultural practices. Both P and C are stored in the sediment of the system while N may exhibit denitrification. The amount of sediment transported into this small GIW system is magnitudes higher than natural systems and exceeds many MSRs in the literature. Peaks in MSR and pigments show land disturbance and erosion as the driver of primary productivity in this system rather than excess nutrients. P profiles show the potential for wetland sediments to be used to connect improved farming practices with changes in nutrient erosion. This study has implications for landowners, environmentalists, and land managers to maintain the integrity of GIWs in agriculture watersheds to receive and store erosional materials.

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Chapter 3

Biogeochemical heterogeneity of sediment characteristics between agriculture and forest influenced geographically isolated wetlands

Introduction

3.1 Geographically Isolated Wetlands in an Agricultural Watershed

Geographically isolated wetlands (GIWs) are wetlands surrounded by uplands and lack a surface connection to other aquatic environments (Tiner 2003a). Whereas GIWs provide numerous ecosystem services such as flood mitigation, pollution filtration, habitat for biodiversity, and nutrient cycling and storage (Marton et al., 2015), the absence of hydrologic connections to other surface waters precludes GIWs from legal protections under the Clean Water Act (USEPA, 2015a). The lack of legal recognition has led to a gap in research of GIWs despite their ability to provide extensive ecosystem services (Marton et al. 2015, Cohen et. al 2016).

As GIWs receive runoff from their surrounding uplands, the accumulation of clays and silts transported into the basin leads to the formation of a clay lens. Because clay and silt are *low-permeable sediment,* interactions between the wetland system and the groundwater are restricted (Hendricks & Goodwin, 1952, Hayes et. al, 1983, Gomez et al., 2014). The formation of these perched systems allows for the biogeochemical processing and storage of nutrients prior to the flow of water to other aquatic ecosystems or groundwater (Cohen et. al 2016). However, the biogeochemical composition of GIWs is based on the sediment received and varies based on the surrounding landscape.

The function of GIWs is dependent on the regional geology, surrounding land use and land cover. The Dougherty plain of southwest Georgia is composed predominantly of intensive row-crop agriculture and pine silviculture. Agriculture in the region produces corn, soybeans, cotton and over half of the countries' peanuts (USDA, 2022). Crop production produces important commodities however, intensive agriculture creates land alterations, soil erosion, degrades water quality and impacts biodiversity (Foley et al., 2005). Yet wetlands can provide ecosystem services that can ameliorate some of the environmental degradation found in agriculture landscapes (Craft & Casey, 2000, Rogers et. al, 2022,). In the Dougherty Plain, there are also upwards of 11,000 GIWs susceptible to influence by landscape alterations (Martin et al., 2013). Given the large number GIWs, the materials received and stored from the landscapes can additively amount to a significant biogeochemical component of the entire area.

Agriculture causes extensive landscape alteration by clearing native vegetation, historical tilling, plowing, and harvesting (Nearing et. al, 2017) leading to elevated rates of soil erosion (Pimentel, 1987). Various improvements have been made in farming practices to maintain soil health and limit erosion of sediments to adjacent waterways through precision agriculture techniques, changes in tillage, cover crops and others (Pierce & Nowak, 1999), but the many GIWs that are scattered throughout agricultural landscapes have previously been overlooked as sentinels for sediment storage and nutrient processing. GIWs in agriculture fields maintain many of the distinct features of wetlands such as hydric soil, wetland vegetation, and seasonal inundation; but the surrounding land use alters their nutrient dynamics, sediment mechanisms, and vegetation making it important to assess their integrity as functioning wetlands. As a result, GIWs change through time and season with variable water levels depending upon precipitation and irrigation changes, erosion related to crop rotation and harvest, and processing related to GIW primary producers living in and around the wetland. While much research has focused on soil being lost to adjacent waterways (Cooper, 1993, Walker, 2019), less is known about how sediment loading from agriculture landscapes effects the biogeochemical composition of GIWs as well as the spatial distribution of eroded soils within wetland systems. Here, I compared the biogeochemical capability of GIWs influenced by intensive agriculture with forested reference GIWs in terms of nutrient, elemental and additional sediment characteristics using a spatial surface sediment assessment.

3.2 Methods

3.2.1 Study Site

The Dougherty Plain of southwest Georgia contains more than 11,000 GIWs with a majority of them less than 1 hectare in surface area (Martin, 2013). The dominant land uses are pine silviculture and intensive irrigated row-crop agriculture. The primary source of water for irrigation is groundwater from the upper Floridan aquifer which extends north from Florida into southwestern Georgia (Miller, 1986, Blood, 1997). Center pivot irrigation systems introduced in the 1970's allow landowners to access groundwater as a readily available and reliable water source for crops independent of alterations in rainfall (Rugel et al., 2012, Bartels, et al 2013, New & Fipps, 2000, Harrison and Hook, 2005). Common row-crops generally include peanuts, cotton, soybeans, and sweet corn.

This project examined six GIWs: four GIWs on two working private farms (agriculture wetlands) and two reference GIWs. The reference wetlands (W53, W37) are located at the Jones Center at Ichauway: an ecological research center dominated by mature second growth long-leaf pine forest, with scattered wildlife food plots, and 1,000 acres of wetlands. The 33,000-acre forest is situated on the west bank of the Flint River south of Newton, Georgia. The land is managed for wildlife and conservation using biennial, low-intensity prescribed burning. The reference GIWs are freshwater marshes comprised of dense understory of sedges and other hydrophytes. W53 is large (3.17 ha) and completely surrounded by forest while W37 is smaller

GIW (0.89 ha) and abuts a county road (Figure 2). The agricultural GIWs are either embedded (completely surrounded by agriculture land use) or adjacent (abutting agriculture land use with some mixed land use of forest). OS79 is an embedded GIW and receives run-off of sediment and nutrients (C, N, P) from solely agricultural practices making this system unique when compared to other systems receiving materials from a variety of land uses. 'Adjacent' agricultural wetlands lie on the edges of fields having catchment with both agriculture and forest. OS78 is an adjacent GIW with partial agriculture input from two different fields as well as a portion of forest land use. OS78 is deeper than most wetlands (~2 meters) with steeper catchment slope compared to the other shallow-basined GIWs in the study. OS80 is an embedded wetland with an oblong shape and subdivided into 3 basins. The constructed berms permit the passage of the pivot irrigation wheels allowing for widespread irrigation of the field. For this study I am assessing OS80 both as a whole system for our agriculture and reference GIW comparisons as well as comparing individual basins to each other to identify homogeneity or heterogeneity among basins. The basins are hydrologically connected through spillage and through culverts constructed in the berm.

3.2.2 Field work:

Surface sediment samples throughout each wetland site to provide a spatial distribution of sediment deposition. Samples were collected using clear polycarbonate core barrels inserted into the wetland using manual percussion, removed, and capped to be transported to the lab. GPS coordinates of core locations were recorded using a handheld Garmin GPS device. Once wetland sediment was retrieved from the site, each core was sectioned into 1-2cm increments up to 8cm in depth to be analyzed as independent samples. The choice to section sediment into small intervals allowed for high resolution essential for observation of systems with low sedimentation rates. Samples were then refrigerated and kept in the dark.

3.2.3 Lab work:
Archive and Loss-On-Ignition

A wet aliquot was removed from each section and used for gravimetric analysis (Heiri et al., 2001). A known volume of sediment was weighed and set in a drying oven set to 50 degrees Celsius. The sediment was reweighed, and bulk density was measured as g dry cm^{-3} wet. Organic matter was calculated as loss-on-ignition where dried sediments were placed in a muffle furnace set to 500 degrees Celsius for 3 hrs. and expressed as a percentage. The remaining wet sediment was freeze-dried and ground using a mortar and pestle.

Elemental analysis

To measure element concentrations, an ICP method was used at Waters Agricultural Lab, Camilla GA. Homogenized ground dry sediment was analyzed for phosphorus and other elements including heavy metals following acid digestion in a heated block and measured using ICP-ARL following standard Environmental Protection Agency methods (US EPA, 2015).

Nutrient analysis
Carbon and nitrogen were measured using a Costech Carbon and Nitrogen elemental combustion system with attached auto sampler to measure inorganic and organic carbon (C) and nitrogen (N) percentages. For organic carbon, samples were acidified for 24 hours in HCl vapors to remove inorganic C. Carbon and Nitrogen stoichiometric relationships were made using methods from Meyers and & Ishiwatari.

Statistical Analysis

To compare differences among reference and agriculture GIWs for nutrients and elemental parameters, Mann-Whitney tests were run to establish statistical significance. Normality was tested using a Shapiro-Wilk normality test proving non-normality. Averages, p-values (<0.05) and confidence intervals are reported. A Principal Component Analysis (PCA) was run in R with missing data removed using the *na.omit()* function. PC1 and PC2 values are reported to establish relationships between measured variables. When comparing subbasins in OS80 (A, B, C), an ANOVA was used to initially establish if significance existed among groups. To determine differences among specific sites, a Tukey's Honest Significance Difference (Tukey's HSD) was used, and p-values were reported.

Geographical Analysis

ESRI ArcMap software was used to do a spatial assessment of measured parameters. Symbology using natural breaks visually represented concentration differences throughout each wetland system.

3.3 Results

3.3.1 Agricultural versus Reference

A Principal Component Analysis (PCA) showed ordinational differences between the two site types using the following variables: organic carbon, total nitrogen, C/N, N/P, P, Fe, Al, K, Mg, Ca, S. PC 1 accounted for 47.7% of the explained variance and PC 2 accounted for 28.4% of the explained variance between the two site types (Figure 15). While most sediment variables ordinated with PC1 and the ag sites, variables TN, OC and N/P ordinated with the reference sites.

Results from statistical comparisons show that agriculture GIWs differ from reference GIWs in most nutrients and sediment measurements. Statistical Mann-Whitney tests results show a significantly higher percent organic matter in the reference site (p=0.003) (Table 4) (Figure 16). Conversely, bulk density was higher in the agriculture site (p-value = 0.0013). Total nitrogen was lower in the agriculture sites (average = 0.289%) compared to the reference sites (average = 0.716%) (p-value = < 0.0001) Phosphorous levels between the agriculture and reference GIWs differed greatly with the phosphorous in the agriculture sites being more than 2 times greater (Agriculture P average =1.13, Reference P average = 0.40) (p-value = p < 0.0001). This trend was reversed for organic carbon with values double in the reference site (average = 9.63) compared to the agriculture site (average = 4.37) (p-value = < 0.0001). The C/N between the two sites was significant (p-value 0.0044), with the agriculture sites having slightly higher C/N (average = 16.61) compared to the reference sites (average = 12.17). The N/P between the two site types was a magnitude different with the reference sites having an average N/P of 44.8 compared to 4.9 N/P in the agriculture sites (p-value = < 0.0001).

Agriculturally associated elements were also elevated in the agriculture GIWs. Iron values in the agriculture sites are a magnitude higher (average = 26.9) compared to the reference sites (average = 2.22) (p-value = p < 0.0001) (figure 17). Aluminum values in the agriculture sites are also more than double (average = 29.8) than in the reference sites (average = 13.4) (p-value = p < 0.0001, 95% CI [-19.7, -13.3]). Potassium was almost double in the Ag sites on average (0.63 mg g-1) than in the reference sites (0.35 mg g-1) (p-value = p < 0.0001). Magnesium values are elevated in the agriculture sites (average = 0.67) compared to their counterpart reference sites (average = 0.39) (p-value p < 0.0001). Calcium values are more than double in the agriculture sites (average = 2.52) than in the reference sites (average = 1.18) (p-value = p < 0.0001). Sulfur values on the contrary are lower in agriculture GIWs with the average being 0.67 compared to the reference counterpart GIWs (average = 0.92) and results do not show significance (p-value=0.027).

3.3.2 Within wetland variability

Site OS80 is broken up into three basins from constructed berms utilized for the passage of the center-pivot irrigation system through the inundated wetland. Using this as a preexisting experimental scenario, I compared the basins to identify homogeneity or heterogeneity of the entire wetland.

Using a one-way ANOVA, percent organic matter showed the most variance among groups (p-value = 0.0049) (Table 5) (Figure 18). A Tukey Honest Significant Differences (Tukey HSD) test identified a difference between OS80 A and B (p-value = 0.0038). Bulk density only differed between OS80 A and C (p-value =0.013). There was no statistical difference between the basins of OS80 for organic carbon. Total nitrogen varied between basins A and B (p-value = 0.015). Phosphorous varied between basins A and B (p-value = 0.042) and basins A and C (p-value = 0.0017). Iron was only different among basins B and C (p-value = 0.024). Aluminum, potassium, magnesium and calcium showed no statistical difference between basins. Sulfur showed significance between basins A and B (p-value = 0.0079) and A and C (p-value = 0.0074).

3.4 Discussion

3.4.1 Comparison of Agriculture and Reference Wetlands

Agriculturally influenced GIWs have elevated nutrients and trace elements compared to their reference counterparts. Phosphorous values are much greater in the Ag GIWs due to chemical applications to adjacent fields (fertilizers); P lacks a gaseous state and complex microbial transformation resulting in long term sequestration once it has entered wetland sediment. I hypothesized that P mineralization from prescribed burning would elevate P values in reference wetlands that are consistently burned on a bi-annual basis (Battle & Golladay, 2003).

However, the P entering from prescribed forest fires was significantly less that P entering the Ag GIW. Subsequent nutrients C and N have the opportunity to degas into the atmosphere while P remains buried showing elevated concentrations; yet reference GIWs show little to no change in concentration downcore and no higher value than Ag GIWs. Carbon:Nitrogen ratios should give indication of source material. Both C/N values for the sites are in the middle ranges representative of a macrophyte dominated system or a combination of algal and terrigenous input. Although there is very little difference between the two sites; C/N in the Ag sites is 4 units higher suggesting crop residue. There was also visible evidence of algae in the water column during time of sampling which would bring a terrigenous ratio of 25 C/N down to the middle range given that macrophytes are not abundant in the system. The mid-range C/N values in the reference wetlands however are a result of primarily macrophyte presence and terrigenous material. The lack of algal presence abides by what is seen in most lake systems where macrophyte dominance and algal dominance are often mutually exclusive (Bachman et al., 2000). The elevated N/P in the reference sites indicates N excess and lower P being stored in the sediments and most likely sourced from natural sources with lower P similar to oligotrophic lakes (Downing & McCauley, 1992). Ag wetlands possessed much lower N/P further suggesting the presence of denitrification in the system (Downing & McCauley, 1992). While it is known that N and P routinely erode from agricultural fields, the dramatic differences in N/P suggest post-delivery biogeochemical transformations most likely associated with denitrification.

Elements associate with agricultural amendments were significantly elevated in the agriculture sites. Trace elements or macronutrients (C, K, P, S) and micronutrients (Fe and Na) are essential to plant growth, however; they are either naturally occurring in the soils or supplemented through anthropogenic chemical application to agricultural fields (He et al., 2005).

Phosphorous and iron, for instance, are commonly applied as fertilizer to crops (He et al., 2005). Although it is undiscernible to identify the source (natural or anthropogenic) of the elements it is interesting to note that the high sedimentation rate (Eggert thesis Chapter 2) in the Ag GIWs compared to the reference GIWs suggests that anthropogenic activity such as soil tillage and irrigation can transport materials (Pierce & Nowak, 1999) both naturally occurring trace elements and anthropogenically applied chemicals into GIWs (He et al., 2005). The trace elements (P, Fe, Al, K, Mg and Ca) (Figure 16) in the Ag GIWs are statistically elevated and, in some cases, double the concentration than in reference GIWs.

Reference GIWs have greater percent organic matter because of the increased terrestrial and macrophyte input from the dense vegetation coverage within the wetland and surrounding terrestrial forest. Furthermore, decay rates in reference wetlands are slowed due to the recalcitrance of the terrestrial organic matter entering the system as supported by higher C/N in the reference sites (Meyers & Ishiwatari, 1993). Agriculture wetlands however lack the sole source of recalcitrant vegetation throughout the open body and possess a mixture of allochthonous material transported from seasonal harvests of crops and autochthonous algae and cyanobacteria generated within. The high rates of sediment transport identified from the sedimentation rate that is two magnitudes higher in the agriculture wetland (C. Eggert thesis, Chapter 2) could also suggest dilution of organic matter from sediment containing high sand components. This is backed by the elevated bulk density in the Ag GIWs showing possibility of higher sand composition compared to organic materials.

An unexpected result of this study was low nitrogen values in the agricultural sites. Previous work on sediment cores also showed low N storage through time when compared to C and P. However, nitrogen additions to fields and N runoff from agricultural activities is well documented (Davidson et. al, 2012) suggesting additional pathways of N flux are occurring. Previous work on agricultural wetland areas suggests these systems have environmental conditions favoring denitrification (Seitzinger et. al, 2006, Racchetti et. al, 2011, Power et al., 2012, Rogers et. al, 2022). The presence of labile organic matter, anoxic conditions and denitrifying bacteria promote denitrification transforming nitrates and nitrites to gaseous N_2 (Poe et al., 2003). Other studies suggest the two pathways of N removal from aquatic systems are burial and denitrification (Finlay et al. 2013). Given the conditions for denitrification and the lack of burial from long sediment core work (C. Eggert thesis Chapter 2), the data show that GIWs could be extreme hotspots for N removal in agricultural settings. However, a unique feature of this system is the access to groundwater irrigation capable of keeping most GIWs inundated longer than naturally irrigated systems. Furthermore, N could be leaching from the system to the groundwater (Beck et al., 1991, Hubbard & Sheridan, 1989) further reducing N concentrations concentrated in agriculture GIWs. Regardless, the magnitude of denitrification should be the focus of future studies on GIWs especially given the findings of Barton et. al, 1999

3.4.2 Impacts of Bermed Wetlands

Due to the pivot irrigation systems frequently used in areas with adequate groundwater, many of the GIWs encountered for this research contained berms within the wetland system to allow for the pivot wheels to travel on solid ground through the wetland. For this study, wetland OS80 is subdivided into 3 sections because of the construction of berms and was further analyzed to discern any differences in nutrient and elemental concentration between subbasins. Although no encompassing conclusions can be made about the entire bermed site, there were some differences among basins for various parameters. It was believed that the basin closest to the center of the field (OS 80 C) would contain elevated concentrations of nutrients due to proximity and percent Ag land cover while the basin closest to the forest (OS80 A) would more closely resemble characteristics of reference GIWs. However, statistical analysis showed very few statistical differences apparent between sites. One difference that was identified was elevated iron concentrations in OS80C possibly explained by higher sediment loading in the basin closest in proximity to the center of the field. Iron is both present geologically and anthropogenically and can be transported with sand which is potentially elevated in the same basin from the BD measurements (Baranoski et al., 2014). Phosphorous on the contrary was elevated in the furthest basin (OS80A) that had fringing forest land cover suggesting that P; which is likely originated from agricultural amendments, travels easiest throughout basins and remains elevated in the outermost basin. While I anticipated differences among basins, it appears that material exchange is occurring among the three subbasins. There are constructed culverts installed with each berm to allow for hydrologic transport and to limit erosional destruction of the berms. These constructed pathways allow for the mixing of water and sediment throughout the three basins. Despite limited connectivity among subbasins, the bermed wetland is still functioning as a whole system. Given that many landowners encounter this problem of wetlands inhibiting passage of their pivot systems throughout wetlands, it is of benefit to know that the physical amendments made to their systems are no more deleterious than typical agriculture practices in terms of spatial sediment distribution.

3.5 Conclusion

Land cover and land use influences GIW composition by altering source materials entering and being stored in the sediment. Agriculture influenced GIWs vary in biogeochemical composition compared to reference forested wetlands. Phosphorous concentrations were more than double in agriculture sites as a result of application of fertilizers to fields, but N values were higher in the reference wetland suggesting high amounts of denitrification in the Ag GIW. Elemental concentrations (Fe, Al, K, Mg, and Ca) were also all elevated in the agriculture sites indicative of anthropogenic application of chemicals and altered sedimentation rate creating a mechanism of elevated erosion to transport naturally and anthropogenically occurring elements into GIWs. In the case of OS80, no apparent heterogeneity was observed suggesting hydrologic connectivity despite constructed berms. Agriculturally influenced GIWs differ in biogeochemical composition compared to reference forested sites and gives implication for the many GIWs in the region coupled with the intensive agriculture of the southeastern USA.

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Tables

Table 1: Forested-Reference Sites and Agriculture sites including Type, Location in landscape, Coordinates (DMS), Wetland Area (hectares) and Watershed area (hectares). *Adjacent means that the dominant land cover is the wetland type with the agriculture wetlands having predominantly agriculture land use with some surrounding forested land cover.

Site	Wetland Type	Wetland Location	Coordinates (DMS)	Wetland Area (ha)	Watershed (ha)
W53	Reference	Embedded	31.271169, -84.496386	3.17	14.34
W37	Reference	Embedded	31.26358, -84.535914	0.89	4.97
OS78	Agriculture	Adjacent*	31.230233, -84.362067	4.22	40.20
OS79	Agriculture	Embedded	31.235840, -84.427451	0.54	11.81
OS80 A, B, C	Agriculture	Adjacent* - Bermed	31.239083, -84.431635	1.54	16.31

Table 2: Reference wetland W53 and agriculture wetland OS79 cumulative storage in the datable history (125 and 136 years respectively) showing nutrients C, N and P in units Kg, Tons, and lbs. to appeal to various stakeholders.

Wetland Cumulative Storage (for ^{210}Pb datable years)								
Agriculture Wetland OS79 (0.5 ha)		Kilograms	Tons	Pounds	Reference Wetland W53 (3.17 ha)	Kilograms	Tons	Pounds
	Carbon	24719	25	54447		9135	10	20139
	Nitrogen	1406	1	3097		606	0.67	1337
	Phosphorous	13319	13	29337		159	0.175	350

Table 3: Monetary values of ecosystem services agriculture wetlands provide through nutrient storage of C, N and P in US$ (2019).

Agriculture Wetland OS79 Monetary Value of Ecosystem Service Nutrient Storage			
Nutrient	Tons per wetland (136 yr history)	Societal Cost 2019 (US$ per metric ton)	Monetary Value (US$)
Carbon	25	114	2850
Nitrogen	1	2620	2620
Phosphorus	13	3117	40521
		Total Value (US$)	**45991**

Table 4: Mann-Whitney test results of reference GIW and agriculture GIW comparison for each nutrient and elemental parameter. Non-significant p-values highlighted in red text, p-values recorded with a threshold of 0.05 for significance.

Mann-Whitney Comparison Tests	
Parameter	**P-value**
LOI	0.00307
BD	0.001272
TN	< 0.0001
OC	< 0.0001
C/N	0.004353
N/P	< 0.0001
P	< 0.0001
Fe	< 0.0001
Al	< 0.0001
K	< 0.0001
Ca	< 0.0001
Mg	< 0.0001
S	0.02715

Table 5: Statistical comparison tests (ANOVA and Tukey HSD) of OS80 A, B, C identifying differences among subbasins of the berm wetland for each measured parameter. Insignificant p-values are highlighted in red text, upper and lower limits and p-values are reported for the Tukey HSD test.

OS80 A, B, C Nutrient and Elemental Comparison Statistics						
Parameter	**ANOVA**	Tukey HSD				
	P-value	Sites	lwr	upr	p	adj
LOI	0.00488	A-B	-3.2	-5.4	-1.1	0.0038
		A-C	-1.5	-3.7	0.62	0.19
		B-C	1.7	-0.28	3.6	0.10
BD	0.0166	A-B	0.092	-0.052	0.23	0.25
		A-C	0.18	0.038	0.32	0.013
		B-C	0.089	-0.042	0.22	0.21
OC	0.177	A-B	-0.20	-1.2	0.83	0.87
		A-C	-0.73	-1.7	0.30	0.19
		B-C	-0.53	-1.5	0.40	0.33
TN	0.0161	A-B	-0.080	-0.14	-0.015	0.015
		A-C	-0.062	-0.13	0.0022	0.059
		B-C	0.017	-0.04	0.08	0.73
P	0.0024	A-B	-0.15	-0.30	-0.0049	0.042
		A-C	-0.24	-0.39	-0.094	0.0017
		B-C	-0.09	-0.22	0.045	0.23
Fe	0.0241	A-B	-0.83	-4.8	3.2	0.86
		A-C	3.3	-0.67	7.4	0.11
		B-C	4.2	0.52	7.8	0.024
Al	0.616	A-B	0.19	-2.7	3.1	0.98
		A-C	1.0	-1.9	3.9	0.65
		B-C	0.82	-1.8	3.5	0.71
K	0.979	A-B	0.0040	-0.062	0.070	0.99
		A-C	0.0051	-0.061	0.071	0.98
		B-C	0.0010	-0.059	0.061	1.0
Mg	0.0551	A-B	-0.048	-0.11	0.012	0.13
		A-C	-0.060	-0.12	0.00072	0.053
		B-C	-0.012	-0.067	0.044	0.85
Ca	0.344	A-B	-0.39	-1.08	0.29	0.32

		A-C	-0.29	-0.97	0.40	0.54
		B-C	0.11	-0.51	0.73	0.89
S	0.00435	A-B	-0.28	-0.49	-0.074	0.0079
		A-C	-0.28	-0.49	-0.076	0.0075
		B-C	-0.0023	-0.19	0.19	1.0

Figures

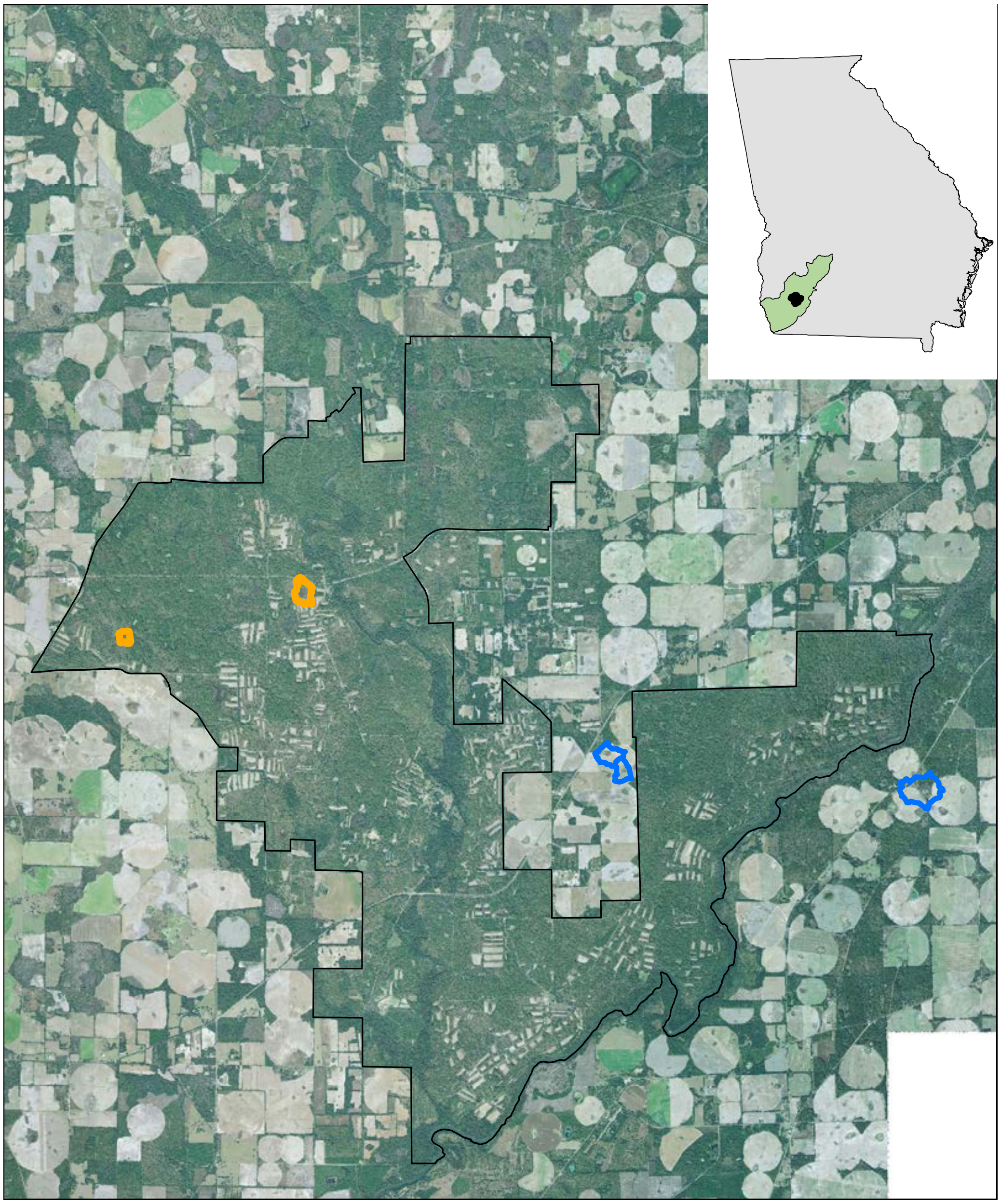


Figure 1: Site map of sample sites with orange representing reference wetlands and blue representing agriculture wetlands. State of Georgia, the Dougherty Plain and the Jones Center of Ichauway identified in inset.

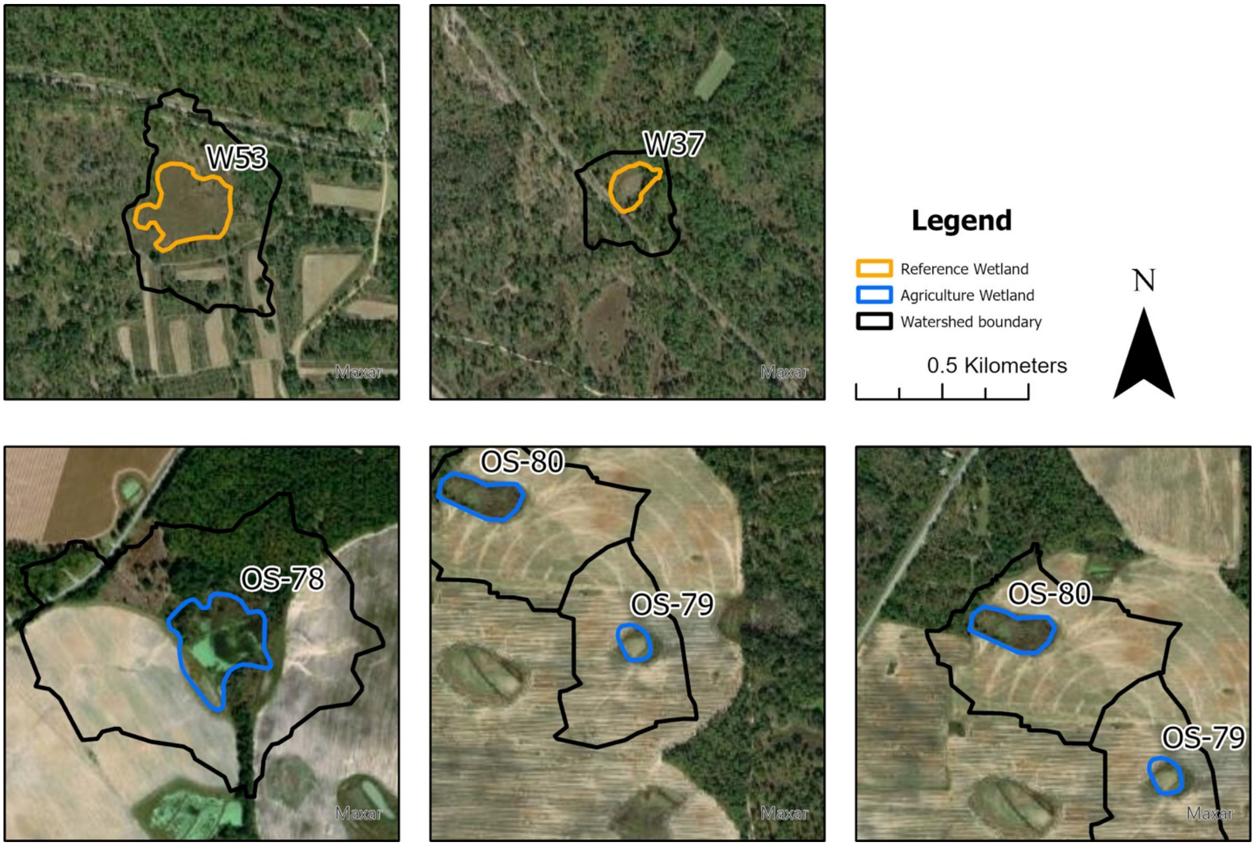


Figure 2: Site specific reference and agriculture wetlands with watershed boundaries. W53 is 3.17 ha, W37 is 0.89, OS78 is 4.22 ha, OS79 is 0.54 ha and OS80 is 1.54ha in size.

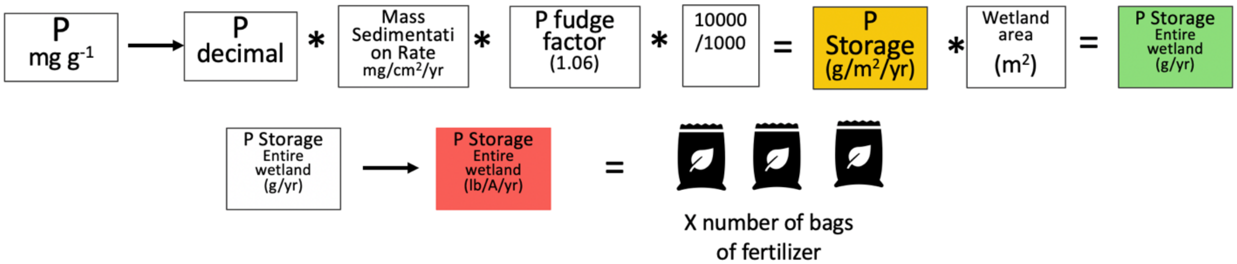


Figure 3: Calculation for nutrient storage per wetland area with sediment focusing factor and appropriate unit conversions. Sediment focusing factor is calculated as the ratio of unsupported ^{210}Pb flux measured at the core site to the measured atmospheric fallout for the region to account for regional differences in atmospheric ^{210}Pb fallout. Calculation was replicated for nitrogen and carbon.

Figure 4: Reference Wetland W53 Core that is 50cm in length collected September 2020.

Figure 5: Sediment core from Agriculture Wetland OS79. Total length of core is 61cm with the bottom 10cm appearing darker and richer in organic matter. Collected February 2021.

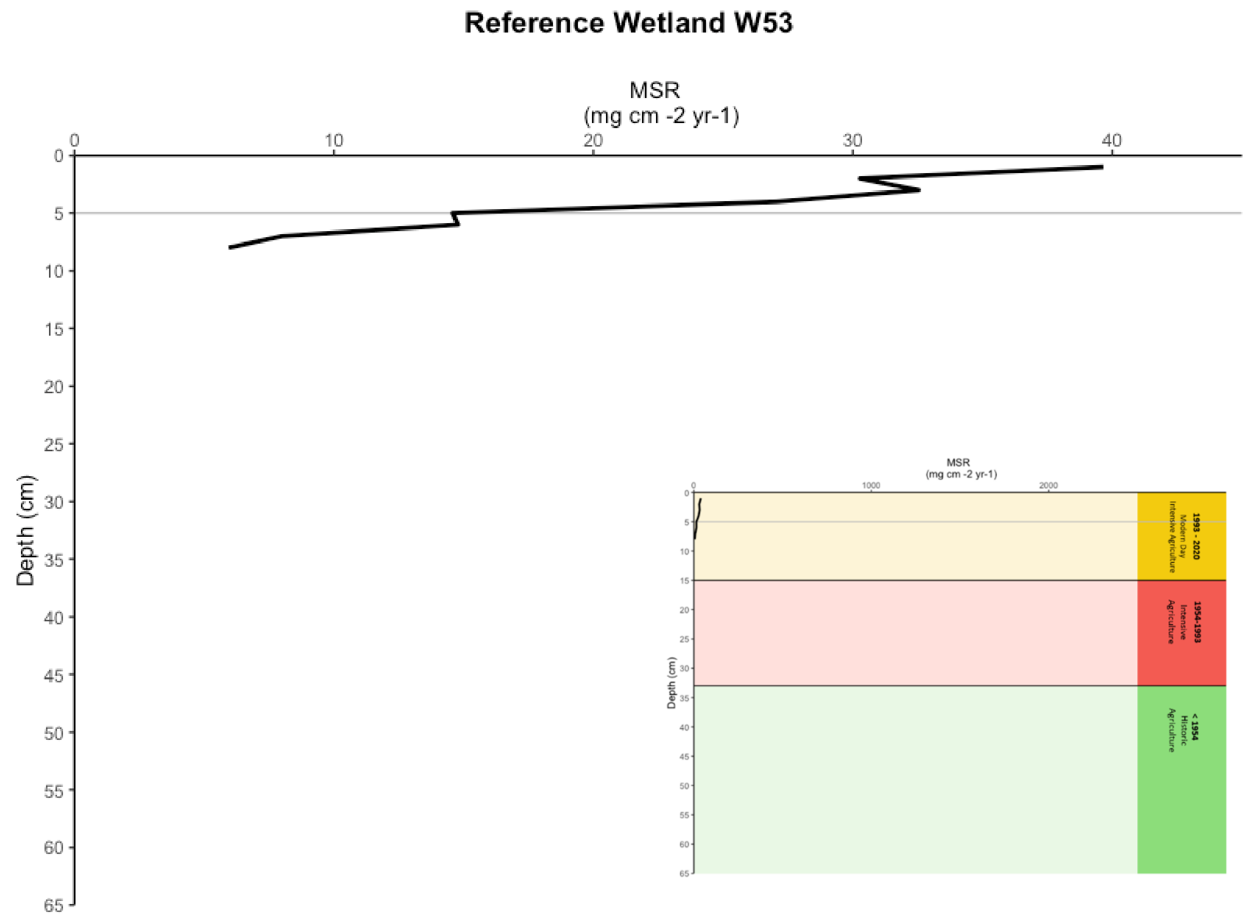


Figure 6: Mass Sedimentation Rate of reference wetland W53 with grey bar indicating 5cm. Inset shows MSR of W53 according to scale of MSR of OS79.

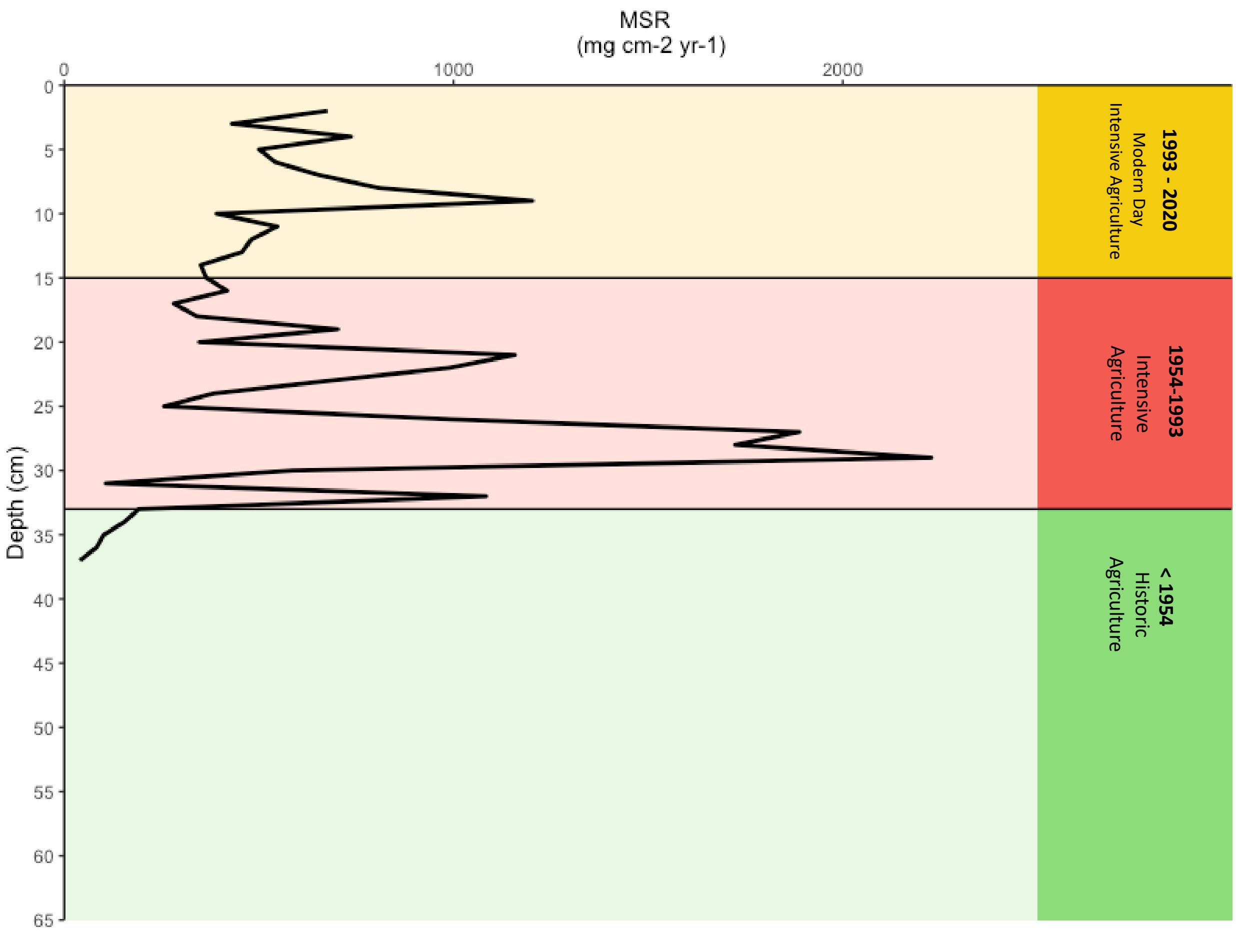


Figure 7: Mass Sedimentation Rate (MSR) in mg cm-2 yr-1 per depth in cm for agriculture wetland OS79 using radiometric dating via ^{210}Pb.

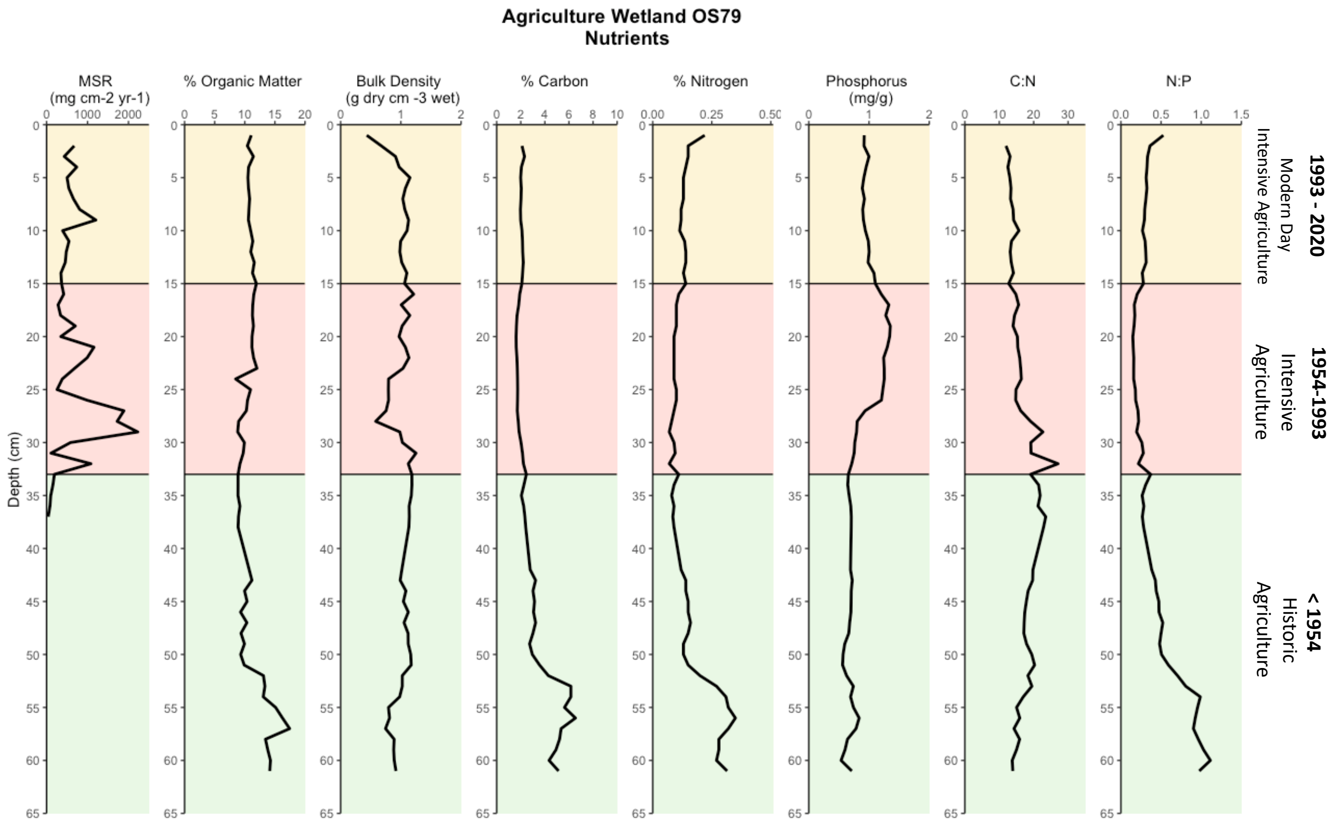


Figure 8: Nutrient concentrations of agriculture wetland OS79 for each historical era.

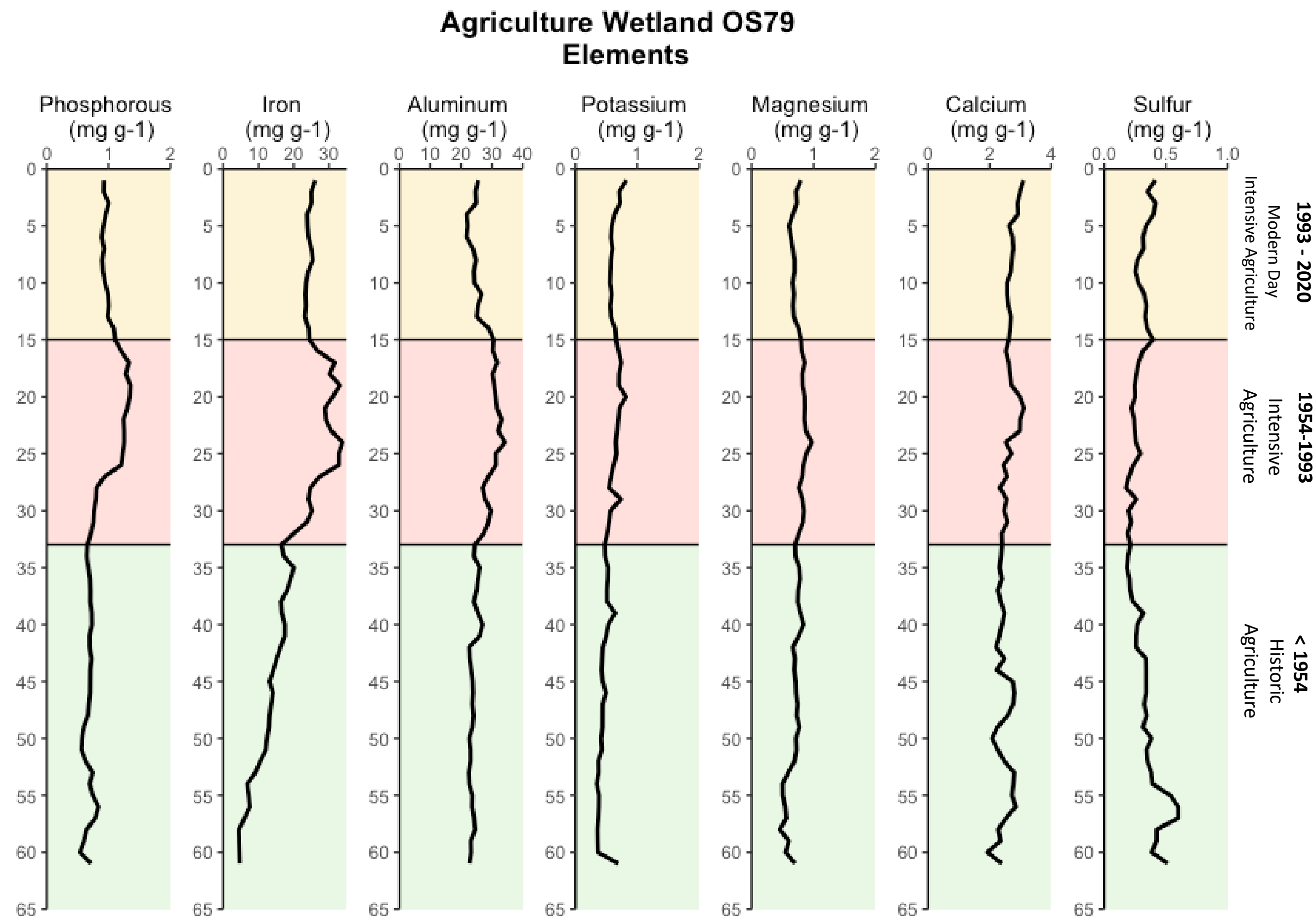


Figure 9: Elemental concentrations of agriculture wetland OS79 for each historical era.

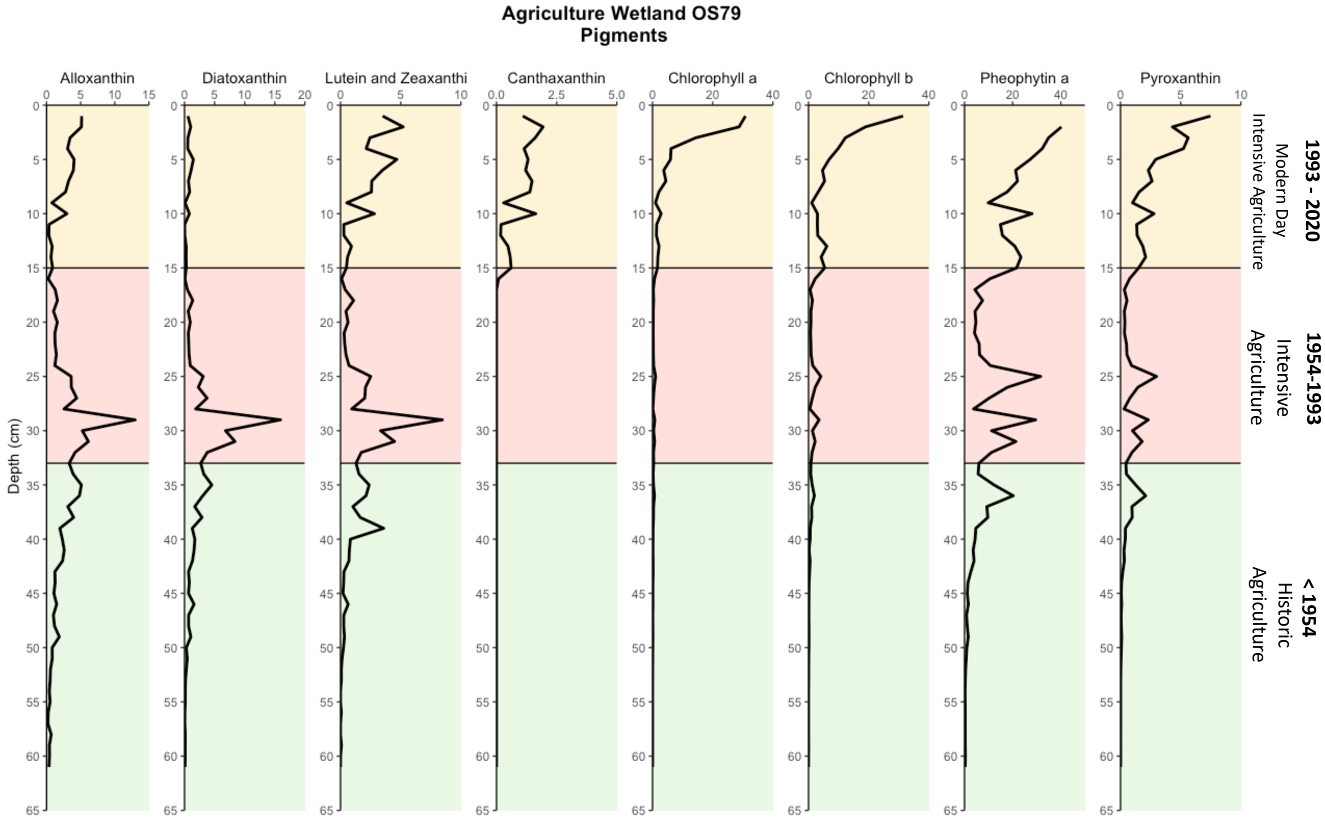


Figure 10: Photosynthetic pigments of agriculture wetland OS79 for each historical era.

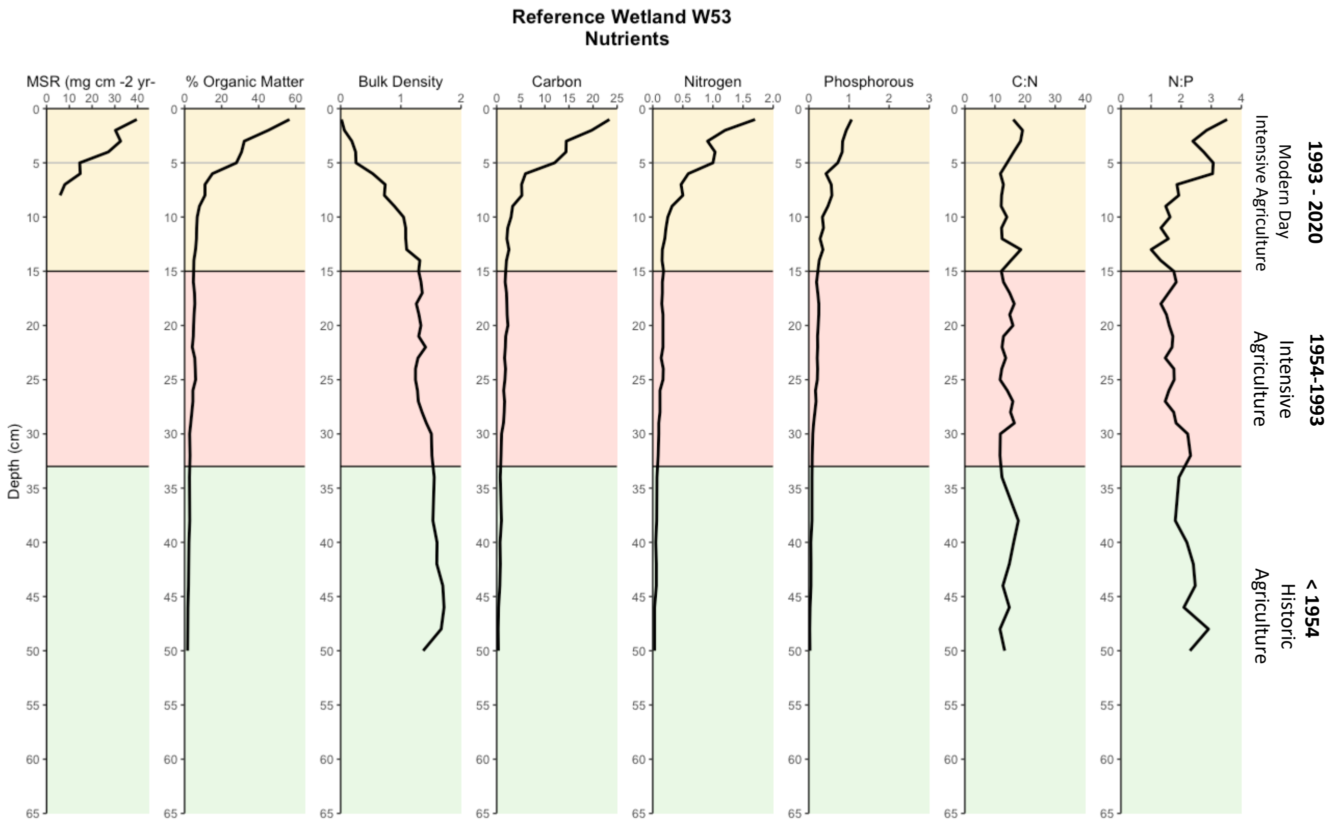


Figure 11: Nutrient concentrations of reference wetland W53.

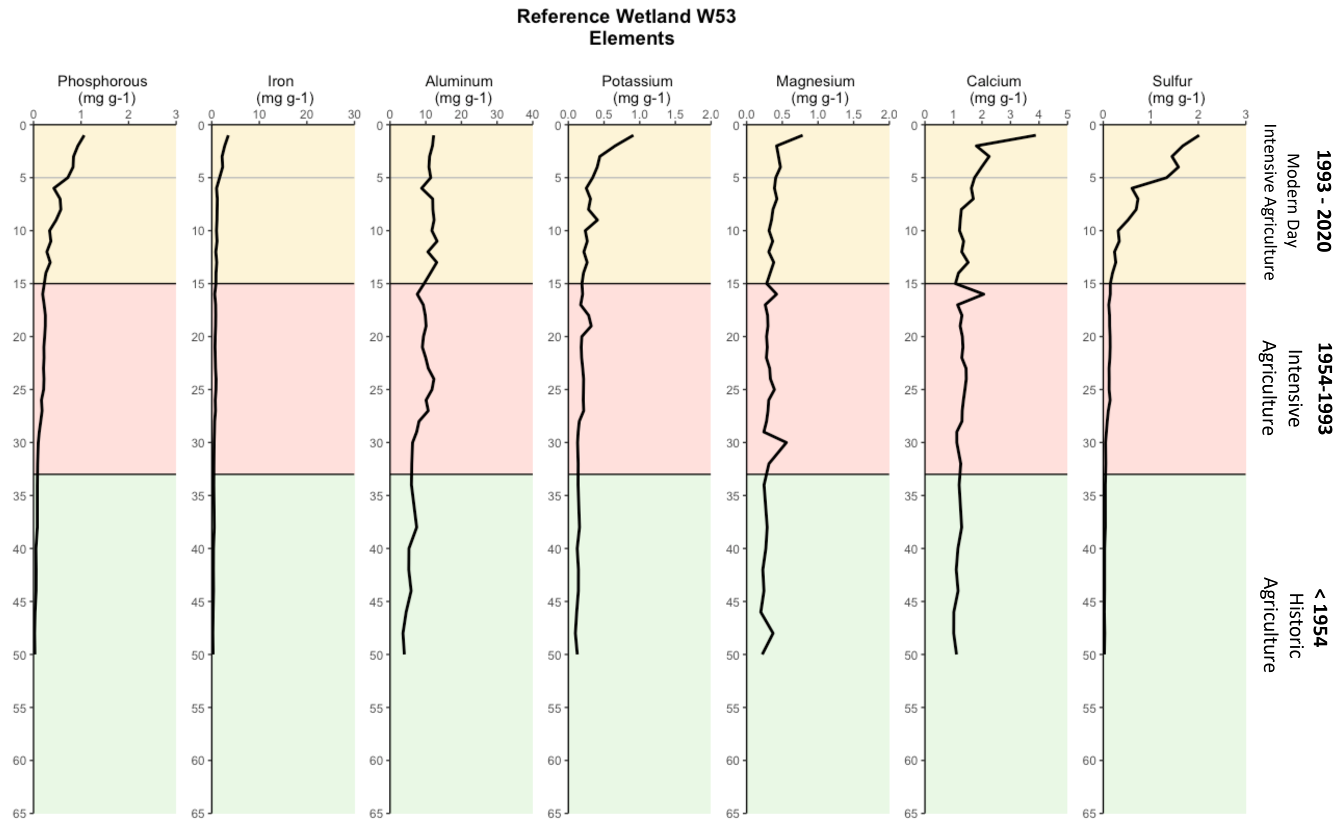


Figure 12: Elemental concentrations of reference wetland W53.

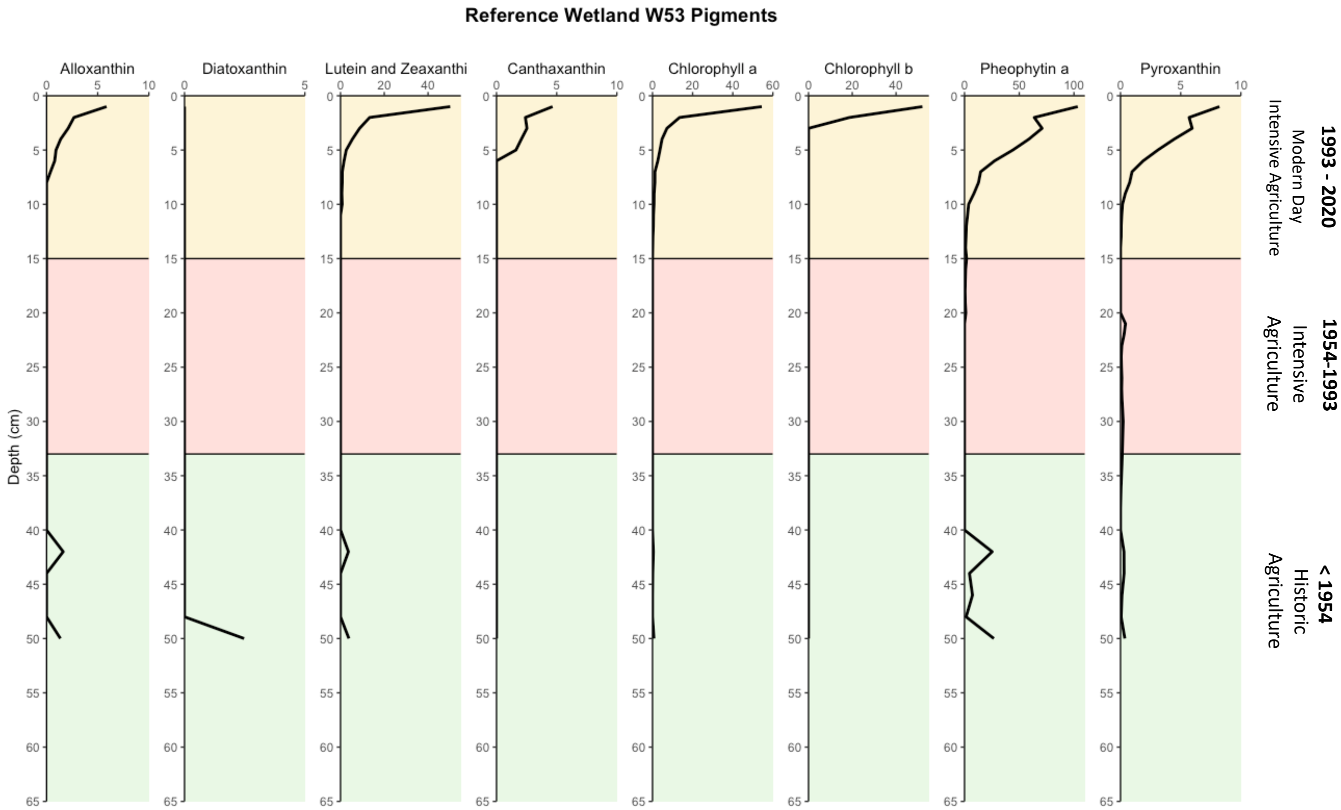


Figure 13: Photosynthetic pigment concentration of reference wetland W53.

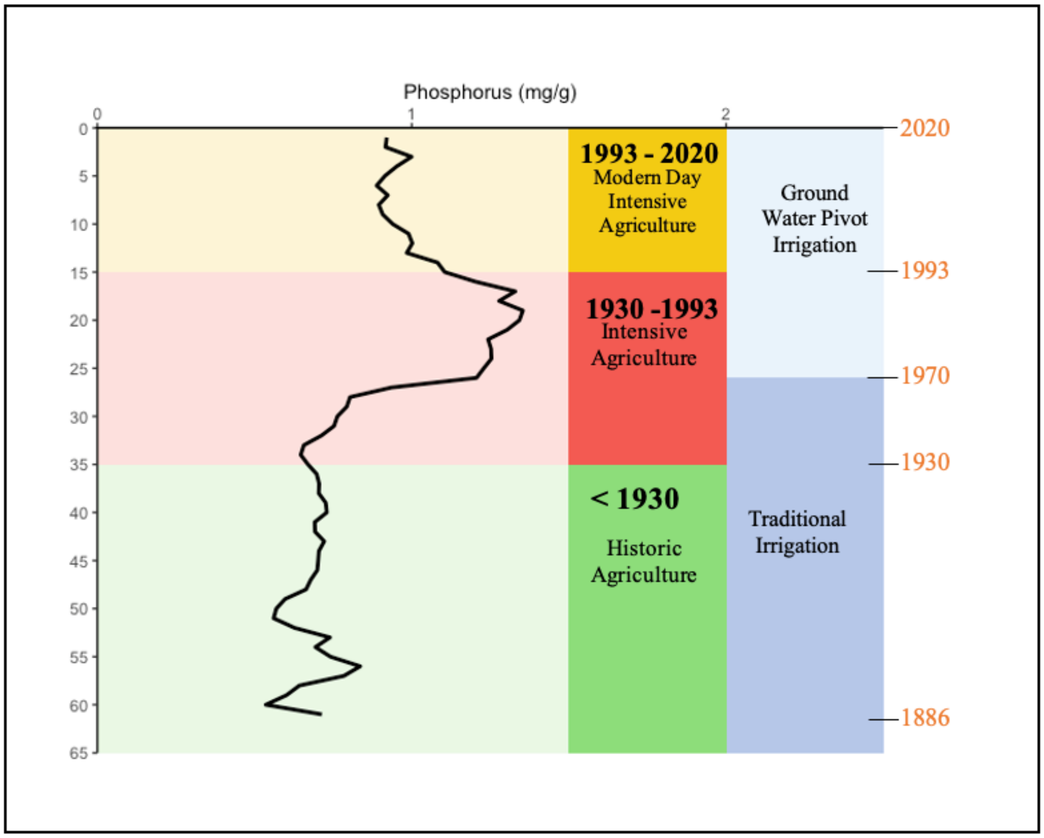


Figure 14: Detailed Phosphorous profile of agriculture wetland OS79 indicating historical eras, timeline of irrigation changes and key dates in orange.

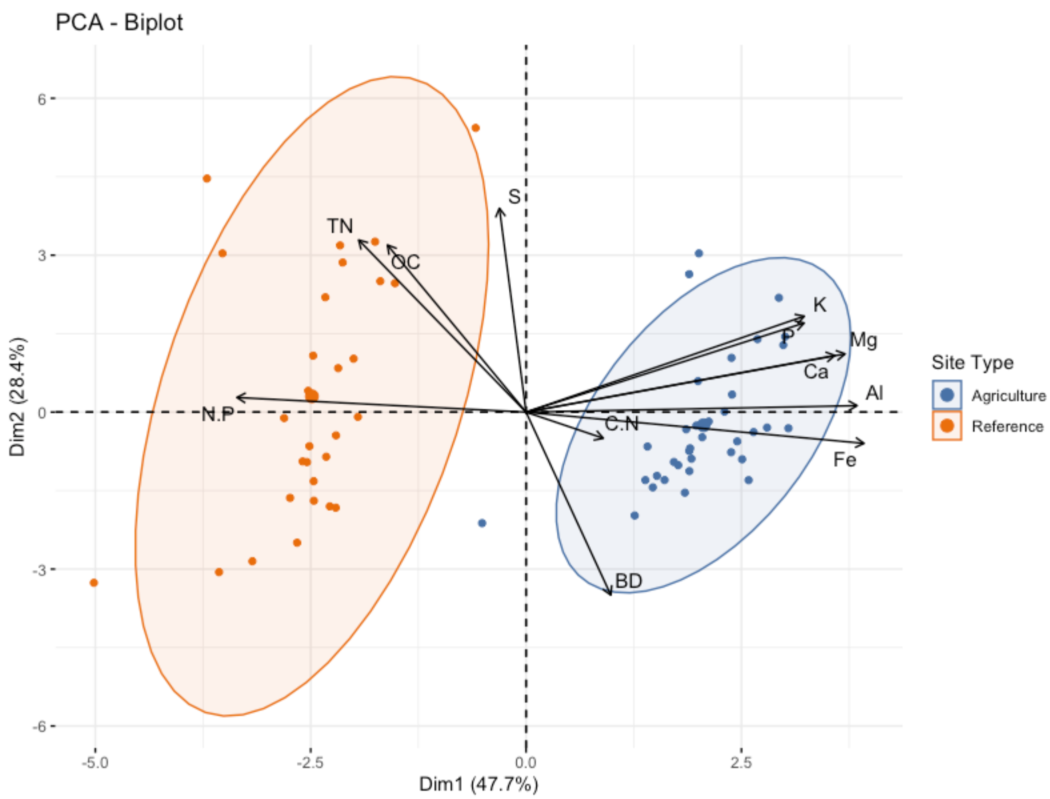


Figure 15: Principal Component Analysis of measured parameters between agriculture and reference sites. Dim1 identifies PC1 and explains 47.7% of the variance between sites while Dim2 identifies PC2 and explains 28.4% of the variance among the site types.

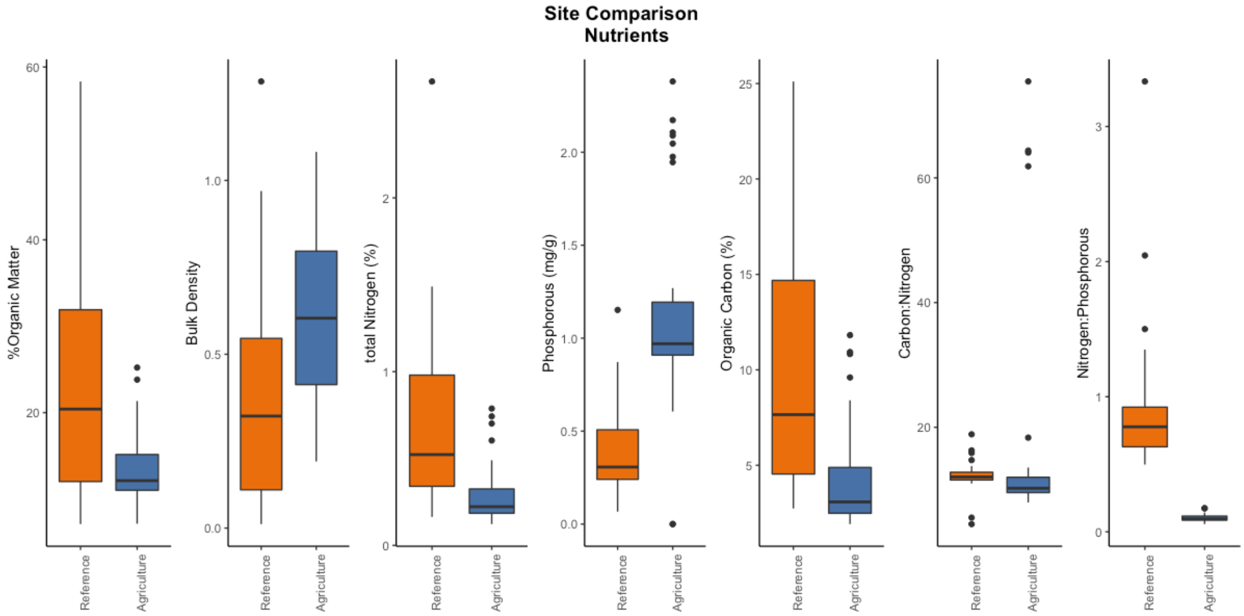


Figure 16: Boxplots of reference and agriculture nutrient concentrations to identify differences among site types.

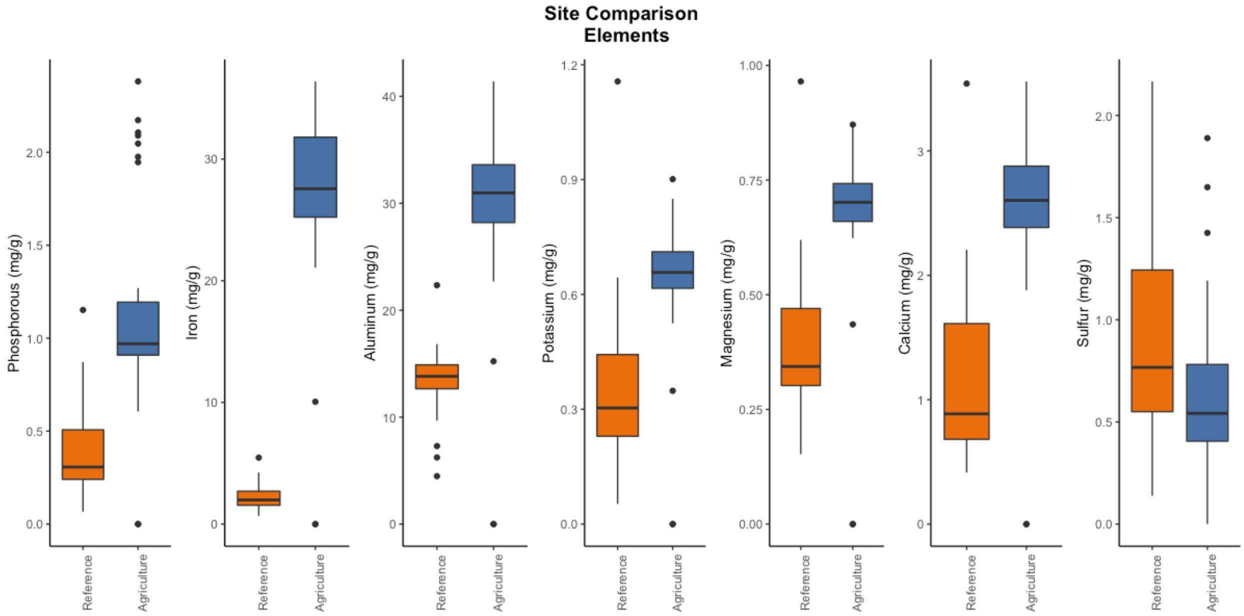


Figure 17: Boxplots of reference and agriculture elemental concentrations to identify differences among site types.

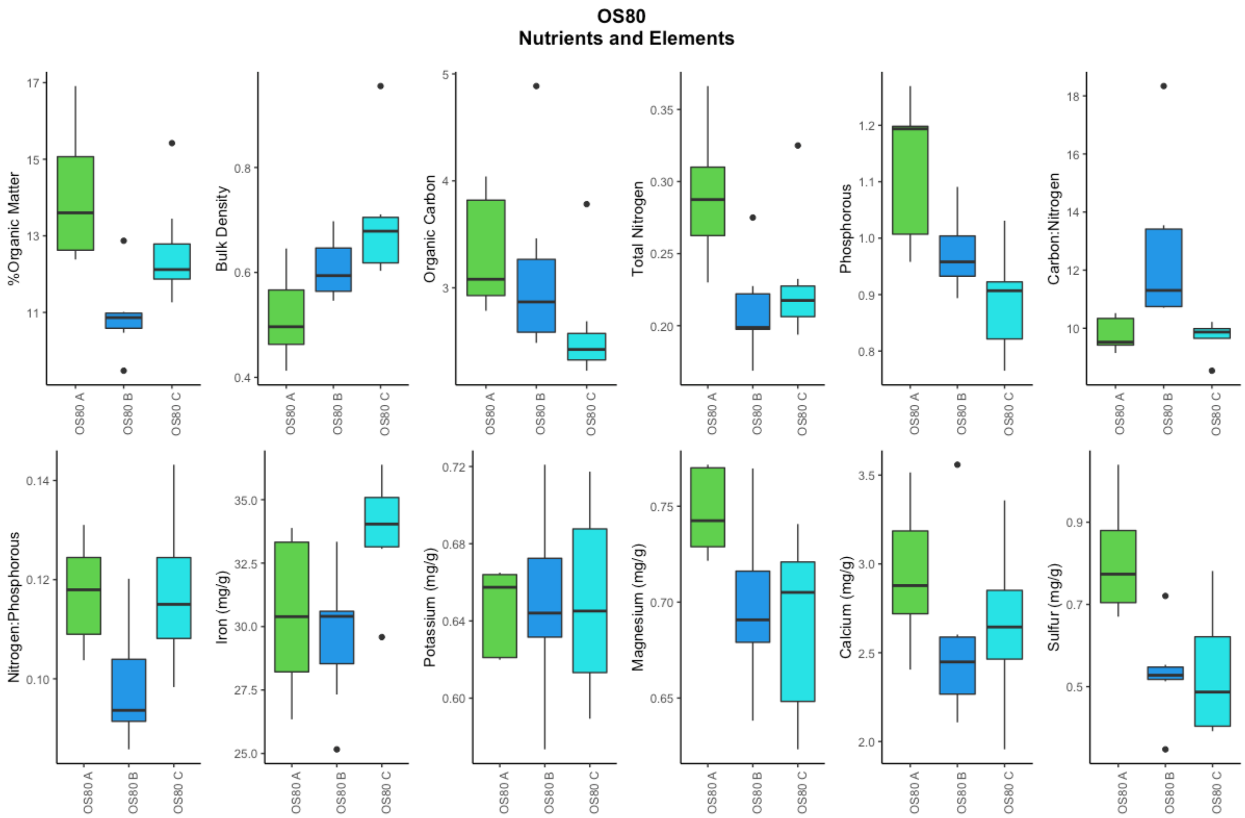


Figure 18: Boxplots of OS80 and subbasins A (closest to forest) B (middle), and C (closest to the center of the agriculture field) to identify nutrient and elemental differences among basins.

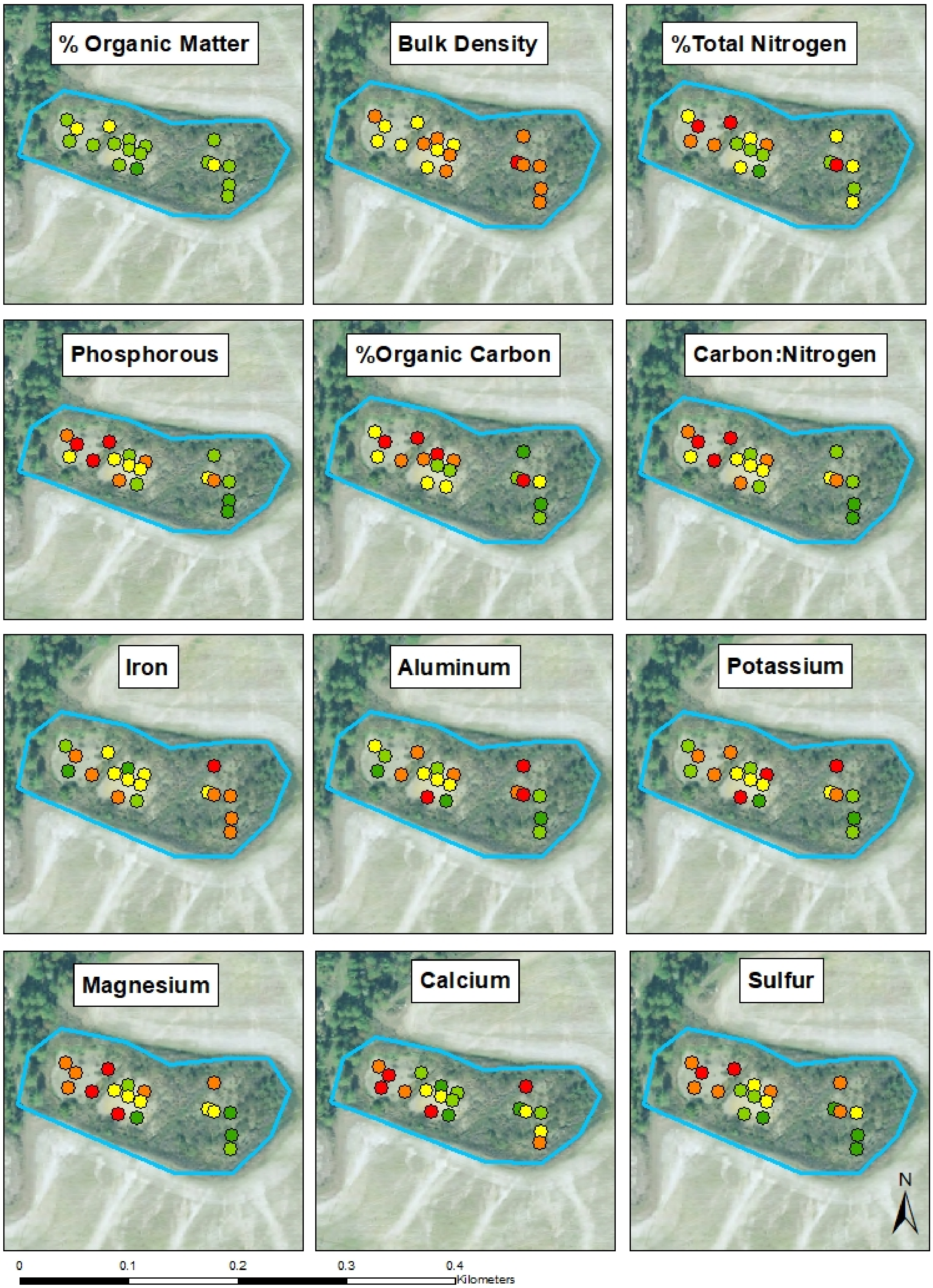
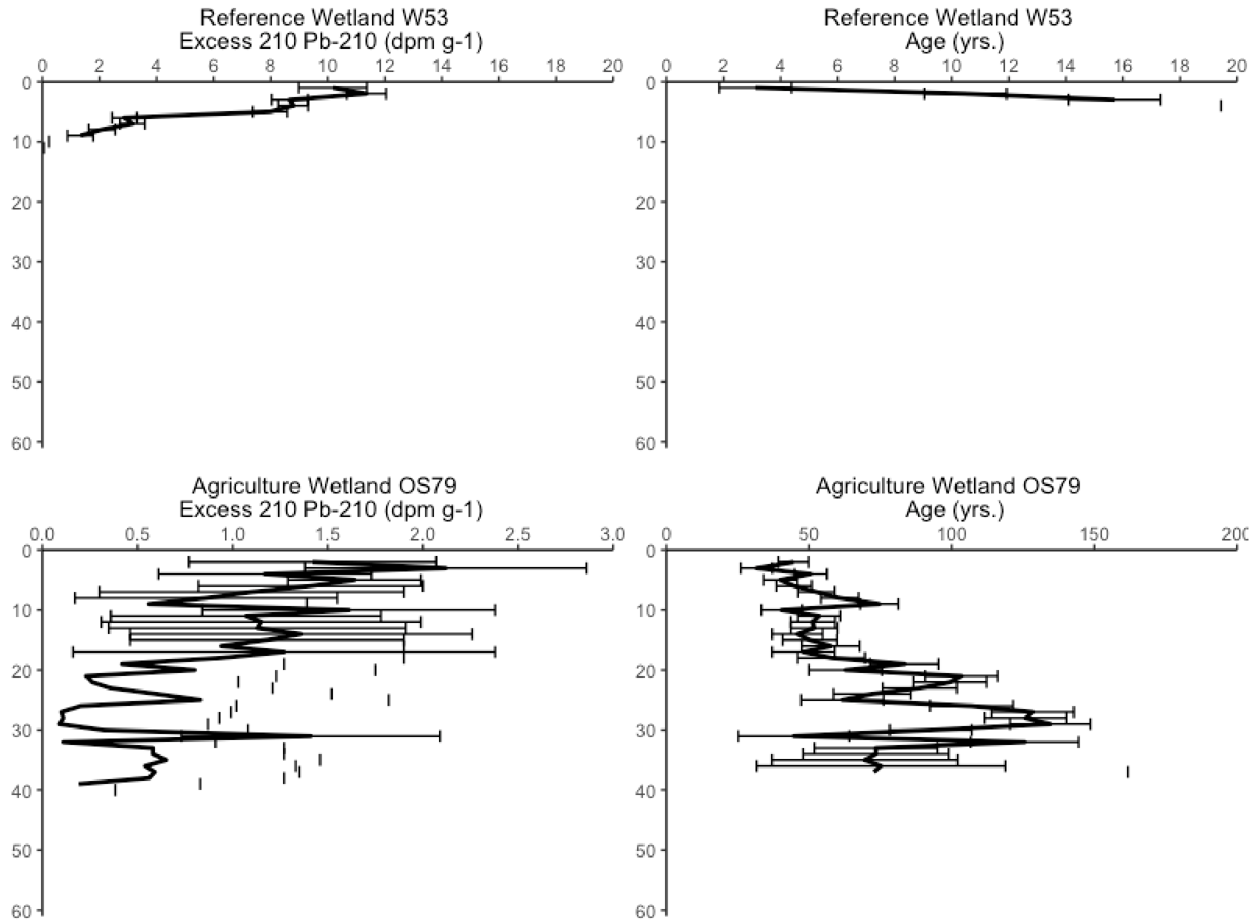


Figure 19: Heat maps of OS80 A, B, C basins for each nutrient and elemental parameter.



Appendix A: Reference Wetland W53 (top) Excess ^{210}Pb in dpm g^{-1} with error bars (left) and Age in years with error bars. Agriculture wetland OS79 Excess ^{210}Pb in dpm g^{-1} with error bars (left) and Age in years with error bars

Appendix B: Sedimentation rate (MSR) of agriculture wetland OS79 versus dates with top 10 drought years indicated in red with lowest annual precipitation and top 10 years with highest annual precipitation highlighted in in blue.