

LONG TERM ACCRETION OF PHOSPHORUS IN WETLANDS: THE EVERGLADES
STORMWATER TREATMENT AREAS AS A CASE EXAMPLE

By

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To my parents, Suresh and Santosh Bhomia

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LIST OF ABBREVIATIONS

ADW	Agricultural Drainage Water
AFDW	Ash Free Dry Weight
Al	Aluminum
BD	Bulk Density
BMP	Best Management Practices
C	Carbon
Ca	Calcium
CAB	Cellulose Acetyl Butyrate
CPT	Change-point Technique
EAA	Everglades Agricultural Area
EAV	Emergent Aquatic Vegetation
ECP	Everglades Construction Project
ENRP	Everglades Nutrient Removal Project
EPA	Everglades Protection Area
FAV	Floating Aquatic Vegetation
Fe	Iron
FEFA	Florida Everglades Forever Act
FL	Florida
FCS	Floc Carbon Storage
FNS	Floc Nitrogen Storage
FPS	Floc Phosphorus Storage
FWMC	Flow-Weighted Mean Concentrations
FWS	Free Water Surface
HCl	Hydrochloric Acid

HSSF	Horizontal Subsurface Flow
LOI	Loss on Ignition
Mg	Magnesium
N	Nitrogen
NaOH	Sodium Hydroxide
NMR	Neutron Magnetic Resonance
NPDES	National Pollution Discharge Elimination System
NPP	Net Primary Productivity
P	Phosphorus
PS	Phosphorus Storage
PAR	Phosphorus Accretion Rate
POR	Period of Record
RAS	Recently Accreted Soils
REE	Rare Earth Elements
RPM	Revolution per Minute
SAR	Soil Accretion Rate
SAV	Submerged Aquatic Vegetation
SD	Standard Deviation
SET	Sediment Elevation Table
SFER	South Florida Environment Report
SFWMD	South Florida Water Management District
SCS	Soil Carbon Storage
SNS	Soil Nitrogen Storage
SPS	Soil Phosphorus Storage
SRP	Soluble Reactive Phosphorus

STA	Stormwater Treatment Area
TC	Total Carbon
TN	Total Nitrogen
TP	Total Phosphorus
USACE	United States Army Corps of Engineers
USEPA	United States Environmental Protection Agency
VF	Vertical Flow
WCA	Water Conservation Areas
XANES	X-ray Absorption Near Edge Structure

Abstract of Dissertation Presented to the Graduate School
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The presence of excess nutrients in an environment can negatively affect the ecological integrity of natural systems and lead to loss of ecosystem functions. Aquatic ecosystems experience impairment of natural structure and functions due to high nutrient inputs. Constructed treatment wetlands are often utilized to transform, modify or store excess nutrients and protect downstream ecosystems. This study was conducted to enhance our understanding of select biogeochemical processes that control treatment performance, efficiency and long-term sustainability of such constructed wetlands. Large constructed wetlands in south Florida, the Everglades Stormwater Treatment Areas (STAs), were selected as the experimental sites for this research. These STAs were built to treat surface runoff originating in the Everglades Agricultural Area (EAA) by removing excess phosphorus (P) from the water before it flows into the Everglades.

The overarching goal of this dissertation research was to understand key processes that control and regulate transformation of P from the reactive (potentially bio-available) fraction into the non-reactive (stable) fractions. Associated pathways for this transformation were also investigated to determine treatment wetlands (STAs)

capability to provide long-term sustainable storage of the sequestered P. This task was carried out by analyzing long-term soil P data obtained from various STAs and conducting experiments to quantify and characterize soil P storage pools and functional chemical P forms within the STAs that have been in operation for 10-16 years.

Spatio-temporal variation in floc, recently accreted soil (RAS) and pre-STA (antecedent) soil P storage pools was calculated by utilizing existing information from soils monitoring. Stratigraphic properties of soil profiles were utilized to determine the boundary between RAS and pre-STA soil, which were then used to calculate accretion rates in the STAs. An inverse relationship was found between accretion rates and operational age of the STAs, suggesting that the rate of new soil formation decreased over time. Using soil P pools, and P retained from the water column, P mass balances for the STAs were developed. Phosphorus mass balance calculations indicated that a large portion of P in RAS sections was probably mined from deeper soil sections.

The quality and quantity of sequestered P has profound implications for the interaction and fate of P in the STAs, hence chemical characterization of accreted P was done by using operationally defined P fractionation schemes. Effects of STA age and dominant vegetation on chemical partitioning of accreted P were investigated. Fractionation analysis showed that about 70% of P in the RAS section was in reactive form, i.e., potentially vulnerable to mobilization. The relative proportion of reactive and non-reactive P pools within emergent and submerged aquatic vegetation cells were similar across the studied STAs. Greater proportions of reactive P pools were observed in floc and RAS sections of SAV cells in comparison to EAV cells. In other words, floc and RAS sections of SAV cells contain larger proportion of reactive P than in floc and

RAS of EAV cells. Strong positive correlation between TP and calcium (Ca) in floc and RAS layers suggested Ca-P co-precipitation as the dominant mechanism of P removal in SAV cells. Among reactive P pools, the P_i pool was higher in SAV cells while P_o pool was greater in EAV cells.

Long-term effectiveness and sustainability of treatment wetlands is important to meet treatment targets and protect downstream targets. This dissertation research was designed to advance our understanding of the extent and quality of P pools in treatment wetlands to allow for better planning and management under conditions of environmental uncertainty.

CHAPTER 1 INTRODUCTION

Wetlands are dynamic ecosystems characterized by unique hydrology, soils, vegetation and high net primary productivity (NPP) (Keefe, 1972; Westlake, 1963). As a transitional ecotones between terrestrial and aquatic ecosystems, wetlands fulfill a vital role in the landscape continuum (Sheaves, 2009). These productive ecosystems are a source of many direct and indirect benefits (Blackwell and Pilgrim, 2011; Costanza and others, 1997) and more recently wetlands have been a major catalyst in transforming modern society's perspective on the value of ecosystem services offered by other natural ecosystems (Maltby and Acreman, 2011).

As natural systems, wetlands are increasingly considered valuable capital assets¹ (Barbier, 2011; Daily and others, 2000) that provide important services including water quality improvement (Gilliam, 1994; Kadlec and others, 1979; Moshiri, 1993; Van der Valk and Jolly, 1992; Verhoeven and others, 2006), flood abatement (Potter, 1994), ground water discharge-recharge (Acharya, 2000), biodiversity enhancement (Erwin, 1990; Mitsch and others, 2009), and a variety of recreational (Bergstrom and others, 1990) and educational opportunities (Sukhontapatipak and Srikosamatara, 2012). These services are a net outcome of several biophysical processes that take place within a wetland. These complex processes are often bundled together in a single term, 'wetland functions', which is used frequently in discussions pertaining to valuation of nature (De Groot, 1992). The ability of natural wetlands to improve water quality is one such function that depends on existing biogeochemical and physical conditions uniquely present in a wetland environment. Recognition of a wetland's potential to treat polluted

¹ Asset can be defined as an economic resource that can produce a flow of beneficial goods and services over time.

waters resulted in efforts to create artificial wetlands for abating unwanted contaminants in water. Early research in this direction began in 1952 when Dr. Käthe Seidel, Max Planck Institute, started experimenting with macrophytes to treat wastewater (Bastian and Hammer, 1993). Currently thousands of functioning constructed wetlands are located globally across multiple geographic regions in both developed and developing nations.

Treatment Wetlands

Constructed wetlands are used for reduction of nutrient loads in surface runoff to protect downstream ecosystems. Impacts from excess nutrient availability are known to degrade the natural balance of aquatic ecosystems (Belanger and others, 1989; Smith, 2003; Verhoeven and others, 2006), hence constructed wetlands are specifically designed and strategically positioned on the landscape to transform and assimilate excess nutrients by utilizing natural biogeochemical processes (Brix, 1993; Solano and others, 2004; USEPA, 2000; Vymazal, 2005). Given their ability to ‘treat’ water, constructed wetlands specifically created for water quality enhancement purposes are referred to as ‘treatment wetlands’.

Constructed treatment wetlands are usually managed to function as buffers to retain or transform excess nutrients and harmful contaminants (Kadlec and Wallace, 2009; Shutes, 2001). Surface waters that do not meet water quality standards because of point or nonpoint sources of pollution can be treated by these wetlands (Babatunde and others, 2008; Day and others, 2004). In the past two decades, treatment wetlands have gained considerable popularity as an effective, low-cost alternative to conventional wastewater treatment approaches (Table A-1, Appendix A). Treatment wetlands are mechanically simple, require low energy inputs, and generally have low operational and

management costs except where cost of land is high since treatment wetlands are often land intensive (Iovanna and others, 2008). Additionally, treatment wetlands can be designed across a broad realm of operational scales ranging in size from smaller units capable of treating wastewaters from only a few households to large systems covering many hectares and treating high volumes of agricultural or stormwater runoff (Chen, 2011).

Treatment wetlands often are designed based on outflow nutrient (pollutant) target concentrations and operating condition (local climatic conditions). Various configurations are available to meet desired performance goals, efficiency, biotic community and preferred level of intervention (Brix, 1993). Three major categories of treatment wetlands based on hydraulic flow are:

- Free-water surface (FWS) wetlands: Water flows on the surface and contains areas of open water, just like natural marshes. These wetlands support emergent aquatic vegetation (EAV) and submerged or floating aquatic vegetation (SAV or FAV; Figure 1-1).
- Horizontal subsurface flow (HSSF) wetlands: Water flows horizontally within the substrate from the inlet to the outlet. The substrate is usually coarse gravel planted with wetland vegetation.
- Vertical Flow (VF) wetlands: Water flow is predominantly vertical from the substrate to the overlying water column, and the site of treatment is mostly the plant root zone.

This dissertation research is focused on FWS treatment wetlands, which are widely popular because of their resilience to adverse climatic factors, and ability to cope with pulse flows and changing water levels (Kadlec and Wallace, 2009). FWS wetlands resemble natural marshes, with submerged and emergent vegetation communities interspersed with patches of open water. These wetlands are commonly used to treat

urban, agricultural and industrial runoff; however, their use in treating mine waters, leachate and polluted ground water has also been successfully demonstrated.

Biogeochemical Processes

Water quality improvement by treatment wetlands is achieved by modification, transformation and storage of excess nutrients and pollutants (Kadlec and Wallace, 2009; Shutes, 2001). The main processes that remove contaminants from water include sedimentation, mechanical filtration, oxidation, reduction, adsorption, absorption, precipitation, microbial immobilization, transformation and vegetative uptake. This is possible primarily as a consequence of air-soil-water-vegetation 'interfaces' where the vegetation and microbial communities interact and participate in various biogeochemical processes (Reddy and DeLaune, 2008). The relative rates of these coupled biogeochemical processes vary across time and space, with incidences of intermittent fast reactions - 'hot moments'² and the presence of active action sites - 'hot spots' (McClain and others, 2003). Wetlands are therefore well suited to transform influent chemicals into products that could be internally assimilated or exported from the system. Gaseous products (N_2 , CH_4 , CO_2 , H_2S , NH_3 , and N_2O) are often lost to the atmosphere whereas dissolved forms (NH_4^+ , PO_4^- , NO_3^- , etc.) are immobilized by the microbial or vegetative communities (Reddy and DeLaune, 2008; Vymazal, 2007). Particulate forms can be exported from the system as a result of high hydraulic flows, or can remain trapped in low flow conditions. The physical settling of suspended organic and inorganic particulates and deposition of plant litter result in the formation of new

² Biogeochemical hot spots are patches that exhibit disproportionately high reaction rates relative to the surrounding matrix, whereas hot moments are defined as short periods of time that exhibit disproportionately high reaction rates relative to longer intervening periods.

material at the soil-water interface (DeBusk and Reddy, 1998). This newly accumulated organic layer is composed of both allochthonous and autochthonous material and may represent various stages in the 'decay continuum' as labile constituents are slowly lost while recalcitrant fractions accumulate over time (Melillo and others, 1989). The residence time of recalcitrant constituents in accreted soils is often high, and due to this long-term storage capability, wetlands are often characterized as nutrient sinks (Nichols, 1983; Reddy and Gale, 1994).

At the elemental level, carbon (C) is the primary driver of all the biogeochemical processes in wetlands (Prairie and Cole, 2009; Reddy and DeLaune, 2008) and phosphorus (P), nitrogen (N), and sulphur (S) cycling is tightly coupled with organic matter turnover in wetlands (Reddy and others, 1999a; Wetzel, 1992). Numerous studies have been conducted to understand the scope, scale and associated pathways for macro-elemental processing in natural and treatment wetlands. Some noteworthy examples include - carbon (Alvarez-Cobelas and others, 2012; Battin and others, 2009; Boon and Mitchell, 1995), nitrogen (Bachand and Horne, 2000; Lund and others, 2000; Spieles and Mitsch, 2000), phosphorus (Fennessy and others, 2008; Lund and others, 2001; Nairn and Mitsch, 2000; Pant and others, 2002; Reddy and others, 1999b; Wang and Mitsch, 2000) and sulphur (Mandernack and others, 2000; Morgan and Mandernack, 1996; Rudd and others, 1986; Spratt and Morgan, 1990). These studies have advanced our knowledge to refine design criteria for meeting performance targets in treatment wetlands. Although more than a thousand treatment wetlands are currently operational throughout the world (Kadlec and Wallace, 2009), active research efforts to optimize performance have been undertaken only on a small proportion of them (Reddy

and others, 2006). This dissertation presents one such effort aimed towards a detailed understanding of the complex processes controlling pollutant removal mechanisms in treatment wetlands. By studying selective wetlands constructed for trapping excess P from runoff originating on farms in the Everglades Agricultural Area (EAA), an attempt is made to understand key regulators of treatment performance over time, and assess the long-term sustainability outlook of those treatment wetlands.

The Everglades, historically an oligotrophic ecosystem, experienced an unprecedented input of P as a byproduct of agricultural and urban development during the mid-twentieth century (Richardson, 2010). The impacts due to excessive P influx has been widely documented for the greater Everglades ecosystem (Noe and others, 2001; Reddy and others, 2011). These impacts include reduced productivity of submerged plants and benthic periphyton, depletion of dissolved oxygen in the water, and changes in invertebrate and vertebrate community structure (Crozier and Gawlik, 2002; Smith and others, 2009). The most conspicuous change in the Everglades has been the expansion of monotypic stands of cattail (*Typha spp.*) that displaced the indigenous sawgrass community (*Cladium jamaicense Crantz*) (Daoust and Childers, 2004; Sklar and others, 2005; Vaithyanathan and Richardson, 1999).

Phosphorus is included in fertilizers and feed supplements to meet the requirement of agricultural crops and livestock and enable continued higher yields, however unutilized P is susceptible to loss from the agricultural fields or livestock feed lots. Because P in all its various forms is non-volatile, it follows hydrologic pathways and often gets concentrated in wetlands and inland water bodies after being introduced in the environment (Reddy and others, 1999a). In the past two decades much effort has

gone into restoring the Everglades to its original hydrologic flow and ecological condition (Chimney and Goforth, 2006). As a potential remedy, thousands of hectares of artificial treatment wetlands, Stormwater Treatment Areas (STAs), were created to remove excess P from surface runoff before this water reaches the Everglades. STAs are actively managed to maintain optimum operational status and meet performance goals mandated by the Everglades Forever Act (EFA). The National Pollutant Discharge Elimination System (NPDES) provides regulatory framework under which STA's operating permits are administered.

Phosphorus Removal Mechanisms

In wetland soils, P predominantly forms complexes within organic matter in peat lands (Cheesman and others, 2010; Fisher and Reddy, 2010) or inorganic sediments in mineral-soil wetlands (Walbridge, 1991). Phosphorus occurs as soluble or insoluble organic or inorganic complexes. The relative proportion of each form depends on soil, vegetation and land-use characteristics of the drainage basin. The particulate and soluble organic fractions can be further separated into labile and refractory components. Physico-chemical transformations convert organic and particulate P into biologically available inorganic forms which is utilized by micro-organisms and vegetation. The bioavailable P fraction triggers growth responses in flora and fauna and can cause a shift from oligotrophic to eutrophic state when P concentrations are sufficiently high. It is essential that the STAs operate to maximize production and storage of refractory components while minimizing loss of bioavailable P fractions to meet Everglades restoration goals.

The relative rates of coupled biogeochemical processes in the STAs regulate long-term accretion of P. In general, two classes of processes, biotic and abiotic,

mediate these transformations (Withers and Jarvie, 2008). Biotic processes include assimilation by vegetation, plankton, periphyton and microorganisms. Abiotic processes include sedimentation, adsorption by soils, precipitation, and exchange processes between sediment and the overlying water column. These abiotic and biotic processes are detailed in Figure 1-2 with a cross-section view of a typical FWS wetland. The STAs are representative examples of FWS wetlands.

In general, four main processes contribute to P retention in the STAs - sorption to soil solids, sedimentation, co-precipitation and biological uptake. Movements of P onto and off of sites on the surface of soil solids are called adsorption and desorption, respectively. Adsorption/desorption equilibria are reached shortly after there is a change occur in pore water P concentration (e.g., in response to external P inputs) (Froelich, 1988). Solid-state diffusion of adsorbed phosphate from the surface into the interior of particles occurs over a longer duration (Froelich, 1988). The soil-water interface controls nutrient concentrations (Li and others, 1972; Patrick and Khalid, 1974) in overlying waters (net flux on or off the soil particles) as governed by the equilibrium phosphorus concentration (EPCo) (Carritt and Goodgal, 1954). In wetlands, the amount of P that can be adsorbed to the soils is often related to the soil iron (Fe) and aluminum (Al) content (Lijklema, 1976). However, in the alkaline soils of south Florida, soil calcium (Ca) also is an important determinant of soil P sorption capacity (Reddy and others, 1998). With regards to treatment wetlands' potential for continued P removal, soil adsorption is not considered a sustainable P removal mechanism because of relatively fast reaction time and the finite sorption capacity of soils for P (Kadlec, 2009; Kadlec and Wallace, 2009).

The suspended solids influx (load) to STAs includes eroded soil particles, macrophyte detritus, and algae or other planktonic organisms, all of which contain P (Stuck and others, 2001). The suspended forms settle out due to gravity under reduced flow velocities or by being trapped within the litter layer or adhering to the biofilms (Schmid and others, 2005). Sedimentation of suspended solids can account for a significant portion of total P removal by STAs, and sustainability is constrained by increase in bottom elevation due to sediment accretion that eventually will prevent surface water flows.

Precipitation of P with Ca, Fe, Al and Mg cations represents an additional pathway of P removal in wetlands (Reddy and others, 1999b; Reddy and others, 2005). It is not easy to differentiate precipitation from adsorption because precipitates often form on the surfaces of soil particles (Scinto and Reddy, 2003); hence this mechanism is referred to as co-precipitation. Reddy and DeLaune (2008) provide a thorough discussion on the conditions that promote P co-precipitation with available cations and explain the processes that result in the formation of apatite ($\text{Ca}_5(\text{Cl})(\text{PO}_4)_3$) and hydroxylapatite ($\text{Ca}_5(\text{OH})(\text{PO}_4)_3$) within Everglades soils (Reddy and D'Angelo, 1994; Reddy and others, 1993). The actual mechanism underlying Ca-P association may be either adsorption of P onto the surface of CaCO_3 precipitates or the formation of mixed crystals during co-precipitation (Otsuki and Wetzel, 1972; Scinto, 1997).

High primary productivity and associated P requirements make biological uptake an important mechanism contributing to wetland P removal. Plants and microorganisms typically utilize only dissolved P_i . Prior studies have investigated P uptake potential of wetland plants (Greenway, 2003; Reddy and Debusk, 1985; Tanner, 1996) and algae

and other microorganisms (Havens and others, 1999). Nearly all of the P incorporated into microbial biomass and majority of the macrophyte-P is returned to the P cycle through decomposition (Kadlec and Wallace, 2009; Reddy and others, 1995). However, reducing conditions in wetlands slow decomposition and, over time, results in organic matter accumulation. The P fraction that is stored in refractory biomass compounds in accrued sediments contributes to long-term sustainable P removal. The conditions supporting and enhancing each of the above mentioned, four P removal mechanisms depend on soil characteristics, vegetation type and abundance and water-column chemistry, including cation availability and the distribution of the total P pool among the various functional P forms. Maximizing P treatment in STAs requires an understanding and quantification (and manipulation) of the relative contributions of each of these processes to net P removal.

Performance of the STAs in terms of P removal is assessed by monitoring inflow and outflow water quality parameters on a short time-scale (weekly or bi-weekly). In addition, periodic soil and vegetation monitoring is conducted. The lack of detailed information on P cycling among the active storage compartments (including water column, plant biomass, surface litter and soil) is responsible for the 'black box' approach still used to evaluate the Everglades STAs (Zurayk and others, 1997). In-depth knowledge of key biogeochemical processes that regulate continued accrual of organic matter, and promote transformation of reactive P forms into non-reactive forms is necessary for designing interventions that will help STA to maintain optimum treatment efficiency and meet mandated performance goals in future. Consolidation and sophisticated integration of available information is required to derive critical

understanding that may be useful for long-term sustainability of the STAs. By using the STAs as a case example, this dissertation examined the role of wetland vegetation, age and soil nutrient storage in regulating P treatment efficiency. This study also explored the relative stability of sequestered P in an attempt to determine long-term sustainability of treatment wetlands, specifically in response to disturbances e.g. extreme weather events or changes in the immediate environment such as pH and redox shifts.

Site Description

The study was conducted in the Everglades STAs, which are located south of Lake Okeechobee in the state of Florida. The current network of six STAs occupies approximately 18,000 hectares of land area and provides an economically feasible means of reducing P inputs to the Everglades Protection Area (EPA) (Figure 1-3 and Figure 1-4). A detailed description of the STA's operational history and performance is presented in Appendix B. The STAs are operated and managed by the South Florida Water Management District (SFWMD). This dissertation presents results of studies conducted in STA-1W, STA-2 and STA-3/4.

Dissertation Overview

The quality and quantity of sequestered P has immediate and profound implications for STA treatment performance. A complex set of bio-geochemical processes controls and regulates P cycling and dictates long-term stability of stored P. Transformation of P from reactive pools to non-reactive pools within the STAs can be considered a predictor of the long-term sustainability of STAs. The ultimate goal of this dissertation was to investigate the fate of sequestered P in relation to the treatment efficiency of the STAs over time.

This study began with the examination of spatio-temporal changes in P storages in STA soils and then progressed to develop a novel technique for measuring soil accretion rates in STAs. Relationship between soil accretion rates and operational age of STAs was explored to determine impacts in P removal efficiency with time. Phosphorus mass-balances were developed by quantifying P pools in recently accreted soil (RAS) and antecedent pre-STA soil to determine allocation of P transferred from the water column to various P storage compartments. Floc and RAS were characterized to identify the relative proportions of various functional P forms to assess treatment efficiency of the STAs. Finally, this information was synthesized to provide insights into STA performance over the entire period of operation and assess the long-term sustainability outlook for the STAs in the future.

Dissertation Objectives and Hypotheses

The first objective of this dissertation was to review available datasets on STA soil physico-chemical variables and determine spatio-temporal changes in surface and sub-surface soil nutrient storage to explore relationship between hydraulic and water quality parameters, soil nutrient storages and STA age. These data were further used to perform preliminary P mass balance. The hypothesis for this objective was that STAs' treatment efficiency or P removal efficiency declines after a protracted period of operation (Chapter 2). Objective 2 was to determine the soil accretion rate in the STAs, by utilizing stratigraphic characteristics of the soil profiles to identify the boundary between recently accreted soil (RAS) and antecedent pre-STA soil. The hypothesis behind this objective was that the STAs are accreting systems and accumulating organic matter conserves attributes of prevailing conditions (e.g. nutrient loading, vegetation community). Changes in these stratigraphic characteristics can be exploited

to identify the depth of RAS deposited on top of pre-STA soil (Chapter 3). Objective 3 was to explore the relationship between soil accretion rates and operational age of the STAs and perform P mass balance using P storages in RAS and pre-STA soil and the amount of P removed from the water column. Cycling of P within different P storage compartments of the STAs was also estimated. The main hypothesis for this objective was that most of the P retained from the water column is stored in RAS, which has a higher P concentration than pre-STA soil. With increasing age, the rate of soil and P accretion declines, resulting in higher outflow P concentrations. Internal re-distribution of P within RAS and pre-STA soil is mediated by vegetation. This controls whether the STAs function as a nutrient source or sink (Chapter 4). Determination of the relative proportion of reactive and non-reactive P pools in the STAs and assessment of the influence of wetlands vegetation communities (EAV vs. SAV) on reactivity of P pools was the fourth objective, addressed in (Chapter 5). I expected that differences in the wetland vegetation types (EAV vs. SAV) will influence the proportion of P forms incorporated into RAS and sequestered in the STAs. The presence of more reactive (i.e., potentially mobile) P forms will reduce the long-term sustainability of the STAs.

Dissertation Layout

The dissertation is organized in 6 chapters. Chapter 1 (this chapter) introduces the main processes occurring in the treatment wetlands, factors critical in controlling long-term treatment efficiency and provides an overview of the objectives and rationale behind the dissertation. This is followed by Chapter 2, which presents an analysis of datasets on STA soil physico-chemical variables and spatio-temporal changes in surface and sub-surface soil nutrient storages. After exploring the relationships between hydraulic and water quality variables, soil nutrient storage and STA age, a preliminary P

mass-balance for STAs was conducted. Chapter 3 presents detailed information about a novel change-point technique (CPT) that was developed to measure soil accretion rates in wetlands. The CPT was used to determine the depth of recently accreted soil (RAS) in select STAs. Chapter 4 focuses on the soil and P accretion rates that were determined using RAS depths and operational age of the STAs. The relationship between accretion rates and STA age is also presented. Influence of wetland vegetation on accretion rates and P mass balance using RAS depth is also presented to show P cycling through various P storage compartments in the STAs. Chapter 5 contains results from the study on chemical characterization of functional P forms in RAS. This was performed to determine the relative proportion of reactive and non-reactive P storage pools. The role of vegetation and other geochemical variables were explored and long-term sustainability of STAs was examined. Finally, Chapter 6 provides a synthesis of conclusions drawn from all the dissertation studies.

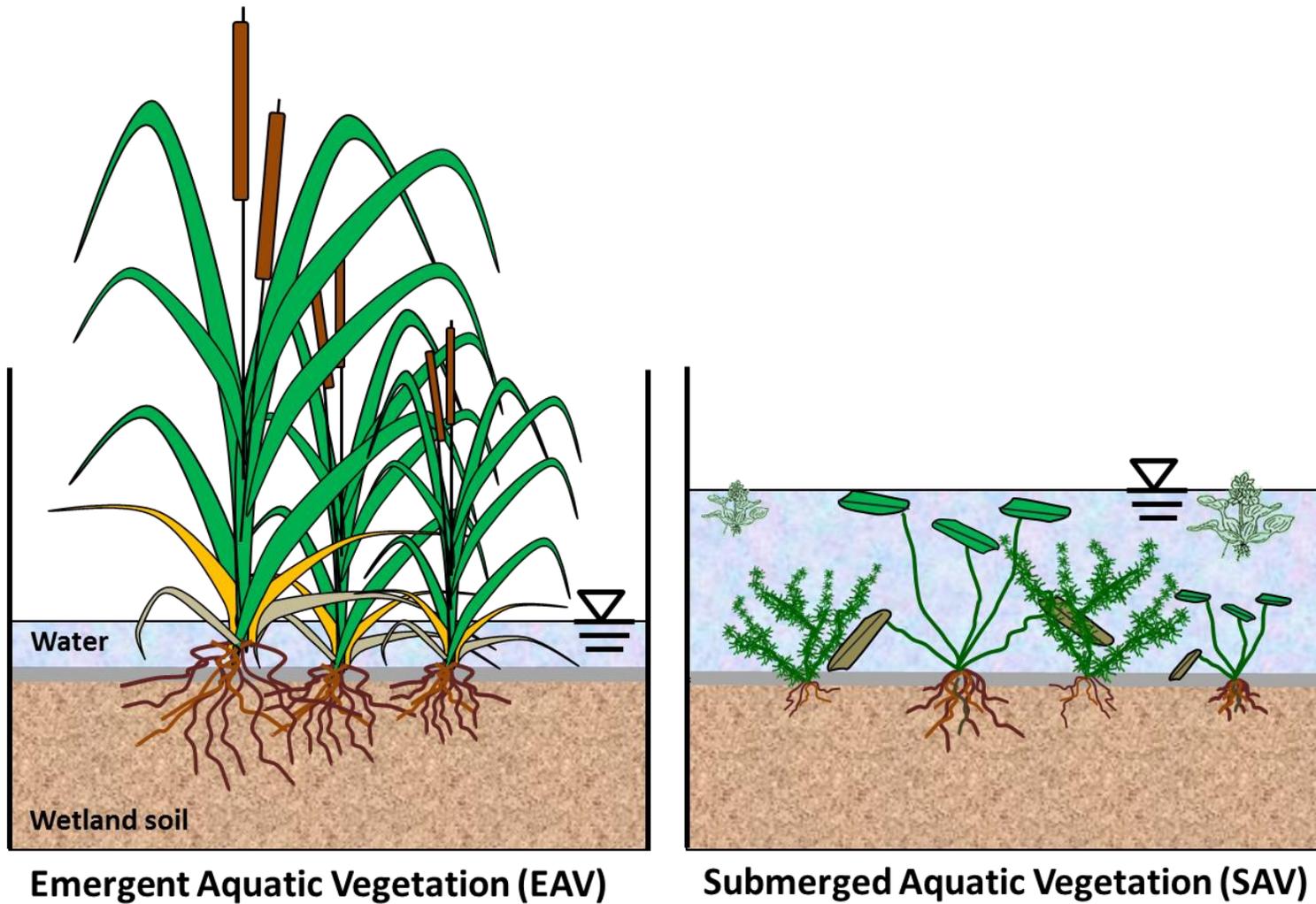


Figure 1-1. Cross section view of emergent and submerged aquatic vegetation in FWS wetlands. Higher water depth enables growth of submerged and floating aquatic vegetation.

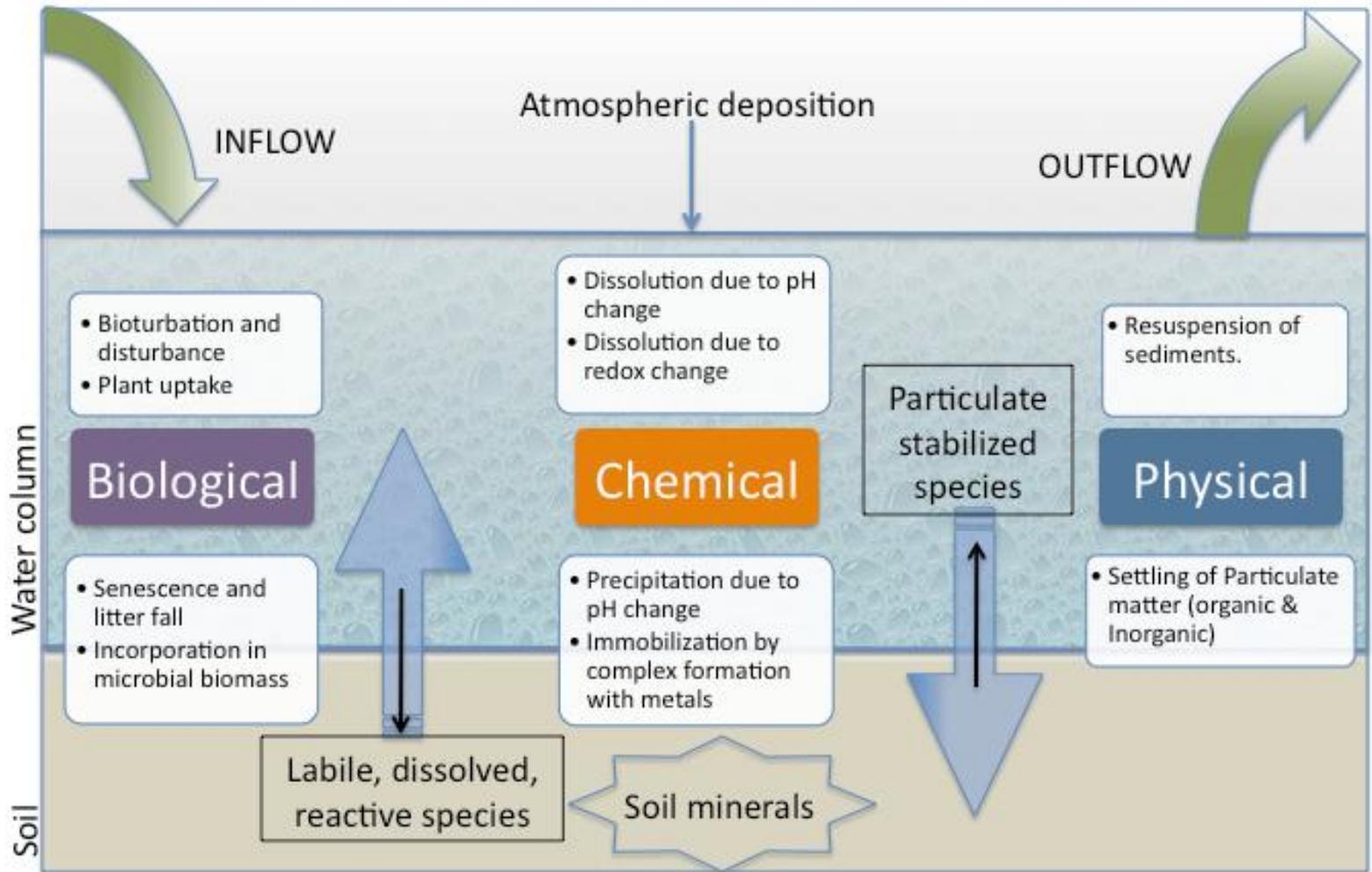


Figure 1-2. Common biogeochemical processes with regard to phosphorus cycling in typical free water surface (FWS) wetland. Arrows show direction of movement; size does not necessarily represent relative mass or volume of processes.

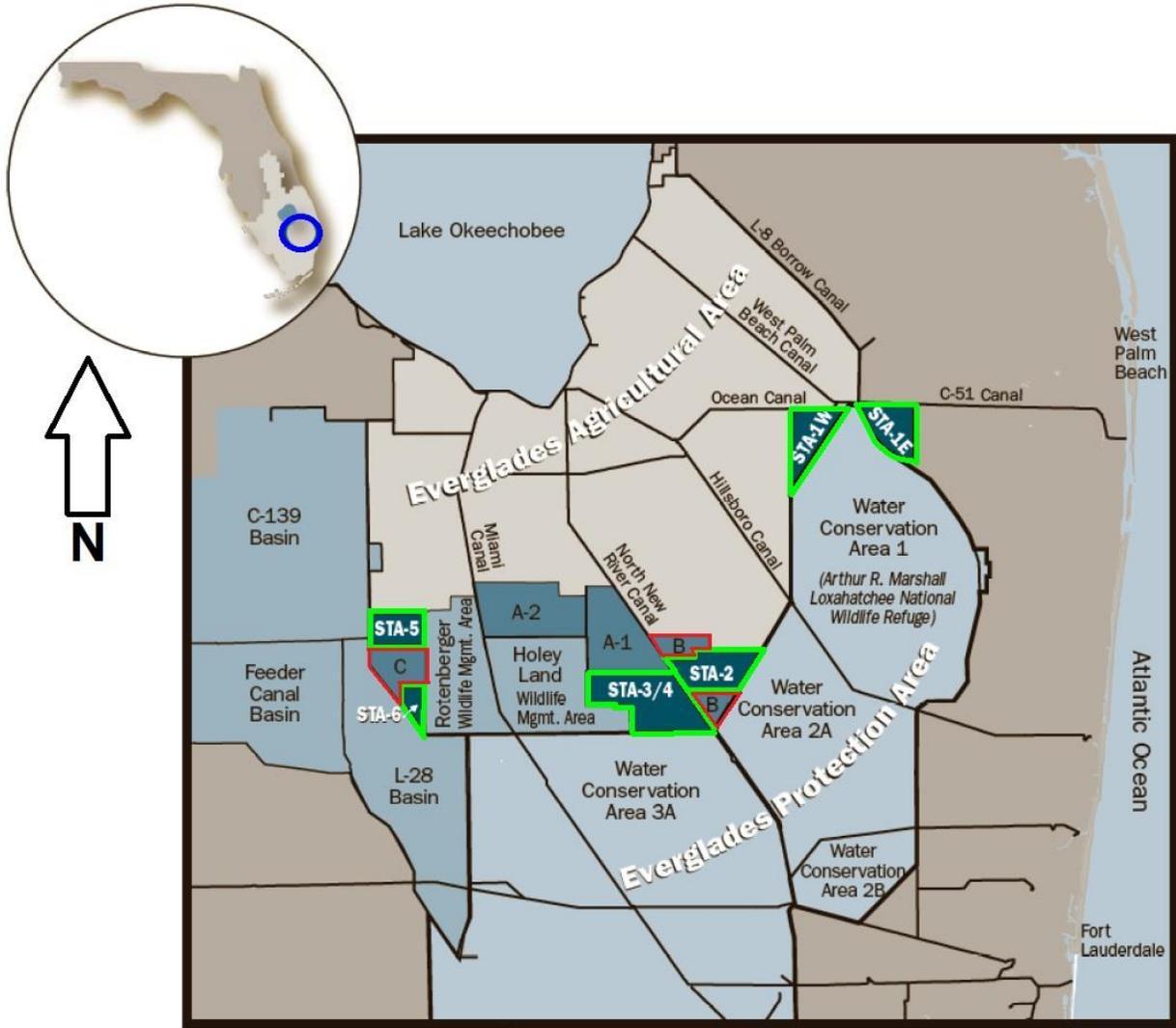


Figure 1-3. Map showing the locations of the original six Stormwater Treatment Areas (STAs; in green), the Everglades Agricultural Area and the Everglades Protection Area in South Florida. Compartments B and C are expansions to the STAs and are indicated in red (Germain and Pietro, 2011).

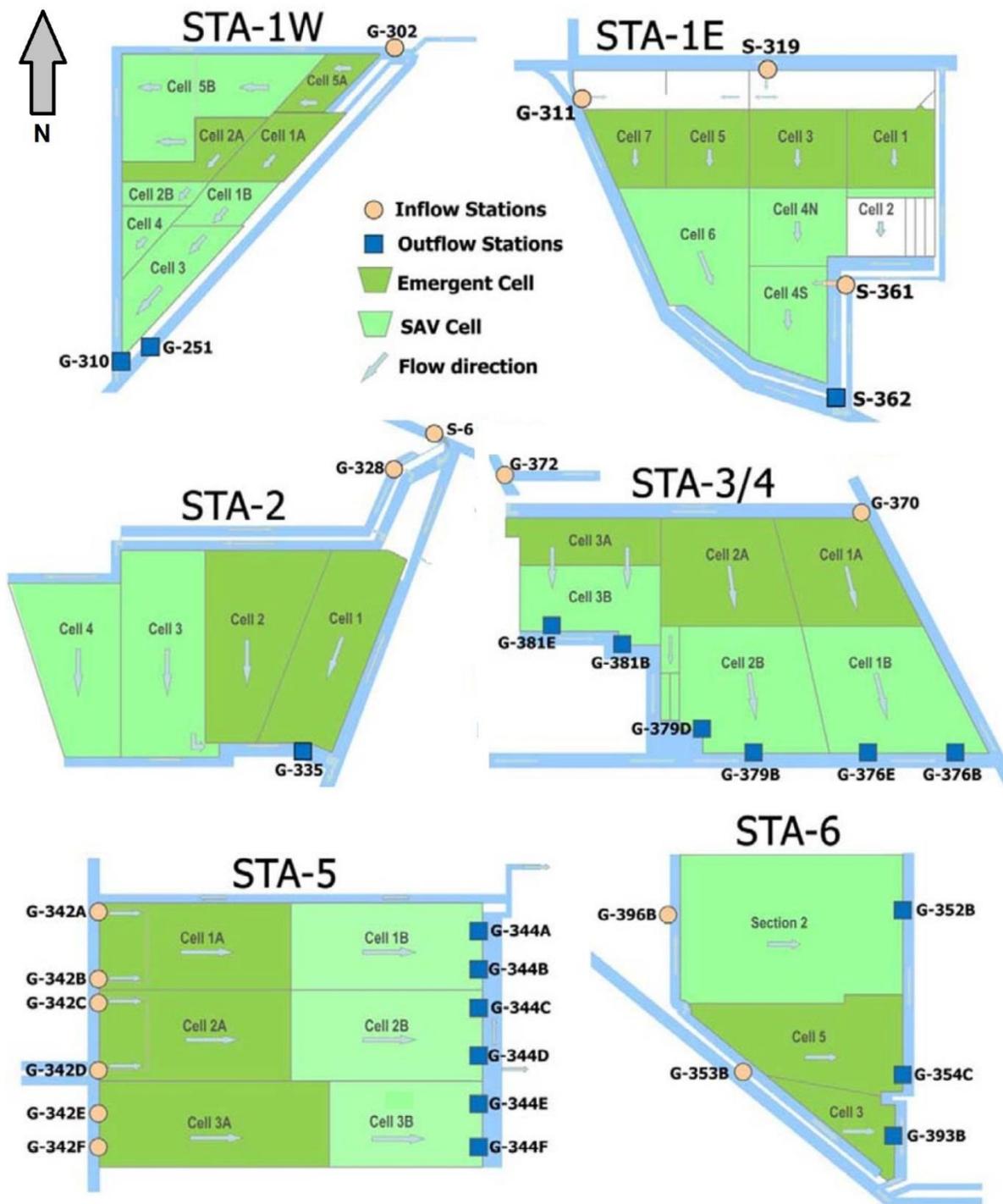


Figure 1-4. Configuration of the treatment cells within each Stormwater Treatment Area (STA). The dominant vegetation type in each cell is also indicated (Germain and Pietro, 2011)

CHAPTER 2
SPATIO-TEMPORAL CHANGES IN SOIL NUTRIENT STORAGE IN THE
EVERGLADES STORMWATER TREATMENT AREAS: IMPACT ON PHOSPHORUS
REMOVAL PERFORMANCE

Background

Constructed wetlands exhibit a broad range of biogeochemical and physical characteristics, and are utilized worldwide for enhancing aspects of surface water quality (Brix, 1994; Kadlec and Wallace, 2009). These artificial ecosystems are designed to reduce the concentration of water-borne contaminants by either transforming or assimilating pollutants. Constructed treatment wetlands are particularly popular for intercepting agricultural drainage waters (ADW), which often contain high concentrations of nutrients such as nitrogen (N) and phosphorus (P). Such is the case with large-scale treatment wetlands in south Florida, which were constructed as filtration marshes to remove excess nutrients from surface runoff before it enters the Everglades (Figure 1) (Chimney and Goforth, 2001; Goforth, 2001; Perry, 2004; Redfield, 2000). These wetlands are referred to as the Everglades STAs, and are tasked with reducing total P (TP) concentrations in surface runoff to ecologically benign levels (Walker, 1995). The strategic location of the STAs has allowed them to retain over 1,450 metric tons of P, which has resulted in a considerable load reduction of P to the Everglades. STA outflow total P flow-weighted mean concentrations (FWMC) were reduced from $152 \mu\text{g P L}^{-1}$ to $38 \mu\text{g P L}^{-1}$ during the period from 1994 to 2011 (Ivanoff and others, 2012).

High P loads in an oligotrophic system are known to cause a shift in the ecosystem's biotic communities by disrupting natural nutrient characteristics and can ultimately lead to eutrophic or hyper-eutrophic conditions (Khan and Ansari, 2005).

Following excessive P inputs, the northern Everglades ecosystem has exhibited signs of widespread impaired ecosystem function, including extensive growth of *Typha spp.* (cattail) in place of the natural inhabitant, *Cladium jamaicense* (sawgrass) (Hagerthey and others, 2008; Vaithyanathan and Richardson, 1999).

To counter these undesirable changes, the Comprehensive Everglades Restoration Plan (CERP) was developed with a goal to restore, protect and preserve the remaining Everglades ecosystem (USACE and SFWMD, 2000). The CERP is broadly aimed at improving quality, quantity, timing and flow of water for both ecological integrity and human needs in south Florida. A major component of this plan, water quality improvement, includes reduction of P inputs by implementing best management practices (BMPs) in the EAA (Diaz and others, 2005; Izuno and Capone, 1995; Rice and others, 2002) and subsequent treatment of ADW that leaves the EAA. Treatment is carried out by intercepting ADW in the STAs where biogeochemical processes remove P from the water column (DeBusk and others, 2001a; Gu and others, 2001; Nungesser and Chimney, 2001).

The first full-scale treatment wetland in south Florida, known as the Everglades Nutrient Removal Project (ENRP), became operational in 1994 (Chimney and others, 2006; Guardo and others, 1995). Subsequent expansion of the ENRP and addition of new STAs led to the current STAs' total footprint of approximately 18,000 ha of effective treatment area (Ivanoff and others, 2012). Although the STAs have sequestered a substantial amount of P during their operational history, they are known to exhibit variable treatment performance in terms of P removal efficiency over time (Pietro and others, 2008). The spatio-temporal variability in STA treatment performance has been

attributed to factors such as antecedent land use, vegetation condition and species composition, nutrient and hydraulic loading, hydraulic residence time, hydroperiod, soil characteristics and P content, cell topography and configuration, extreme weather events, construction activities and regional operations (Germain and Pietro, 2011). A study conducted on 49 treatment wetlands found that TP removal was more a function of mean hydraulic residence time than mean hydraulic loading rate (Carleton and others, 2001). However, a broader overview of P removal performance across a range of FWS wetlands suggested that background concentrations, P loading rates (PLR), temperature and seasonal effects and ecological variables such as water depth and vegetation type and cover, etc. are the main controlling factors (for details see Chapter 10, Kadlec and Wallace, (2009)). This review also recognized constraints in P processing when low outflow concentrations are required, which highlights the challenges experienced by the Everglades STAs where outflow TP FWMCs are currently mandated to be in the 13-19 $\mu\text{g P L}^{-1}$ range.

A thorough examination of 21 variables including inflow TP concentration, hydraulic and TP loading rates, TP fractions, calcium (Ca) and pH did not yield a single variable that has greatest influence in controlling TP concentration or TP areal settling rate in STAs (Jerauld, 2010). This study, however, emphasized the importance of background soil P concentration and also showed an inverse relationship between STA ages and outflow TP concentrations (Jerauld, 2010). STA age could be a key factor in determining STA performance because it is a lumped term that represents multiple wetland characteristics that change over time, such as soil P and plant biomass and tissue P concentrations. Further information on key factors affecting performance of

treatment wetlands in general, and the STAs in particular, are presented in Chapter 1 as a review of published literature (Carleton and others, 2001; Carleton and others, 2000; Carleton and Montas, 2010; Chimney and Pietro, 2006; Dierberg and others, 2002a; Dierberg and others, 2005; Fisher and Reddy, 2010; Gu and others, 2001; Gu, 2006; Gu, 2008; Ivanoff and others, 2012; Juston and DeBusk, 2006; Juston and DeBusk, 2011; Kadlec, 1997; Kadlec, 1999; Kadlec, 2005; Kadlec and Hammer, 1988; Kadlec and Wallace, 2009; Luderitz and Gerlach, 2002; Martin and Anderson, 2007; McCormick and Odell, 1996; Moustafa and others, 1996; Nouri and others, 2010; Nungesser and Chimney, 2001; Pietro and others, 2006; Reddy and others, 1999a; Richardson, 1985; Richardson and Qian, 1999; Walker and Kadlec, 2011).

Juston and DeBusk, (2006) explored relationships between mass loading of P and subsequent outflow concentrations within the STAs and compared them with seven other treatment wetlands in Florida. Their analysis of historic data concluded that a long-term average annual PLR at or below $\sim 1.3 \text{ g m}^{-2} \text{ yr}^{-1}$ is conducive to outflow TP concentrations less than $\sim 30 \text{ } \mu\text{g P L}^{-1}$ irrespective of vegetation type (Juston and DeBusk, 2006). An extensive study of the Everglades STAs for the entire period of operation (1994- 2011) found a significant positive correlation between PLR and outflow TP concentration, with dramatic increases in outflow concentrations from STAs when PLR was greater than $\sim 1.0 \text{ g m}^{-2} \text{ yr}^{-1}$ (Ivanoff and others, 2012). This analysis also elucidated differences in vegetative response to PLR, with a substantially greater increase in outflow TP concentration in EAV cells in comparison to SAV cells at PLRs greater than $\sim 1.0 \text{ g m}^{-2} \text{ yr}^{-1}$ (Ivanoff and others, 2012). However, EAV cells are typically

situated in the front end of STA flow-ways, which experience higher inflow TP concentrations, which may affect outflow TP concentrations.

Performance of the STAs for regulatory compliance is quantified by measuring hydrologic parameters, i.e. volume and chemical characteristics of inflow and outflow waters to and from STAs. This approach overlooks the complex biogeochemical processes that regulate P removal from the water column and controls the stability of sequestered P pools in the STAs. With continued STA operation, P removed from the water column accumulates as recently accreted organic soil and contributes to the incremental enrichment of the surficial layer of soil, potentially leading to the saturation of internal P storage compartments (Lowe and Keenan, 1997). Recently accreted soils (RAS) share an active interface with floc (unconsolidated detritus that is deposited on the consolidated wetland surface layer) and the overlying water column, and depending on the existing biogeochemical factors, nutrient concentrations in the RAS layer could potentially influence STA TP outflows (White and others, 2006). Therefore, an understanding of the complex processes that regulate long-term sustainable P removal in the STAs is desired for effective management and for meeting Everglades restoration goals. An assessment and characterization of nutrient storages in STA soils could be the first step towards dismantling the black-box-like approach (Zurayk and others, 1997) used to evaluate treatment wetland function. Investigation of changes in soil P storages over temporal and spatial scales could provide meaningful insights into STA performance and P removal efficiency over time.

Objectives and Hypotheses

The main objective of this study was to review available datasets on STA soil physico-chemical parameters and determine spatio-temporal changes in surface and

sub-surface soil nutrient storages. Subsequently, relationships between hydraulic and water quality parameters, soil nutrient storage and STA age were investigated to explore the trajectory of TP removal efficiency in aging STAs. A preliminary TP mass balance was performed to understand where the bulk of retained P was distributed within the STA soil profile. These objectives were supported by the hypothesis that TP removal efficiency of STA declines after a continued period of operation. In addition, internal redistribution of P within soil profiles, mediated by vegetation, controls overall P removal efficiency of STAs.

Methods

A comprehensive review of existing information on STA soil nutrient storage was conducted to document changes in soil nutrient status over time and to explore relationships between soil P storage and TP retained from the water column. Surface soil P storages in all six STAs were compared to explore the effect of STA age on TP removal rates. Phosphorus distribution within various compartments of STAs – water column, floc, surface soils (0-10 cm), and sub-surface soils (below 10 cm) was determined. Temporal changes in P storage within these compartments was used to generate estimates of P flux, which was then used to develop overall TP mass balances for the STAs.

Site Description

The Everglades STAs have a combined surface area of approximately 26,300 ha, with about 18,000 ha of effective treatment area (Ivanoff and others, 2012). This area is distributed among six STAs, each of which is comprised of multiple, independently managed units called cells (Figure 1-4). Each cell is actively managed to have one dominant vegetation community depending on the intended treatment

objectives. The two broad categories of vegetation are emergent aquatic vegetation (EAV) and submerged aquatic vegetation (SAV) [SAV cells also contain floating aquatic vegetation (FAV) species]. The South Florida Water Management District (SFWMD) is responsible for operating, maintaining and optimizing the performance of all the STAs to ensure compliance with operating permits. The six operational STAs include: STA-1E and STA-1W, STA-2, STA-3/4, STA-5, and STA-6. A detailed description of STAs and associated TP removal is presented in Table B-3 (Appendix B).

Data Sources

Data used in this study were obtained from the SFWMD and the Wetland Biogeochemistry Lab (WBL), University of Florida. Detailed information regarding operations and management of STAs was obtained from South Florida Environment Reports (SFERs) (Chimney and others, 2000; Germain and Pietro, 2011; Ivanoff and others, 2012; Pietro and others, 2010). Data used for this analysis represented 495 floc samples and 1700 soil samples spanning the entire period of record (POR) for all STAs up to water year (WY) 2008 [Each WY runs from May 1 through April 30 of the following calendar year].

Sampling dates indicated that STA soils were collected approximately every three years from WY2004 through WY2008; however, the earliest data from WY1994 was obtained from STA-1W. Floc depth was variable across sample sites. Soil cores were divided into two sections – surface soils (0-10 cm) and sub-surface soil (10-30 cm).

Floc and soil dataset used for analysis contained physico-chemical information such as bulk density, ash free dry weight (AFDW), organic matter content (loss on ignition; LOI), pH, iron (Fe), Ca, sulfur (S), total carbon (TC), TP and total nitrogen (TN).

Using bulk-density, core depth and soil nutrient concentrations, P, C and N storage within floc, surface soils and sub-surface soils was determined. Nutrient storage was not calculated where floc depth, bulk density or nutrient concentration data was missing.

Soil Nutrient Mass Storages

Total nutrients (C, N and P) storage in floc (variable depth) and soils (0-10 and 10-30 cm) were calculated. Mean floc depth for each sampling event was used for calculating P, N and C storage in the floc fraction while a depth of 10 cm was universally used for surface soil storage calculations. Nutrient storage per unit area (g m^{-2}) for both floc and soil layers was calculated as follows:

$$F_XS = (C_X * D_{fb} * d_f)/100 \quad \dots\dots\dots (2-1)$$

$$S_XS = (C_X * D_{sb} * d_s)/100 \quad \dots\dots\dots (2-2)$$

where,

F_XS = Floc nutrient (X) storage (g m^{-2})

S_XS = Soil nutrient storage (g m^{-2})

X = Nutrient X (carbon, nitrogen or phosphorus)

C_X = Nutrient concentration (mg kg^{-1})

D_{fb} = Bulk density of floc (g m^{-3})

D_{sb} = Bulk density of soil (g m^{-3})

d_f = Depth of floc (cm)

d_s = Depth of soil (cm)

Relationships between TP retained by the STAs and P mass storage (g P m^{-2}) in floc and the top 10-cm surface soils were explored. The effect of STAs age on floc and soil P mass storage was examined for all STAs. Relationships between TP areal storage in the STAs and concomitant C and N mass storage was also explored.

Phosphorus Mass Balance

Mass balances can be calculated with varying degrees of complexity, either considering only the mass of P that entered but did not leave a wetland (by subtraction of outflow from inflow data) (Boyt and others, 1977; Sloey and others, 1978) or, through

quantification of P flux, across various compartments within the wetland (soil and biomass) and finally P storage in soils (Dolan and others, 1981; Fetter and others, 1978; Headley and others, 2003; Lee and others, 2012). Even simple P mass balances are useful in determining the sources of P to the wetland (surface water, groundwater, precipitation) and for calculating gross P removal effectiveness (Bhadha and others, 2011; Chung and others, 2008). More complex 'complete' mass balances are increasingly difficult to assemble owing to sample collection and processing challenges (Correll, 1998), but may aid in illuminating internal processes that could be useful to the understand fate of retained nutrients by the STAs. Phosphorus mass-balances performed as a part of this study utilized an approach with somewhat greater level of complexity involving cumulative TP retained from the water column (P_{Wc} ; $g P m^{-2}$) by STAs over their POR (up through WY2008) and corresponding changes in areal P mass storage ($g P m^{-2}$) in floc and the top 10-cm of surface soil (Figure 2-1).

The difference between floc P storage (FPS; $g P m^{-2}$) and P_{Wc} indicated net movement of P within floc and surface soil layer and was represented as $P_{flux F}$. The sign of $P_{flux F}$, '-ve' or '+ve', indicated direction of P enrichment (movement), with +ve $P_{flux F}$ signifying flux from the underlying surface soil layer into the floc layer. Conversely, FPS smaller than P_{Wc} indicated net movement of P down into the surface soil ($P_{flux F}$; -ve), this would be the case when floc gets consolidated and transformed into soil.

The earliest available soil P storage (SPS; $g P m^{-2}$) for the top 10-cm of surface soil was used as background P (P_{BG}) and was subtracted from WY2007 SPS. A net positive change indicated P enrichment of the surface horizon either from the floc above ($P_{flux F}$; -ve) or from the subsurface soil below ($P_{flux SS}$; +ve; Figure 2-1). Soil P storage in

WY1995 was used as the background (P_{BG}) for STA-1W while SPS in WY2005 was taken as background for both STA-1E and STA-3/4. Soil PS in WY2001 was used as background for STA-2, STA-5 and STA-6. The arrows in Fig. 2-1 indicate the direction of P flux ($g\ P\ m^{-2}$) from one storage compartment to another.

For all practical purposes, soils represent the only long-term nutrient storage pool in wetlands while nutrients in live vegetation serve only as a temporary transient pool (Howard-Williams, 1985), hence P present in vegetation was not considered for TP mass-balance calculations. Critical assumptions made for developing TP mass balances for the STAs are listed below:

- The total mass of TP retained from the water column (P_{Wc}) initially resides as floc, therefore floc P storage (FPS) at any given time reflects the fraction of TP incorporated from the water column as well as contribution from vegetative detrital matter (physical settlement of particulate forms, adsorption-absorption of soluble forms, biological immobilization by microbial communities).
- Floc P contributed by vegetative detrital matter deposition may represent a fraction that could be obtained from underlying soils by rooted plants (EAV) or directly from the water column by submerged and floating plants (SAV/FAV). For comparisons at STA level, both EAV and SAV/FAV cells within one STA were averaged to obtain FPS for that STA.
- Floc becomes soil over time, so with a long observation period some of the water-column TP have passed through the floc and into the surface soil.
- Flux of P from underlying soil ($P_{flux\ SS}$) to overlying soil or floc is regulated by redox conditions and the equilibrium P concentration (EPCo).
- Phosphorus in live vegetation biomass at a given time (i.e., plant standing stock) accounts for only a tiny fraction of TP in the STAs and represents a transient pool which ultimately gets transformed into floc and soil after plant senescence, following the decay continuum pathway.

Data Analysis

All calculations and comparison of nutrient storage pools were performed using Excel. Nutrient mass storages were not calculated if floc depth, bulk density

measurements or nutrient concentrations were unavailable. Total P storage in analyses represented floc and 0-10 cm soil P storages. Area-weighted mean values were used to determine nutrient storages within each STA cell, which were then added together to provide total storage for the whole STA in a given year. Relationships within nutrient mass storages in STA soils, and between STA age and soil and floc P storages were explored using Excel spreadsheet regression models.

Results

Physico-Chemical Properties

Among all STAs, floc and soil bulk density were highest in STA-1E, suggesting these is much higher mineral fraction in the surface soils (Table 2-1). Floc bulk density ranged from 0.04 to 0.26 g cm⁻³ whereas soil bulk density varied from 0.2 to 1.0 g cm⁻³ across all STAs for all sampling events. The range of mean floc depth (cm) across STAs was higher in WY2004 than in WY2007 (Table 2-2). Floc depth decreased in STA-1W and STA-5, whereas it increased in STA-2 during this period.

Phosphorus

Floc and soil P concentrations (mg P kg⁻¹) showed an increase from WY2004 to WY2007 (Table 2-3). Floc P concentration was lowest in STA-2, whereas it was highest in STA-1W. The range of soil P concentration was lowest in STA-1E and highest in STA-5. Floc and soil P storage in STAs is presented in Table 2-4. In WY2007, STA-5 surface soils (0-10 cm) had highest P storage.

Caution should be exercised in comparing SPS in the 0-10 cm depth surface soil across STAs. In older STAs, such as STA-1W, most of the 0-10 cm soil represents consolidated floc and only some antecedent pre-STA soil. However, in younger STAs, much of the 0-10 cm soil depth may represent pre-STA soil with only a small fraction

derived from consolidation of floc. Therefore comparing P storage in the top 10-cm of surface soil across different STAs will represent dissimilar contributions from floc and pre-STA soil depending on the operational age of STA, and the rate of soil accretion. The percentage of TP (floc + soil) derived from water column as a function of STA's operational history is plotted in Figure 2-2. As the STAs aged, the percentage of TP storage derived from water column increased ($r^2=0.86$). However, no clear relationship ($r^2=0.20$) was observed between the mass of TP removed from the water column and TP storage in WY2007 (Figure 2-3). The one to one line in Figure 2-3 differentiates between the proportion of TP in floc + soil derived from pre-STA soil and TP transferred from the water column. This indicated increasing proportion of TP in surface soils because of net P retention from overlying water column with increasing STA's age. A comparison of TP retained from the water column during the operational history of STAs and the amount stored in floc and soil is presented in Table 2-5.

There was no relationship when P storage was regressed against TP retained from the water column for all STAs each water year (Figure 2-4). Similarly, no relationship was obtained when cell averages were analyzed instead of whole STAs (Figure 2-5). Additionally, when floc P concentrations (Figure 2-6) and floc P storages (Figure 2-7) were regressed against inflow TP flow-weighted mean concentrations ($\mu\text{g P L}^{-1}$), no relationship was observed at the cell level.

Nitrogen

Total N concentrations (mg N kg^{-1}) across STAs are shown in Table B-1 (Appendix B), while FNS and SNS are shown in Table 2-6. In most cases, SNS increased over time, except for a slight decrease in STA-1W during WY2008. This decrease may have resulted from rehabilitation activities, which involved removing most

of the surface soil. A similar dip in SPS was observed for STA-1W in WY2008, supporting the assertion above.

Soil N and P storage for WY2007 showed a positive linear relationship ($r^2=0.67$; Figure 2-8). This suggested that P was stored primarily in organic form with approximately 31 to 54 g N per g of P stored per m^2 in the STAs. High N:P ratios suggested that STA soils were P limited.

Carbon

The concentration of C ($g\ C\ kg^{-1}$) in floc and soil is presented in Table B-2 (Appendix B), whereas carbon storages are shown in Table 2-7. Soil PS and soil C storage for WY2007 showed a positive linear relationship ($r^2=0.66$; Figure 2-8). The range of C stored in STAs varied from 470 to 820 g C per g of P stored per m^2 in the STAs. Total mass of N and C (mt) stored in floc and surface (0-10 cm) soil is presented in Table 2-8.

Mass Balance

The outcomes of TP mass balances for five STAs are presented in Figure 2-9 with calculated P storages and fluxes between STA P storage compartments (STA-1E was not included in this calculation because of unavailability of floc data for WY2007). All STAs showed a net positive retention of TP from water column. Soil PS showed positive changes in STA-1W, STA-5 and STA-6 whereas STA-2 and STA-3/4 showed a negative change in SPS in comparison to the background P storage. The negative changes in SPS were interpreted as a redistribution of P into the floc or subsurface soils (below 10 cm). STA-1W and STA-3/4 were considered functioning favorably for long-term P storage as calculations suggested flux of P into sub-surface soils downwards

from surface soils. For the other STAs, net P flux from sub-surface soil to floc and surface soil was observed.

Discussion

Wetlands, in general, accumulate organic matter because of production of detrital material from biota (predominantly vegetation) and suppressed rates of decomposition (Reddy and others, 1993; Rogers, 1983). Accreting organic matter forms the largest sink for influent nutrients, particularly for P, of which up to ~80% is stored in soils (Faulkner and Richardson, 1989; Kadlec, 2009; Reddy and others, 1999a) relative to other ecosystem components such as plant biomass and plant litter (Heliotis and DeWitt, 1983). In the Everglades STAs, long-term sustainability lies in consistently maintaining conditions that are favorable for converting influent reactive P forms into non-bioavailable (non-reactive) forms.

Monitoring and permit compliance of STA performance require quantification of TP load reductions by measuring hydrologic parameters, i.e., volume and chemical characteristics of inflow and outflow waters. Performance determined in this fashion provide only limited information, such that higher than expected outflow P concentrations only serve as an indicator of a problem without providing insight into the underlying causal processes. Such information serves little purpose if the goal is to enhance treatment performance or to forecast future treatment capabilities. The assessment and characterization of stored nutrients (P) therefore provides basic information for maintaining long-term nutrient removal effectiveness of treatment wetlands in general and that of the STAs specifically. Examining the changes in P pools in floc, surface soil and sub-surface soils is a first step in that direction, specifically because nutrient concentrations in floc and soils have the potential to influence the

overlying water column concentration depending on existing biogeochemical factors (White and others, 2006).

Phosphorus Retention

Phosphorus retention in treatment wetlands is mediated by both short-term (Kadlec, 1997; Kadlec, 2005; Reddy and others, 1995) and long-term P removal pathways (Kadlec, 2009; Reddy and others, 1999a), which are regulated by the existing biogeochemical conditions. Although removal of P from the water column may appear to be a rapid phenomenon, formation of stable storage compounds, which are less readily released into solution, can only be achieved after a considerable period (Hamad and others, 1992). This time allows P to diffuse into the soil matrix (an irreversible process with finite capacity) or be incorporated into vegetation (biota) and form refractory organic compounds (infinite capacity). The presence of Ca and Mg in alkaline soils (Moore and others, 1998) and Fe and Al in acidic soils (Lijklema, 1976) influences formation of stable P minerals, whereas uptake by vegetation (and other biota) eventually leads to the production of relatively stable organic P forms. In the former scenario, the quantity of available minerals, which is often finite, constrains unlimited production of stable P mineral forms. On the other hand, formation of stable organic P through vegetation uptake and biomass growth could continue indefinitely as long as favorable conditions are maintained. Therefore, accretion of organic matter as new soil in wetlands provides the long-term sustainable pathway for P removal.

Analysis of physico-chemical attributes of STA soils allowed investigation of temporal changes in nutrient storage, and examination of relationships between nutrient storage changes with respect to STA performance and operational age. The STAs exhibited considerable variability for stored P in floc and surface soils. One possible

reason for this variability could be differences in the periodic cycle of drying and rewetting experienced by each STA. During summer months when STAs experience dry conditions, organic soils oxidized and P may have been lost on soil rewetting (Fisher and Reddy, 2001; Newman and Pietro, 2001; Olila and others, 1997). Thus, drying and rewetting could play a key role in redistribution of P within the STAs as the released P is assimilated by downstream biological communities. This downstream movement of P as an enrichment front has been observed in Water Conservation Area-2A with a zone of greater P impact closer to the inflows (DeBusk and others, 2001b; Debusk and others, 1994; Koch and Reddy, 1992). The large size of the STAs and elongated water flow paths are amenable to establishment of a similar longitudinal gradient in P stored in the water column, vegetation and soils (Walker, 1995). Such internal redistribution and longitudinal P gradients, along with enrichment of surface soils from continuous external loading could be another reason for the variability in P storage in STA soils.

Absence of a clear relationship between inflow TP loads and floc and soil P storages (Figures 2-4 to 2-8) could be a consequence of the following reasons: first, insufficient information on soils (limited data points) to capture inherent spatial variability; second, water-column data represented TP retained only in that particular water year, whereas P measurements in the case of floc and soils were cumulative for the POR; third, the proportion of P in the vegetation and biota was not accounted for in these relationships and fourth, error in measurement of nutrients in soils and the water column could have masked any small relationship that may exist. These reasons only provide a partial explanation for the observed lack of relationship, while there could be many other factors that are sufficiently complex to resolve at STA or individual cell

scales. For example : a) Soils data may not be truly representative of the entire STA, b) There have been differences in vegetation coverage across cells over the POR and insufficient information about the role of plants in P redistribution along soil profile, c) There have been variability in hydraulic residence times and dynamic range of P loading rates (PLR) and, d) There is inherent heterogeneity in STA soils and impacts from extreme weather events such as drying, flooding and hurricanes. The scope of current analysis did not allow examination of each of these individual factors in detail. The analysis however did provide a clear indication that the soil P proportion derived from the water column increased with time (Figures 2-2 and 2-3).

Phosphorus Mass Balance

Long-term sustainability and efficiency of STA operations is contingent on understanding the spatial distribution and accurate quantification of P storage pools in the STAs. The fate of accreted P is influenced by its association with reactive organic substrates and factors controlling its potential mobilization. The change in SPS from pre-STA P levels was manifested as redistribution of P into either the floc or subsurface soils (below 10 cm). These changes were examined by developing P mass balances for the STAs.

Comparison of STAs with varying operational age indicated that STA surface soils for STAs up to 8 years of age function as a source for P (upward $P_{flux F}$) whereas surface soils for STA with longer operation age function as a net sink for P (downward $P_{flux F}$; Figure 2-9). However, since no STA has experienced a net export of P at its outflow, they have been functioning as a net sink for P removal. In STA-1W, after 13 years of operation, net downward P flux from floc layer to the surface soil and into the underlying sub-surface soils was inferred from mass balance calculations. This result

could be an artifact of using a fixed soil core depth (top 10 cm) for mass balance calculations without taking into account the actual depth of RAS, which accumulated after the STA became operational. In the absence of an actual boundary between RAS and pre-STA soil, an accurate mass balance calculation and determination of precise movement of P within the soil profile is not possible. However, this mass-balance approach provides a preliminary understanding of the distribution of P retained from the water column within STA soil profile across the three major compartments– floc, surface soil and sub-surface soil.

Some STAs experienced a drastic increase in their surface soil P storage relative to the background levels (P_{BG}). These increases could not be fully accounted for by TP retained from the water column, suggesting an alternate pathway of P movement from surface soils to floc via vegetation. In such cases, the role of vegetation in mining and redistributing sub-surface P from organic soils to the surface becomes highly important. Results from this study agree with mesocosm experiments conducted with TP surface-water concentrations ($<100 \mu\text{g L}^{-1}$), which demonstrated that emergent macrophytes mined over 50% of their total P requirements from the underlying peat soil (White and others, 2006; White and others, 2004). The P mass-balances in this study also highlighted the need to identify accurately the boundary between RAS and pre-STA soil, to enable more robust P storage calculations and determination of soil and P accretion rates in the STAs.

Impact of STA Age on Phosphorus Retention

The success of Everglades restoration depends on sustainable P removal from surface runoff and continued sequestration of P in non-reactive forms within accreting soils of the STAs. Design of the original six Everglades STAs was based on steady

state model calibrations involving a constant areal rate of P removal dependent on inflow P concentration (Kadlec, 1997; Kadlec, 2005; Walker, 1995). It was assumed that accumulation of refractory stable P forms would continue at a steady rate after an initial brief stabilization period in each STA. However, the STAs experienced a decline in annual floc and surface soil P accretion rates as the systems aged (Figures 2-10 and 2-11) suggesting that smaller annual increments of P were stored in the floc and soil layer over time. Alternatively, in younger STAs, most of the 0-10 cm soil depth may have been native soil with only a small fraction of consolidated floc whereas in older STAs most of the 0-10 cm soil represented consolidated floc and very little native soil (Figures 2-2 and 2-3).

The declining trend in annual P accretion with STA age may indicate exhaustion of localized sites for P adsorption in the soil matrix and saturation of existing demands by vegetation and luxury uptake by microbial communities (Carleton and others, 2001). It is also possible that the PLR in the STAs over their operational history exceeded Richardson's 'one gram rule' (Qian and Richardson, 1997; Richardson and Qian, 1999). This could have resulted in loss of P from STA soils, which was subsequently observed as a declining trend in P accretion over time.

While it is hard to determine if the maximum potential for P uptake by biotic communities has been reached, a comparison of soil P storages using long-term data analysis over the period of each STA's life suggests that a constant measure of refractory organic P was not uniformly accreted over the entire course of STA operation. This observation could, however, be an artifact of the sampling design, where soil samples represented only the top 10 cm of nutrient storage and missed a portion of

accreted P in cases when the RAS depth was greater than 10 cm. In the absence of fixed soil reference points, a valid conclusion cannot be drawn unless a clear boundary between RAS and pre-STA soil is known. With the current soil data, it was not possible to distinguish between native soil and consolidated floc. The amount of error in SPS calculation changed with STA age as the boundary of the 0-10 cm surface soil shifted with new soil accretion. Soil P storage calculations only reflected the top 10 cm of soil, possibly underestimating the total accretion of nutrients over the POR in cases of old STAs where RAS depth exceeded 10 cm.

The observed decrease in SPS in some STAs could therefore represent upward shifting of the 10-cm boundary in the soil layer. Over time, as more detrital material was consolidated and incorporated as soil, the top 10-cm layer accounted for more and more of the newly accreted material while the proportion of the 0-10 cm soil fraction composed of pre-STA soil in previous cores was reduced. Since SPS was calculated only from the top 0-10 cm soil layer, this could have resulted in overall underestimation of total accreted P since the inception of a STA, and eventually being perceived as a declining trend in P accretion.

Summary

The Everglades STAs are unique because of their large size and low target outflow TP concentrations ($\sim 13\text{-}19 \mu\text{g L}^{-1}$). The general range of inflow P concentrations in many other treatment wetlands are 1–2 orders of magnitude greater than the STAs. The large expanse of STAs, past land use (agricultural farm or historic wetland), extreme weather events (e.g., droughts, storms), and suspension of operations due to nesting of migratory water fowl species, are only a few examples of the complex challenges experienced during the management of the STAs. The status of STA

operational phases (start-up, routine operation, or recovery) and management activities (e.g., drawdown, cell rehabilitation, vegetation conversion and control) also influence outflow P concentrations from the STAs. Each of these factors has some bearing on the overall treatment performance of the STAs, and detailed understanding of the fate and transformation of sequestered P in STA soils may help adaptive management to optimize STA efficiency. The results presented in Chapter 1 (this chapter) set the stage for subsequent forays into enhancing our understanding of P processing in wetlands by using the STAs as a case example. The next chapter presents details on development of a simple technique for identifying the boundary between RAS and pre-STA soil by utilizing stratigraphic properties of soils that were formed after startup of the STAs.

Table 2-1. Bulk density (g cm^{-3} ; mean \pm SD) for floc and soil samples from the STAs. Total number of samples is presented in parentheses.

WY	STA-1E	STA-1W	STA-2	STA-3/4	STA-5	STA-6
Floc						
2003	--	--	--	--	0.06 \pm 0.06 (58)	--
2004	--	0.08 \pm 0.04 (88)	0.10 \pm 0.08 (70)	--	0.08 \pm 0.06 (104)	0.04 \pm 0.03 (22)
2007	0.26 \pm 0(1)	0.06 \pm 0.07 (47)	0.15 \pm 0.04(62)	0.11 \pm 0.04 (28)	0.11 \pm 0.03 (15)	--
Soil						
1995	--	0.18 \pm 0.0 6(36)	--	--	--	--
1996	--	0.20 \pm 0.06 (23)	--	--	--	--
2000	--	0.26 \pm 0.06 (31)	--	--	--	--
2001	--	--	0.21 \pm 0.08(10)	--	0.34 \pm 0.14 (10)	0.52 \pm 0.17 (10)
2003	--	--	--	--	0.50 \pm 0.25 (59)	--
2004	--	0.22 \pm 0.06 (89)	0.23 \pm 0.06(74)	--	0.47 \pm 0.24 (108)	0.58 \pm 0.24 (31)
2005	1.07 \pm 0.44(94)	--	--	0.34 \pm 0.1 (323)	--	--
2006	--	0.24 \pm 0.05 (28)	--	--	--	--
2007	1.01 \pm 0.37(103)	0.26 \pm 0.09(133)	0.25 \pm 0.08(115)	0.27 \pm 0.1 (289)	0.34 \pm 0.15 (82)	--
2008	--	0.23 \pm 0.05 (52)	--	--	--	--

Table 2-2. Mean floc depth across the STAs (cm; mean \pm SD) for sampling years.

WY	STA-1E	STA-1W	STA-2	STA-3/4	STA-5	STA-6
2003	--	--	--	--	6.8 \pm 2.7	--
2004	--	18.2 \pm 7.3	5.2 \pm 2.4	--	9.0 \pm 4.0	7.8 \pm 3.1
2007	9.0 \pm 0 [#]	4.4 \pm 2.3*	7.1 \pm 3.6	7.3 \pm 3.8	5.1 \pm 2.7	--

STA-1E: Only one floc sample was recorded.

* STA-1W: Mean floc depth was calculated by using available data from Cells 2, 4 and 5B only.

Table 2-3. Total phosphorus concentration in floc and soils in the STAs (mg P kg⁻¹; mean \pm SD).

WY	STA-1E	STA-1W	STA-2	STA-3/4	STA-5	STA-6
Floc						
2003	--	--	--	--	1180 \pm 444	--
2004	--	726 \pm 272	856 \pm 339	--	824 \pm 325	1028 \pm 520
2007	644 \pm 0*	1192 \pm 261	870 \pm 167	1072 \pm 130	1187 \pm 485	--
Soil						
1995	--	479 \pm 130	--	--	--	--
1996	--	353 \pm 96	--	--	--	--
2000	--	507 \pm 194	--	--	--	--
2001	--	--	521 \pm 157	--	465 \pm 74	236 \pm 103
2003	--	--	--	--	465 \pm 197	--
2004	--	272 \pm 77	506 \pm 133	--	445 \pm 139	455 \pm 236
2005	177 \pm 136	--	--	688 \pm 187	--	--
2006	--	452 \pm 188	--	--	--	--
2007	160 \pm 135	598 \pm 316	511 \pm 186	599 \pm 175	615 \pm 396	--
2008	--	500 \pm 226	--	--	--	--

* STA-1E: Only one floc sample was recorded.

Table 2-4. Total phosphorus areal storage in floc and soils in the STAs (g P m⁻²; mean ± SD). Values represent entire floc depth and top 10 cm of surface soil.

WY	STA-1E	STA-1W	STA-2	STA-3/4	STA-5	STA-6
Floc						
2003	--	--	--	--	3.3 ± 1.7	--
2004	--	9.6 ± 4.8	2.8 ± 2.1	--	4.4 ± 2.3	3.2 ± 2.7
2007	15.1 ± 0*	4.4 ± 1.6	8.7 ± 4.9	8.5 ± 4.6	6.7 ± 3.1	--
Soil						
1995	--	7.7 ± 1.5	--	--	--	--
1996	--	3.5 ± 1.1	--	--	--	--
2000	--	6.9 ± 3	--	--	--	--
2001	--	--	12.7 ± 5.6	--	15.2 ± 2.9	10.8 ± 2.4
2003	--	--	--	--	19.1 ± 9.6	--
2004	--	5.8 ± 2.6	12.2 ± 8.2	--	18.9 ± 8.0	23.3 ± 11.8
2005	13.2 ± 7.8	--	--	23.3 ± 8.5	--	--
2006	--	11.3 ± 6.1	--	--	--	--
2007	10.1 ± 6.2	14.6 ± 5.9	12.5 ± 6	16.1 ± 6.7	20.7 ± 13.7	--
2008	--	10.7 ± 4.7	--	--	--	--

* STA-1E: Only one floc sample was recorded.

Table 2-5. Comparison of total phosphorus removed from the water column and floc phosphorus storage and soil phosphorus storage. STA area used for calculations is shown.

	Water Year	Age (yr)	STA area (ha)	FPS (g P m ⁻²)	SPS (g P m ⁻²)	P storage (g P m ⁻²)	Total P in STA (mt)	Phosphorus removed from water*(mt)
STA-1E	2007	3	2073	--	10.10	10.1	209	24
STA-3/4	2007	4	6683	8.50	16.10	24.6	1644	222
STA-6	2004	6	912	3.16	23.29	26.5	241	25
STA-2	2007	8	3329	8.70	12.50	21.2	706	181
STA-5	2007	8	2462	6.70	20.70	27.4	675	158
STA-1W	2007	13	2695	4.40	14.70	19.1	515	339

*Data source: Pietro and others, (2008), Table 5-2 for all STAs except STA-6; for STA-6 SFER 2005, Table 4-1 (Goforth and others, 2005).

Table 2-6. Total nitrogen areal storage in floc and soils in the STAs (g N m⁻²; mean ± SD). Values represent entire floc depth and top 10 cm of surface soil.

WY	STA-1E	STA-1W	STA-2	STA-3/4	STA-5	STA-6
Floc*						
2003	--	--	--	--	96 ± 61	--
2007	--	92 ± 43	125 ± 66	139 ± 72	170 ± 79	--
Soil						
1995	--	478 ± 122	--	--	--	--
1996	--	637 ± 133	--	--	--	--
2000	--	770 ± 163	--	--	--	--
2001	--	--	605 ± 89	--	809 ± 100	623 ± 172
2003	--	--	--	--	865 ± 193	--
2004	--	622 ± 145	609 ± 117	--	877 ± 203	1029 ± 353
2005	345 ± 246	--	--	832 ± 179	--	--
2006	--	646 ± 123	--	--	--	--
2007	312 ± 141	792 ± 159	642 ± 123	646 ± 178	689 ± 223	--
2008	--	622 ± 115	--	--	--	--

*Total nitrogen concentration for floc was not available for STAs 1W, 2, 5 and 6 during WY2004.

Table 2-7. Total carbon areal storage in floc and soils in the STAs (kg C m⁻²; mean ± SD). Values represent entire floc depth and top 10 cm of surface soil.

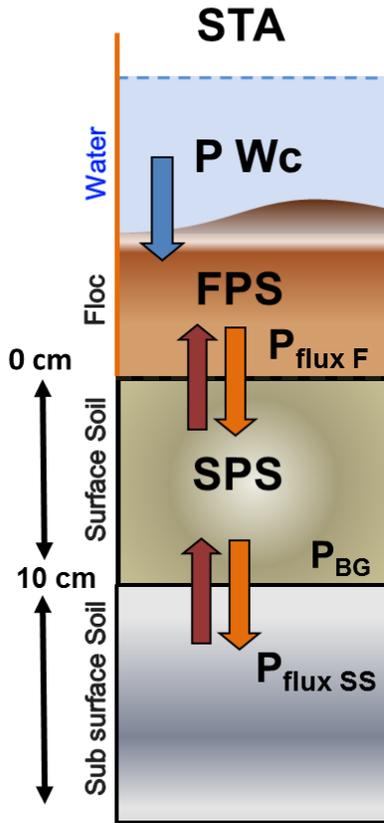
WY	STA-1E	STA-1W	STA-2	STA-3/4	STA-5	STA-6
Floc*						
2003	--	--	--	--	1.30 ± 0.85	--
2007	--	1.52 ± 0.64	2.28 ± 1.2	2.16 ± 1.2	2.41 ± 1.3	--
Soil						
1995	--	10.7 ± 1.6	--	--	--	--
1996	--	8.09 ± 2.9	--	--	--	--
2000	--	6.24 ± 0.74	--	--	--	--
2001	--	--	10.2 ± 1.5	--	11.8 ± 1.6	8.3 ± 2.1
2003	--	--	--	--	12.3 ± 2.5	--
2004	--	10.3 ± 2.2	9.04 ± 2.4	--	12.4 ± 2.6	13.8 ± 3.7
2005	5.17 ± 3.6	--	--	12.69 ± 2.8	--	--
2006	--	10.8 ± 2.0	--	--	--	--
2007	4.55 ± 2.1	8.6 ± 1.4	10.3 ± 2.1	9.7 ± 2.7	9.75 ± 3.2	--
2008	--	10.1 ± 1.5	--	--	--	--

*Total carbon concentration for floc was not available for STAs 1W, 2, 5 and 6 during WY2004.

Table 2-8. Variation in areal and total nutrient storages in the STAs with different ages. Nutrient masses represent entire floc depth and top 10 cm of surface soil.

STA	WY	Age (yr)	Area (ha)	Areal storage (floc + surface soil, g m ⁻²)			Total mass in STA (mt)		
				P	N	C	P	N	C
STA-1E	2007	3	2073	10.1	312	4550	209	6,470	94,400
STA-3/4	2007	4	6683	24.6	785	11870	1644	52,460	793,520
STA-6	2004	6	912	26.5	1,029	13790	241	9,380	125,710
STA-2	2007	8	3329	21.2	767	12570	706	25,530	418,480
STA-5	2007	8	2462	27.4	859	12160	675	21,150	299,450
STA-1W	2007	13	2695	19.1	884	10100	515	23,820	272,160

Phosphorus mass balance for STAs



All values expressed in $g P m^{-2}$

P_{Wc} = To date water column P retained
[Inflow TP conc. – Outflow TP conc.]

FPS = Floc P storage
[WY2007]

$P_{flux F}$ = Floc and soil interface P flux
[$P_{flux F} = FPS - P_{Wc}$]

SPS = Soil P storage
[WY2007]

P_{BG} = Background soil P storage
[Earliest soil sampling data]

$P_{flux SS}$ = Soil and sub surface soil P flux
[$P_{flux SS} = (SPS - P_{BG}) + P_{flux F}$]

Figure 2-1. Phosphorus mass balance calculations for soil P storage with respect to net P retained from the water column. All values are in $g P m^{-2}$. Arrows indicate flux of P between compartments. Top row arrow indicates direction of P movement between water and floc. Middle row arrows show P movement between floc and surface soil (0-10 cm). Lower row arrows indicate P movement between surface (0-10 cm) and sub-surface soil (10-30 cm).

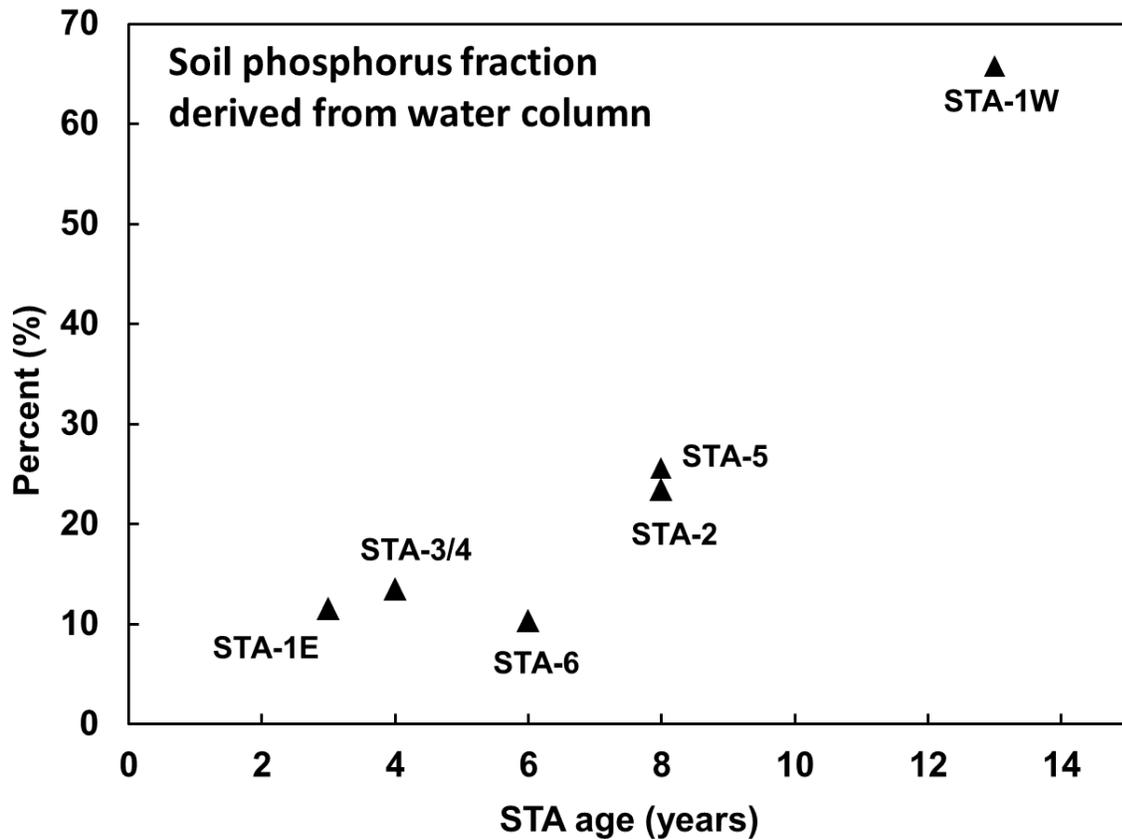


Figure 2-2. Relationship between STA age and fraction of total phosphorus storage in floc + soil derived from the water column.

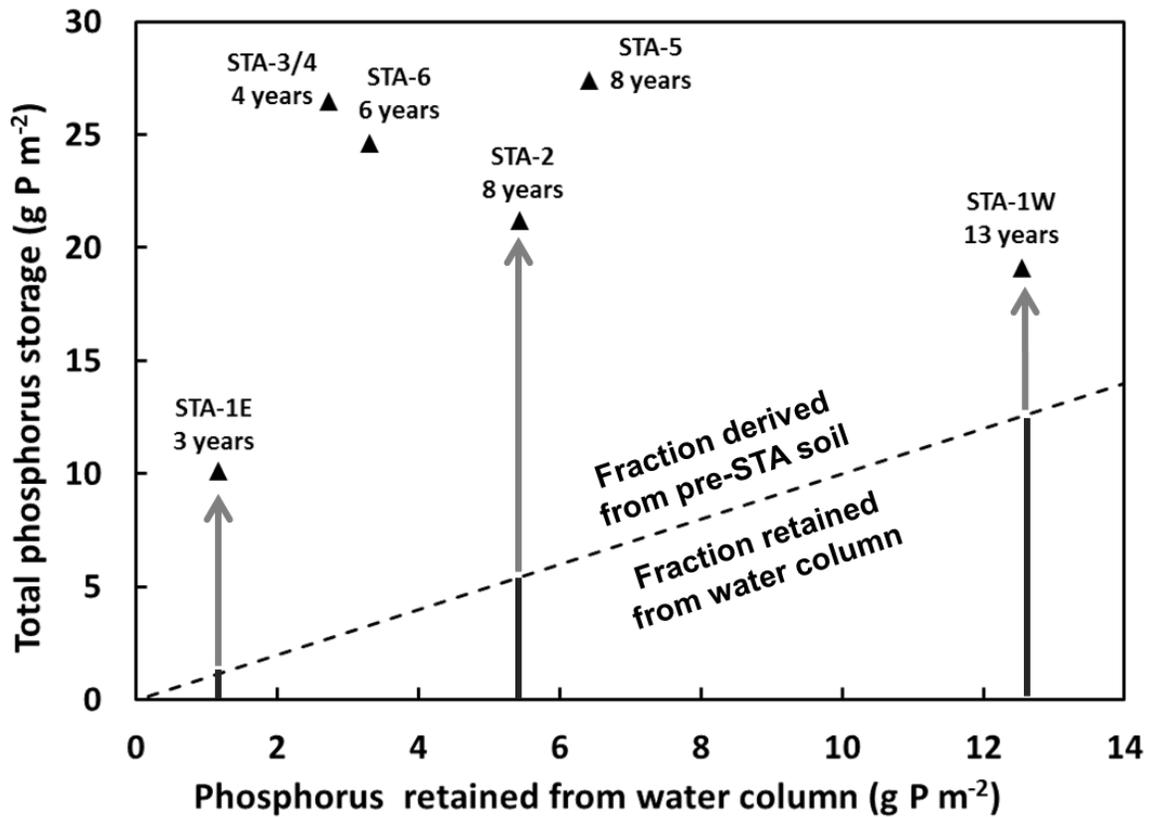


Figure 2-3. Relationship between total P retained from the water column through WY2007 and total P storage in floc + soil (g P m⁻²). A one to one (1:1) line differentiates between P derived from pre-STA soil and P retained from the water column.

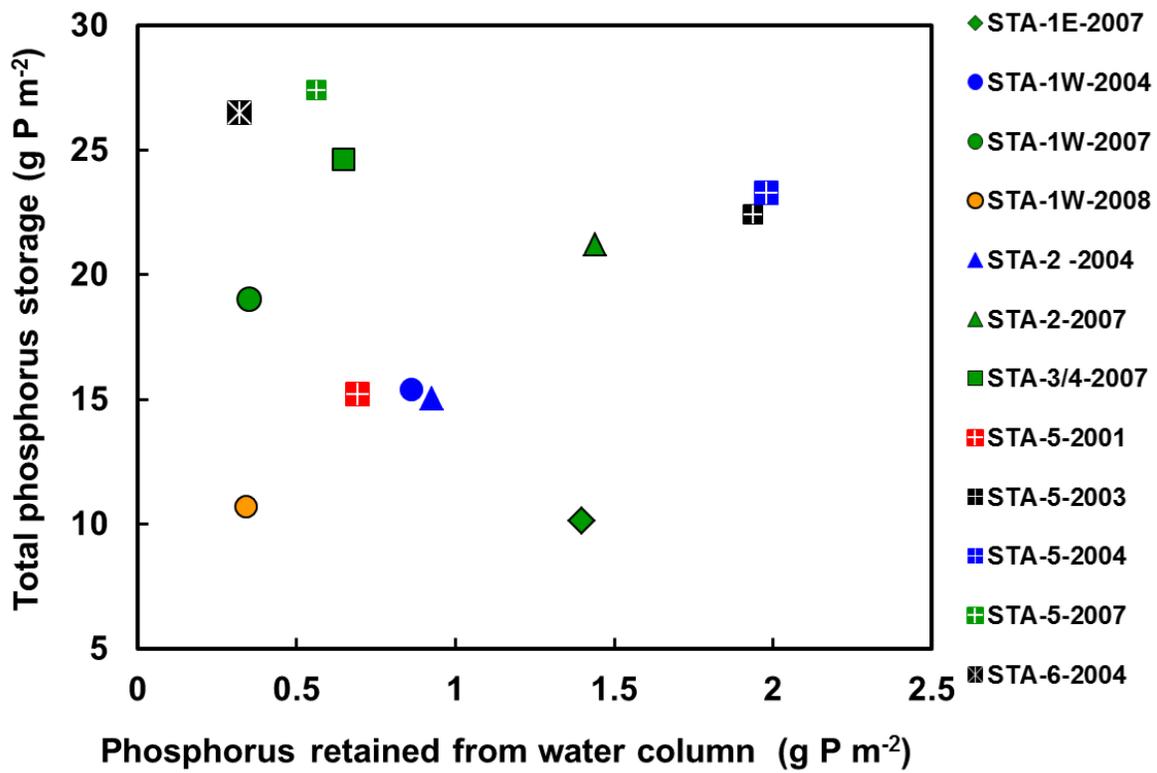


Figure 2-4. Relationship between total P retained (g P m⁻²) from the water column and total P storage in floc + soil (g P m⁻²). Data represent annual STA area-weighted averages.

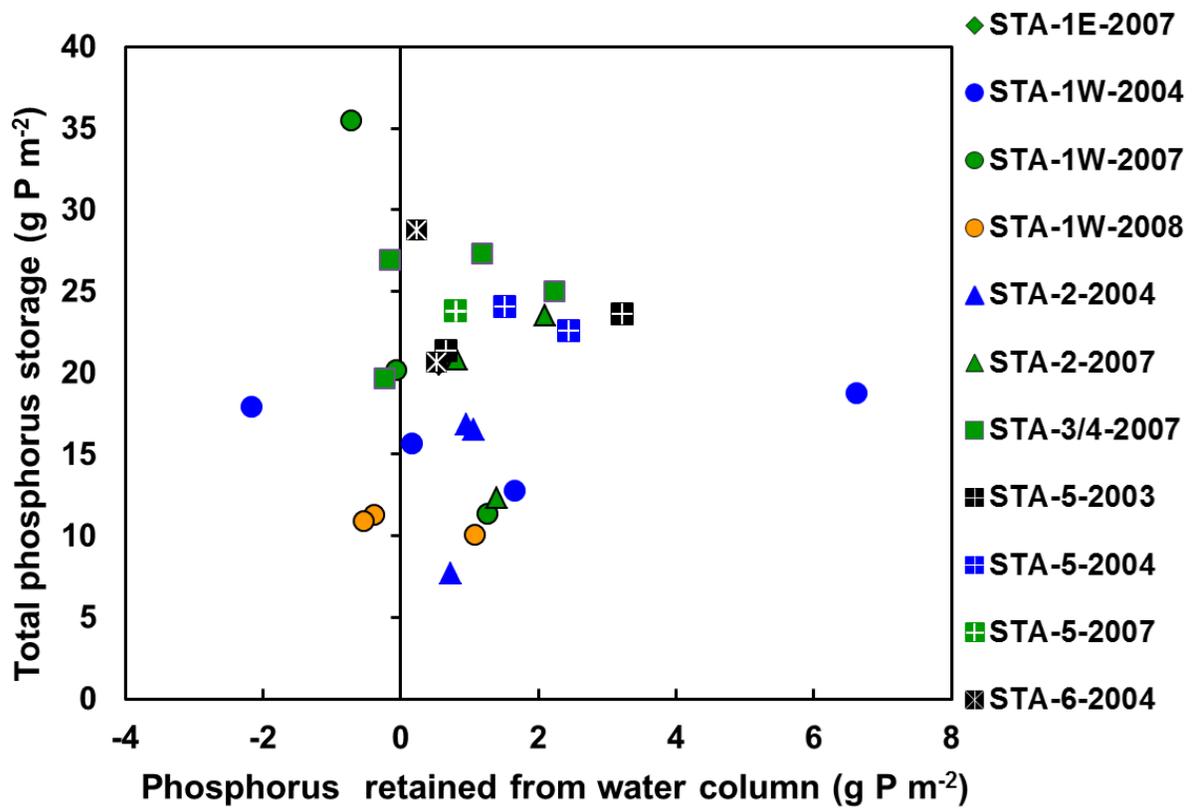


Figure 2-5. Relationship between total P retained (g P m⁻²) from water column and total P storage in floc + soil (g P m⁻²). Data represent annual cell averages (not area-weighted).

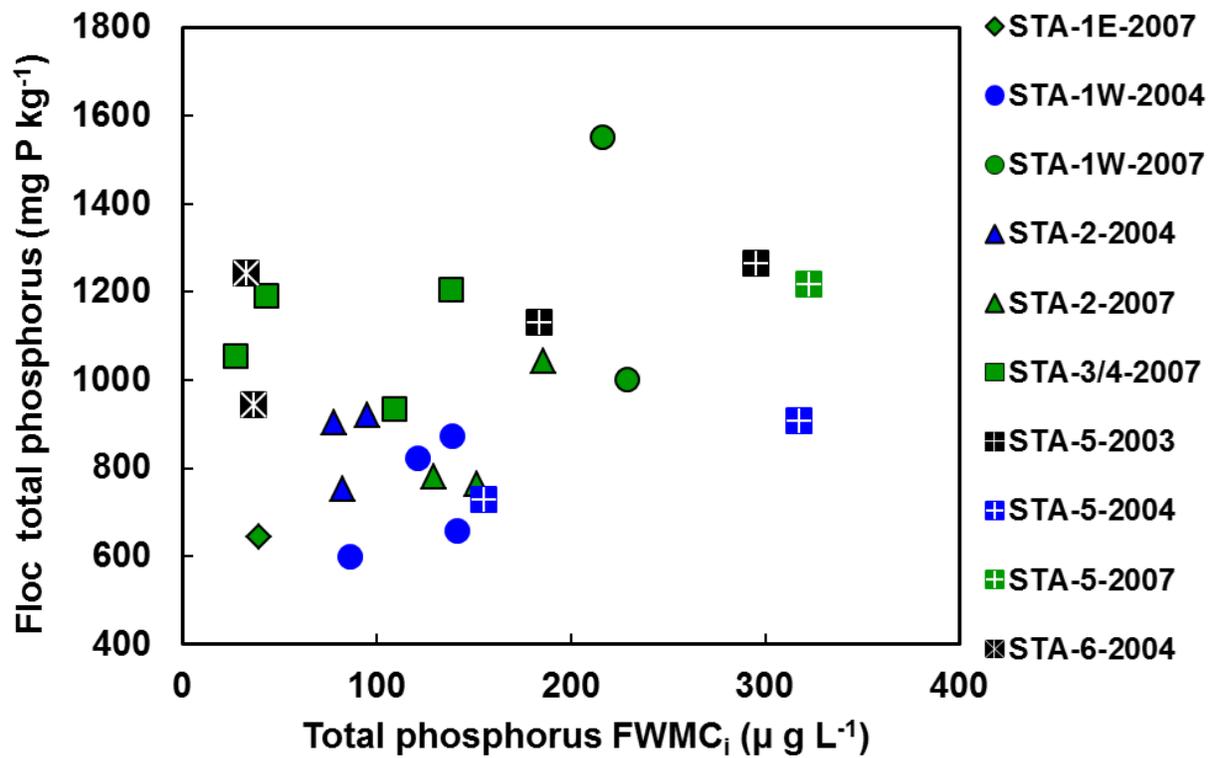


Figure 2-6. Relationship between floc total P concentration (mg P kg⁻¹) and inflow total P flow-weighted mean concentration (FWMC; μg L⁻¹). Data represent annual cell averages.

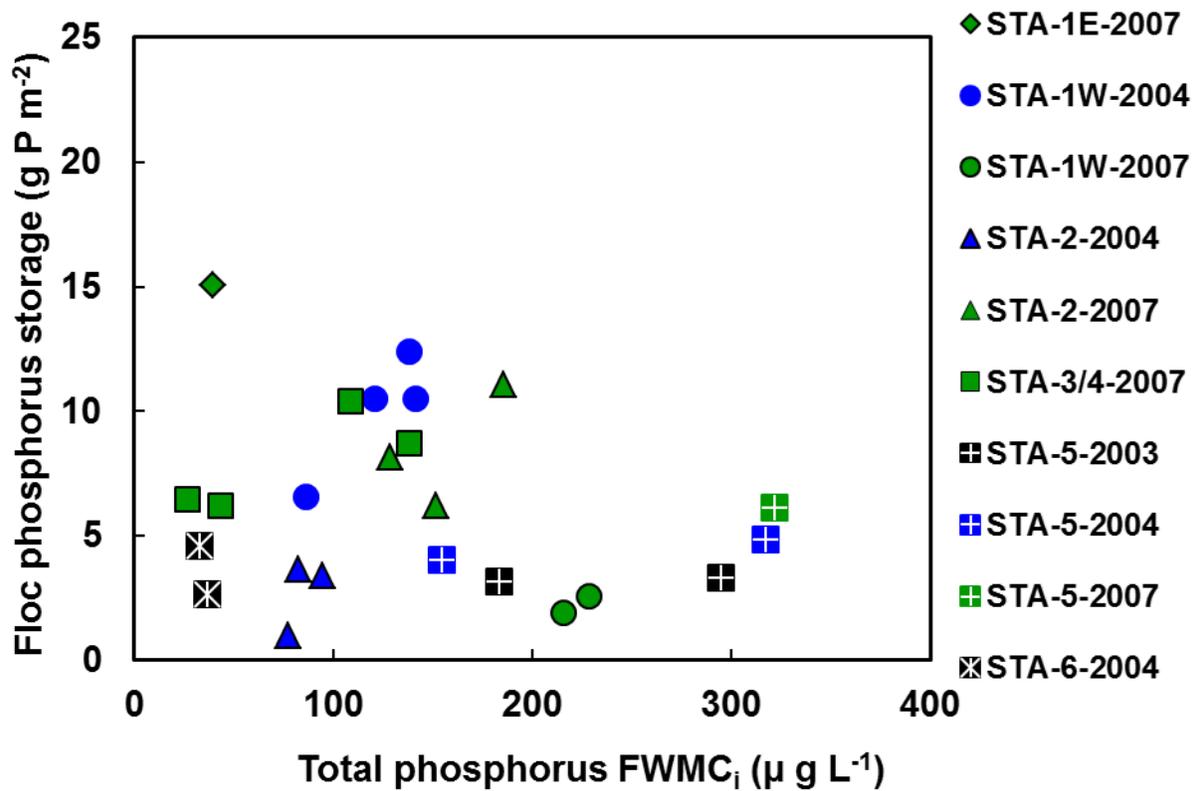


Figure 2-7. Relationship between floc P storage (g P m^{-2}) and inflow total P flow-weighted mean concentration (FWMC; $\mu\text{g L}^{-1}$). Data represent annual cell averages.

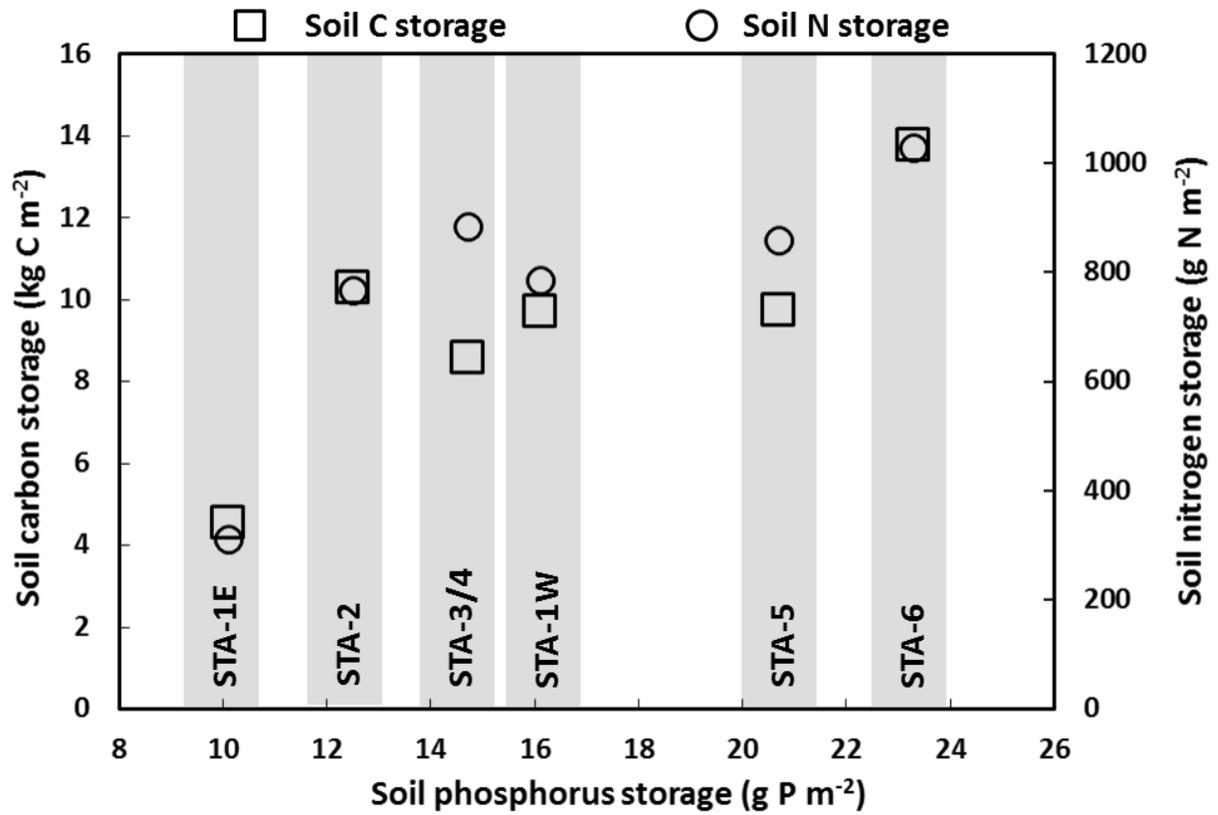


Figure 2-8. Relationship between soil carbon storage (kg C m⁻²) and soil P storage (g P m⁻²) in WY2007 except for STA-6 data, which are from WY2004.

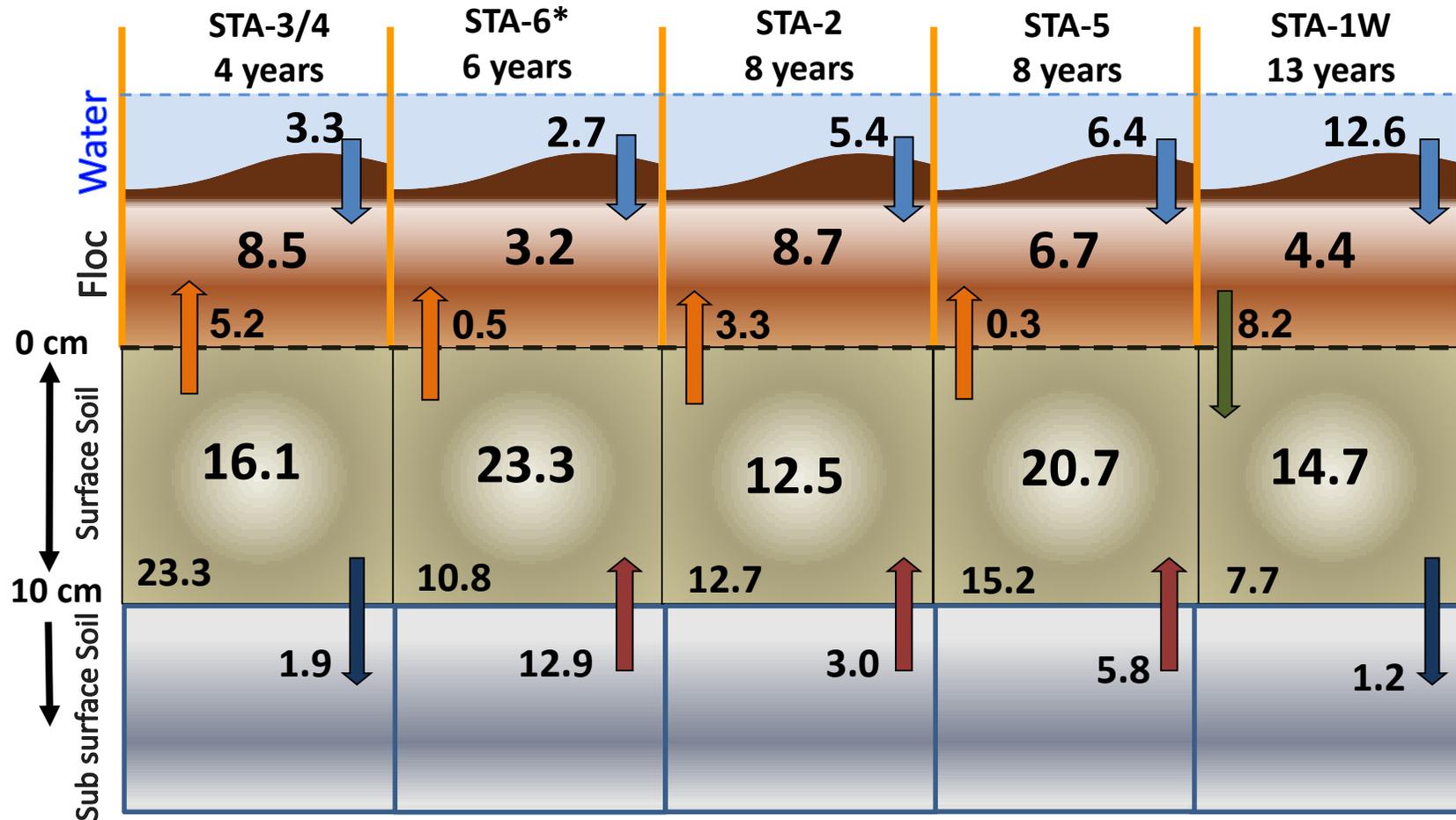


Figure 2-9. Phosphorus mass balance calculations for soil P storage with respect to net P retained from the water column. All values are in $g P m^{-2}$. Arrows indicate flux of P between compartments. Top row arrows indicate direction of P movement between water and floc. Middle row arrows show P movement between floc and surface soil (0-10 cm). Lower row arrows indicate P movement between surface (0-10 cm) and sub-surface soil (10-30 cm).

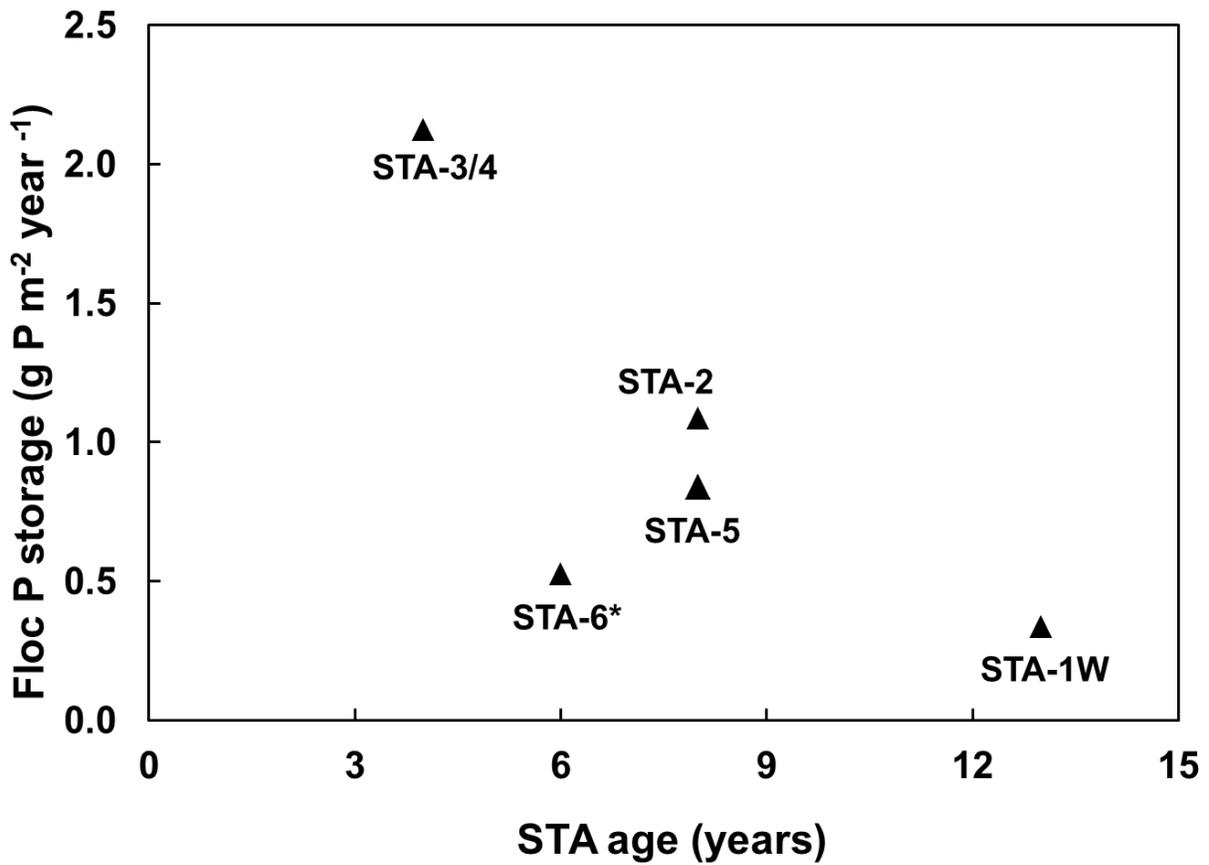


Figure 2-10. Relationship between mean floc P storage per year ($\text{g P m}^{-2} \text{ yr}^{-1}$) and STA age. *STA-6 data pertains to WY2004 while other STAs data represent WY2007.

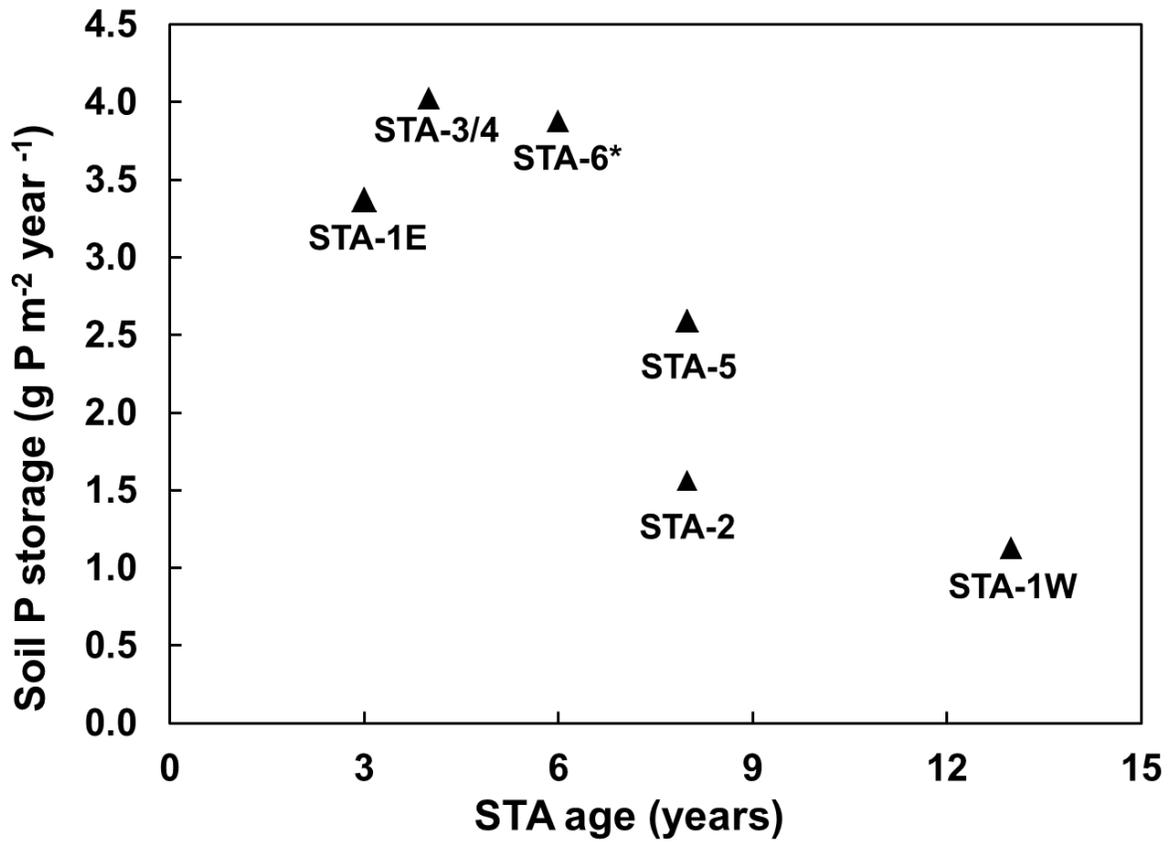


Figure 2-11. Relationship between mean surface soil (0-10 cm) P storage per year (g P m⁻² yr⁻¹) and STA age. *STA-6 data pertains to WY2004 while other STAs data represent WY2007.

CHAPTER 3 CHANGE POINT TECHNIQUE FOR MEASUREMENT OF SOIL ACCRETION RATES IN CONSTRUCTED WETLANDS

Background

Wetlands receive sediments, nutrients, and other contaminants from various point and non-point sources. As such, they serve as sinks, sources, and transformers of influent materials (Kadlec and Wallace, 2009; Reddy and DeLaune, 2008; Rooth and others, 2003). Pollutants removed from the water column are lost to the atmosphere, taken up by vegetation or incorporated in soil. The particulate fraction of inflow and plant litter material accretes in the system. This newly accreted material, referred to as recently accreted soil (RAS), serve as the long-term integrator of prevailing wetland conditions and preserves a record of nutrient loading (Inglett and Reddy, 2006; Reddy and DeLaune, 2008; Smol, 1992). Soil that existed prior to wetland creation or prior to a perturbation in a wetland's natural state generally exhibits physico-chemical characteristics different from RAS. Such differences between RAS and the native soil forms an 'artificial' boundary between the two layers. Therefore, investigation of wetland soil profile characteristics could provide reliable markers that correspond to the transition zone between RAS and native soil in the depth profile. These markers can be utilized for measuring soil accretion rate in wetlands by identifying this boundary and measuring RAS that accrued over a known period.

Wetland soils provide a long-term sink for various pollutants (Reddy and DeLaune, 2008) and therefore soil accretion rates have been related to the performance of treatment wetlands (Kadlec, 2009). In addition, buildup of accreted soils has a potential to adversely affect treatment efficiency of constructed wetlands because of a reduction in hydraulic volume and retention time. Outflow nutrient concentrations are

also impacted by the interaction of RAS with the overlying water column (Kadlec and Wallace, 2009). Hence, measurement of soil accretion rates and quantification of soil elevation changes in wetlands are important for continued treatment efficiency and maintaining long-term nutrient storages in these systems. Soil accretion rates in wetlands are regulated by existing physical, chemical and biological conditions including nutrient and sediment loading, hydrologic regimes and the seasonal cycle of vegetation growth and senescence (Callaway and others, 1997; Callaway and others, 1996a; Craft and Richardson, 1993b; Reddy and others, 1993). Thus, the soil build-up represents an integrated outcome of multiple processes operating simultaneously in a wetland system.

Several methods have been developed to measure vertical soil accretion in coastal marsh areas (Callaway and others, 1997; Church and others, 1981; Ibanez and others, 2010; Langley and others, 2009; Morse and others, 2004). These methods were used to determine soil elevation changes relative to eustatic sea level rise. Few studies, however, have been conducted in inland freshwater wetlands (Craft and Richardson, 1993a; Craft and Richardson, 1993b; Reddy and others, 1993; Rybczyk and others, 2002) and constructed wetlands (Harter and Mitsch, 2003; Kadlec, 2009). Commonly available techniques for soil elevation measurement can be used for measuring accretion over short periods (months to years) (Thomas and Ridd, 2004), or for longer periods (decades to centuries) (Brenner and others, 2001; DeLaune and others, 1978). Accretion rate measurement techniques can also be grouped on the basis of methodology: a) use of tracers (depositional markers), b) direct elevation change measurement (using specialized instruments) and c) topographic surveys.

Accretion measurement methods employ sophisticated techniques that require specific equipment and field conditions for successful implementation. For example, tracer techniques using radiometric markers are only applicable in wetlands that have been functional for a sufficiently long duration to exhibit a signature corresponding to an enrichment peak in accreted sediments. Other accretion methods depend on artificially introduced markers (such as feldspar clay) within the soil horizon to determine accretion of material over time. Use of surface elevation tables (SETs) and surveying requires using specialized equipment in the field. All existing methods depend on specialized skills during deployment, i.e., retrieval of equipment and conducting surveys under submerged conditions. Additionally, the abovementioned requirements limit the application of existing techniques at multiple sites. The absence of a straightforward and simple soil accretion measurement technique for wetlands presents a challenge for estimating the rate of soil formation and how it affects long-term nutrient storage in wetland soils. Wetland managers could potentially benefit from this information to develop appropriate strategies to enhance the longevity and efficiency of treatment wetlands.

This chapter presents results of a study conducted in large sub-tropical treatment wetlands in south Florida to test a new and relatively simple change-point technique (CPT) for determining soil accretion rates.

Methods

Site Description

Three large constructed wetlands (STA-1W, STA-2 and STA-3/4) in South Florida were chosen for this study. These wetlands are part of a network of treatment wetlands known as the Stormwater Treatment Areas (STAs) (Figure 3-1). At the time of

sample collection, the operational age of the selected STAs ranged from 6-16 years. The STAs were constructed with a uniform structural configuration that includes a combination of flow-ways that are comprised of treatment cells, with each cell having one dominant vegetation community – emergent aquatic vegetation (EAV), or submerged and floating aquatic vegetation (SAV/FAV) (Goforth, 2005). Intact soil cores were collected along a transect parallel to the flow direction in each cell. The total number and location of sampling sites was determined by taking into consideration the size and shape of each cell. Existing quarter-mile-grid sampling maps obtained from the SFWMD were utilized to identify the sampling locations in this study. Detailed information about three STAs (Appendix B) and sample collection maps (Appendix C) and sampling sites is presented in Appendix D (Tables D-1, D-2 and D-3).

STA-1W: As a part of the long-term management goals of STA-1W, rehabilitation activities were carried out during WY2007-08, including tilling and demucking in Cell 2B and Cell 4 and an effort to convert from EAV to SAV in Cell 3. Soil samples collected from these cells were not subjected to isotopic ratio analysis, but all other analyses were carried out. Soil sampling took place in July 2009. A total of 41 soil cores were collected (Appendix C, Figure C-1). Triplicate samples were collected from eight sites.

STA-2: Soil sampling was carried out in October 2009. A total of 29 intact soil cores were collected (Appendix C, Figure C-2). Triplicate samples were collected from five sites.

STA-3/4: As of 2008, Cells 1A, 1B, 2A and 3A were designated as EAV and were managed as such. Cells 2B and 3B were designated SAV. However, Cells 1B and 2B were converted to SAV in WY2009, and were considered as SAV for this study. Soil

cores were collected in January and February 2010. A total of 58 soil cores collected from EAV and SAV cells (Appendix C, Figure C-3). Triplicate samples were collected from nine sites.

Soil Sampling and Processing

Soil cores (n=128) were collected using a stainless steel tube (10.2-cm internal diameter [ID], 0.2-cm wall thickness [WT]). Depth of soil cores ranged from 10 - 40 cm, as limited by the depth of bedrock from the wetland soil surface. Soil cores were transferred into clear cellulose acetyl butyrate tubes (10.2-cm ID, 0.16-cm WT) in the field and transported to the laboratory for storage at 4°C until they were analyzed.

Thickness of the unconsolidated surface detrital layer (floc) was measured before removing this material from the soil core. The remaining soil core was then sectioned at 2-cm intervals along its entire length. The total number of such sections were 733 (STA-1W), 505 (STA-2) and 573 (STA-3/4) [For details see Tables C-1, C-2 and C-3 (Appendix C)]. Surface material (floc) and 2-cm soil sections were dried at 70°C for bulk density determination. Dried samples were finely ground using a ball mill and passed through a 2-mm mesh before chemical analysis.

Chemical and Isotopic Analysis

Total P was determined by the ashing and HCl digestion (Andersen, 1976), using standard molybdate colorimetry for analysis (U.S. Environmental Protection Agency, 1993). Total nitrogen (TN), total carbon (TC) and stable isotope ratios of C and N ($\delta^{13}\text{C}$ and $\delta^{15}\text{N}$) were determined using a Costech Elemental Analyzer (Model 4010, Costech Analytical Industries, Inc., Valencia, CA) coupled to a Finnigan MAT Delta^{Plus} XL Isotope Ratio Mass Spectrometer (CF-IRMS, Thermo Finnigan, San Jose, CA) via a Finnigan ConFlo II interface. Elemental calibration was accomplished using peach leaves (2.93%

N, 44.65% C). Inorganic C was removed prior to $\delta^{13}\text{C}$ analysis using the HCl-fumigation (Harris and Horwath, 2001). Soil samples were analyzed separately for $\delta^{15}\text{N}$, TC and TN (non-acid-fumigated samples) and $\delta^{13}\text{C}$ (acid-fumigated samples) to avoid potential error in the $\delta^{15}\text{N}$ measurement due to HCl fumigation. Ratios of C- and N-stable isotopes (R_{sample}) are expressed as per mille (‰) differences from the ratio of a standard (R_{std} , atmospheric N_2 and Pee Dee Belemnite, for N and C, respectively) using delta notation (δ) as : $\delta_{\text{sample}} = [(R_{\text{sample}} / R_{\text{std}}) - 1] \times 1000$.

Change-point Analysis

A change-point (CP) refers to a point along a distribution of values of a variable where the values before and after the change-point are significantly different. The method for identification of a change-point uses deviance reduction along a distribution of points such that the sum of deviances on either side of the change-point is minimized compared to the deviance of the overall dataset. The percent error reduction associated with splitting the data is calculated by an iterative process identifying a point (change-point) that minimizes the deviance (Qian and others, 2003). A schematic depiction of how a CP was used as an indicator of the boundary between RAS and native soils in a treatment wetland is presented in Figure 3-2.

The software programme SegReg¹ (Oosterbaan and others, 1990), was used to identify the CP in soil variables along depth profiles, with a 90% confidence interval (CI). The SegReg identified one or more CPs in the data, whereupon separate linear regressions were run on the data subsets as defined by the CPs. The location where these line segments intersected was interpreted as the boundary between RAS and native soil. The depth from the soil surface to the first CP corresponded to the thickness

¹ <http://www.waterlog.info/segreg.htm>

of RAS layer. The depth profiles for physico-chemical properties such as bulk density, TP, TN, TC, nutrient ratios (N:P, C:P and C:N), and $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ were used to identify CPs in soil cores using SegReg program. Only four variables - bulk density, TP content, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ yielded consistent CPs along depth profiles, and allowed to identify RAS depth. An example of the SegReg output for a representative soil core, using all four variables is presented in Figure 3-3.

The RAS depths obtained by SegReg for each of the four variables - bulk density, TP content, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$ were averaged to obtain mean RAS depth for each soil core. Mean RAS depth for each soil core from a cell were then averaged to obtain the mean RAS depth for that cell. Mean RAS depths for all cells within a STA were subsequently used to calculate a grand mean RAS depth for that STA. Comparison of differences in RAS depths among parameters within each STA were tested with one-way ANOVAs followed by the Tukey-Kramer HSD tests ($p < 0.05$) using JMP (Version 7; SAS Institute Inc., Cary, NC, 1989-2007).

Operational age of STAs at the time of soil sampling was used to calculate mean annual soil and P accretion rates. Operation ages for STA-1W, STA-2 and STA-3/4 were 16, 10 and 6 years, respectively. However, Cells 5A and 5B in STA-1W were constructed much later (WY2009), so the operational age for those cells was taken as 10 years. In cases where the CP depth was an odd value, the average bulk-density of the RAS layer was calculated using the mean bulk densities of the 2-cm soil sections above and below the CP depth, and then using this mean value along with all other RAS sections to calculate mean bulk density for the whole RAS layer. For example, if the CP depth was 7 cm, then the average bulk-densities for the 4-6 cm and 6-8 cm soil

sections were used along with the bulk densities for the 0-2 and 2-4 cm soil sections to calculate the average bulk density for RAS. Average TP (mg P kg^{-1}) for RAS was also calculated in a similar manner. Mean bulk density and TP for the whole RAS layer were used for calculating total P storage in RAS (g P m^{-2}) and for calculating annual P accretion rates ($\text{g P m}^{-2} \text{ yr}^{-1}$).

The robustness of CPT was tested by determining CP depths on pre-existing data available from the Water Conservation Area-2A (WCA-2A) (Reddy and others, 1993). Reddy and others, (1993) used radiometric marker technique for determination of accretion rates where peak concentration of Cesium (^{137}Cs), a radioactive fallout product of nuclear bomb testing, corresponded to year 1963-64. Depth of ^{137}Cs peak along the soil profile represented depth of accumulated soil since 1963-64. Stratigraphic properties of WCA-2 soil cores (bulk density, TP and ^{137}Cs activity (pCi section^{-1})) were used to determine CP depth by SegReg program. The SegReg results were compared with the depth of ^{137}Cs peaks obtained for each sampling station in WCA-2A ($p=0.26$, $\alpha=0.05$, paired t-test).

Results

The mean RAS depth for STA-1W, STA-2 and STA-3/4 was 14.7 ± 5.1 cm, 11 ± 3.3 and 10 ± 4.6 cm, respectively. The mean annual soil accretion rate for STA-1W, STA-2 and STA-3/4 for an operational history of 16, 10, and 6 years, were 1 ± 0.3 cm yr^{-1} , 1.1 ± 0.3 cm yr^{-1} and 1.7 ± 0.8 cm yr^{-1} , respectively.

Within each STA, RAS depths obtained by using different soil characteristics (bulk density, TP, $\delta^{15}\text{N}$ and $\delta^{13}\text{C}$) were similar except for STA-1W (Figure 3-4). In STA-1W, RAS depth estimated by bulk density was twenty-five percent higher than that estimated by TP however this trend was not seen in STA-2 and STA-3/4. In STA-3/4,

RAS depth estimated by bulk density was thirty percent greater than that estimated by using $\delta^{13}\text{C}$, however this was not significant. Three way ANOVA results on the normalized dataset suggested a significant difference in RAS depth predicted by four parameters. Bulk density predicted fifteen percent higher CP depth in comparison to TP, however this effect was dependent on STA (site*soil variable, $p < 0.05$). In all three studied STAs, RAS depths were consistent for other two soil physico-chemical variables ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$). There was no influence of dominant vegetation on mean RAS depths determined by four soil variables across three STAs. This indicated that there was no significant influence of a specific dominant wetland vegetation on CP depths and all four variables offered similar results when used for CP estimation (Figure 3-5).

Discussion

Soil that existed prior to wetland creation (native soils) exhibit characteristics that are dissimilar from RAS (White and others, 2006). This difference in physico-chemical properties between RAS and native soil forms an 'artificial' boundary, marking the divide between two layers. This stratigraphic information conserved in the soil profile was utilized for CPT. The study was undertaken in STAs constructed on erstwhile agricultural farmland containing historically oligotrophic peat soil (Histosols). STAs were established for reducing TP inputs to the Everglades by removing influent P from the water column and sequestering it in RAS. Accreting organic soils did not differ from native soil in C and N characteristics, but had an elevated P signature, which generated a CP when analyzed using the SegReg program. Investigation of depth profiles for total C, total N, and nutrient ratios (N:P, C:P and C:N) did not produce a clear CP along soil profiles. On the other hand, analysis of stable isotope ratios of C and N along soil depth profiles yielded CPs that were consistent with those generated from bulk density and TP

values. In aquatic ecosystems, C and N isotope signatures in soil are widely used to detect changes in plant and microbial processes related to the change in existing conditions (Chang and others, 2009; Inglett and Reddy, 2006). Such changes in biogeochemical properties and processes were elucidated by examining stable isotope ratios of N and C ($\delta^{15}\text{N}$ and $\delta^{13}\text{C}$).

The mean RAS depths across different vegetation types were similar for studied soil variables in all three STAs. This suggested that the SegReg CP determination technique could be applied to wetlands with different vegetation. Additionally, the RAS depth determined using different soil properties were similar except depths estimated by bulk density and TP. It is possible that CP depth predicted by TP represents a better estimate of RAS depth in STAs in comparison to BD estimates. This may be caused by external P loading received by STAs since their inception where CP in TP profile is a better indicator of actual boundary between RAS and pre-STA soil. Bulk density, on the other hand, represents characteristics that are somewhat secondary to the direct P loading. As the mass (weight) of accreted soil increases it compresses soil to a point until the internal resistance to further compression is balanced by the force exerted by the mass of RAS. The resultant increase in BD was noticed as a CP in SegReg program; however the identifiable point of increased BD was slightly deeper than the actual boundary between RAS and pre-STA soil. This may be due to differences in composition of RAS and pre-STA soil and not due to biogeochemical processes occurring in the soil profile. Overall, reasonably accurate CP depth results could be obtained by using selective soil variables for determination of RAS depth using the SegReg CP technique in wetland systems with variable aquatic vegetation.

A decline in soil accretion rate with increasing operational age was observed. This decline in RAS depth over time could be a result of soil compaction as the weight of overlying soil increases over time. Additionally, occurrence of brief dry periods could result in oxidation and loss of STA's organic soils leading to a decrease in RAS depth. The accretion rates determined by CPT for three STAs falls within the average range (0.3-1.9 cm yr⁻¹) as observed by using other measurement techniques (Table 3-1) across a range of wetland systems.

The results obtained by CPT were compared with a well-established marker horizon technique (¹³⁷Cs peak) on an existing dataset (Reddy and others, 1993). The RAS depths and ¹³⁷Cs peak depths were not significantly different across the sampling locations (Figure 3-6, p=0.26, α=0.05, paired t-test). This observation confirmed the utility and reliability of simple CPT as an alternative to the existing methods that usually require elaborate procedures. This served as a test of reliability and robustness of CPT for determination of RAS depths and calculating annual accretion rates.

Available accretion measurement techniques vary widely on the key principle utilized for determining elevation change in wetland soils over time (Table 3-1). Tracer techniques depend on artificially introduced markers (feldspar or plaster) (Cahoon and Turner, 1989; Knaus and Gent, 1989) or atmospherically deposited radioactive Cesium and Lead (DeLaune and others, 1978; Stam, 1999). Sedimentation Erosion Tables (SET) (Boumans and Day, 1993; Eerdt, 1985; Schoot and De Jong, 1982) and Surface Elevation Table (Cahoon and others, 2002) utilize special set of plates and pins for measurement of elevation changes. Stakes and rods (Pestrong, 1965; Reed, 1989), sediment pins (Letzsch and Frey, 1980), Photo-Electronic Erosion Pin (PEEP; Lawler,

(1991)), anchored tiles (Pasternack and Brush, 1998) and the bridge method (Perillo and others, 2003) are examples of techniques using specialized instruments. Surveying methods using eco-sounder system (Takekawa and others, 2010; Verlaan and Spanhoff, 2000), dendro-geomorphic (Hupp and Bazemore, 1993), sediment flux measurements (Noe and Hupp, 2009), peat probing, water surface elevation changes, and topographic surveys (Kadlec, 2009) have also been used for calculating accretion rates in wetland ecosystems.

In comparison, the CPT offers a simple, easily implementable procedure that generates robust results. It does not require presence of a radioactive layer or an introduced marker horizon or specialized instruments for conducting a survey, which enables its rapid replication at multiple sites. The CPT is particularly useful in systems where a natural or anthropogenic perturbation is known to have impacted the biological state of a system, creating a stratigraphic signature embedded in accreted soil corresponding to a specific time in the history of a wetland.

There are, however some scenarios where use of CPT may not be advisable. For instance, high-energy systems that experience frequent suspension and resettling of sediments could result in destruction of CP signature and may not be appropriate for application of CPT. Also, soil accretion rates cannot be calculated for wetlands that lack information about operational history or a specific historical time point which may correspond to a discontinuity in the soil profile. Sequential vertical layering of RAS (Kadlec, 2009; Rybczyk and others, 2002) in low-energy wetland systems (treatment wetlands) are prone to disruption by bioturbation (Robbins, 1986) and by plant-mediated processes that take place in the root zone. Such processes could result in attenuation of

specific signatures and present a challenge to identify CP. In addition, the outcomes of CPT are dependent on a consistent solid phase boundary within the accreting soil profile. Any mobile constituents or chemical processes that occur at the surface, but are different at depth (such as pH-mediated solubility, decomposition, etc.) could artificially cause surface sediments to be different from deep sediments, without there being any change in the system. Pre-existing conditions at a location could have a significant role in soil characteristics and therefore should be considered during selection of variables for examining existence of CP in a soil profile. And lastly, CPT can be applied to soil cores that are deep enough to traverse the boundary between RAS and the native soil.

Nevertheless, CPT presents a new and simple approach for measurement of vertical accretion rates in low-energy systems, such as constructed wetlands. It provides an alternative to existing techniques and offers a simple method for soil accretion rate measurement. It presents a practical option for managers who are interested in evaluating long-term accretion of contaminants as a measure of performance of treatment wetlands.

Table 3-1. Soil accretion measurement methods and published accretion rates from wetland studies.

Location	State/ Country	Method	Accretion Rates (cm yr ⁻¹)	Reference
Waquoit Bay	Massachusetts	²¹⁰ Pb	0.3–0.5	Orson and Howes (1992)
Narragansett Bay	Rhode Island	²¹⁰ Pb	0.2–0.6	Brickerurso et al. (1989)
Farm River	Connecticut	²¹⁰ Pb	0.5	McCaffrey (1980)
Flax Pond	New York	²¹⁰ Pb	0.5–0.6	Armentano and Woodwell (1975)
Great Marsh	Delaware	²¹⁰ Pb	0.5	Church et al. (1981)
Delmarva Peninsula	Virginia	²¹⁰ Pb	0.1–0.2	Kastler and Wiberg (1996)
Chesapeake Bay,	Maryland	²¹⁰ Pb	0.2–0.4	Stevenson et al. (1985)
Chesapeake Bay,	Maryland	²¹⁰ Pb	0.5–0.7	Kearney and Ward (1986)
Chesapeake Bay,	Maryland	²¹⁰ Pb	0.4–0.8	Griffin and Rabenhorst (1989)
Floodplain wetland	Las Tablas de Daimiel, Spain	²¹⁰ Pb	1.6–3.8	Sanchez-Carillo et al.(2001)
Severn Estuary	England	²¹⁰ Pb	0.4	French et al. (1994)
St. Johns River Basin	Florida	²¹⁰ Pb	0.2–0.4	Brenner et al. (2001)
Pamlico Sound	North Carolina	¹³⁷ Cs	0–0.5	Craft et al.(1993a)
Everglades	Florida	¹³⁷ Cs	0.1–1.2	Reddy et al. (1993)
St. Johns River Basin	Florida	¹³⁷ Cs	0.3–0.5	Brenner et al. (2001)
San Francisco Bay	California	¹³⁷ Cs	0.4–4.2	Patrick and DeLaune (1990)
Tidal fresh water marsh	Virginia	¹³⁷ Cs	0.8	Neubauer et al.(2002)

Table 3-1. Continued

Location	State/ Country	Method	Accretion Rates (cm yr ⁻¹)	Reference
Multiple sites	Oregon and Washington	¹³⁷ Cs	0.2–0.7	Thom (1992)
Eastern Scheldt	Netherlands	¹³⁷ Cs	0.4–1.6	Oenema and DeLaune (1988)
Multiple sites	England, Netherlands, Poland	¹³⁷ Cs	0.3–1.9	Callaway et al. (1996a; 1996b)
Chesapeake Bay	Maryland	²¹⁰ Pb and ¹³⁷ Cs	0.3–0.8	Kearney and Stevenson (1991)
Everglades	Florida	²¹⁰ Pb and ¹³⁷ Cs	0.1–0.8	Craft and Richardson (1998)
Chesapeake Bay	Maryland	²¹⁰ Pb and ¹³⁷ Cs	0.3–0.8	Kearney et al. (1994)
Long Island Sound	Connecticut	²¹⁰ Pb and ¹³⁷ Cs	0.1–0.7	Anisfeld et al. (1999)
Barn Island	Connecticut	²¹⁰ Pb and ¹³⁷ Cs	0.1–0.4	Orson et al. (1998)
Nauset Marsh	Massachusetts	²¹⁰ Pb and ¹³⁷ Cs	0–2.4	Roman et al. (1997)
Louisiana coast	Louisiana	²¹⁰ Pb and ¹³⁷ Cs	0.5–0.9	DeLaune et al. (1989)
Island of Sylt	Germany	²¹⁰ Pb and ¹³⁷ Cs	0.6–1.5	Kirchner and Ehlers (1998)
Louisiana	Louisiana	Stable tracers using REE ^a	0.8 –3.0	Knaus and Van Gent (1989)
Multiple sites	Maine	Marker horizon	0–1.3	Wood et al. (1989)
Sapelo Island	Georgia	Marker horizon	0.2–0.7	Letzsch (1983)

^a rare earth elements

Table 3-1. Continued

Location	State/ Country	Method	Accretion Rates (cm yr ⁻¹)	Reference
Barn Island	Connecticut	Marker horizon	0.1–0.4	Orson et al. (1998)
Eastern Scheldt	Netherlands	Marker horizon	0.4–1.6	Oenema and DeLaune(1988)
Nauset Marsh	Massachusetts	Marker horizon	0–2.4	Roman et al.(1997)
Rookery Bay	Florida	Marker horizon and SET ^b	0.4–0.8	Cahoon and Lynch (1997)
Louisiana coast	Louisiana	Feldspar Marker Horizon	0.7–1.0	Cahoon and Turner (1989)
Scolt Head Island,	England	Marker horizon	0.1–1.4	Stoddart et al.(1989)
Scolt Head Island,	England	Marker horizon	0.1–0.8	French and Spencer (1993)
Tijuana Estuary		Marker horizon	0.1–8.5	Cahoon et al. (1996)
STA-1W (n=28) ^c	Florida		1 ± 0.3	
STA-1W Cell 5A and 5B (n=12) ^c	Florida	CPT (using bulk density, TP content, δ ¹⁵ N (‰) and δ ¹³ C (‰))	1.2 ± 0.6	This dissertation study
STA-2 (n=29) ^c	Florida		1.1 ± 0.3	
STA-3/4 (n=39) ^c	Florida		1.7 ± 0.8	

^b sediment elevation table^c values in parentheses indicate the number of soil cores analyzed

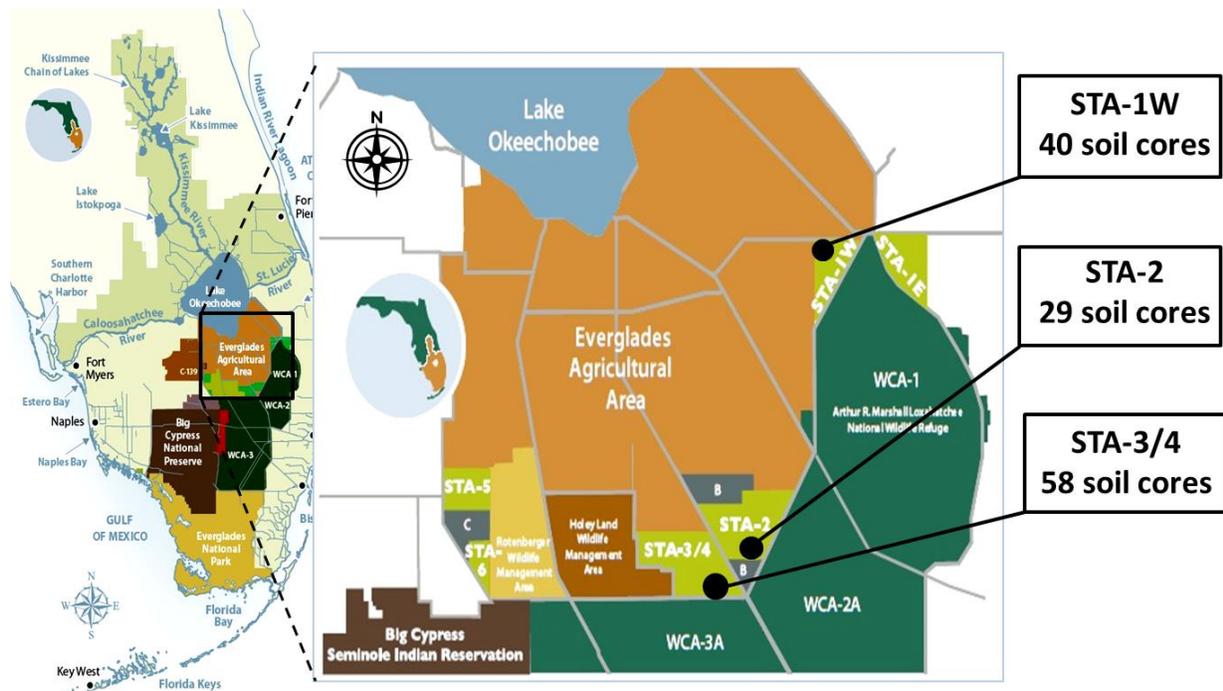


Figure 3-1. Location of the three Stormwater Treatment Areas (STA-1W, STA-2 and STA-3/4) used in this study and the number of soil cores collected from each STA.

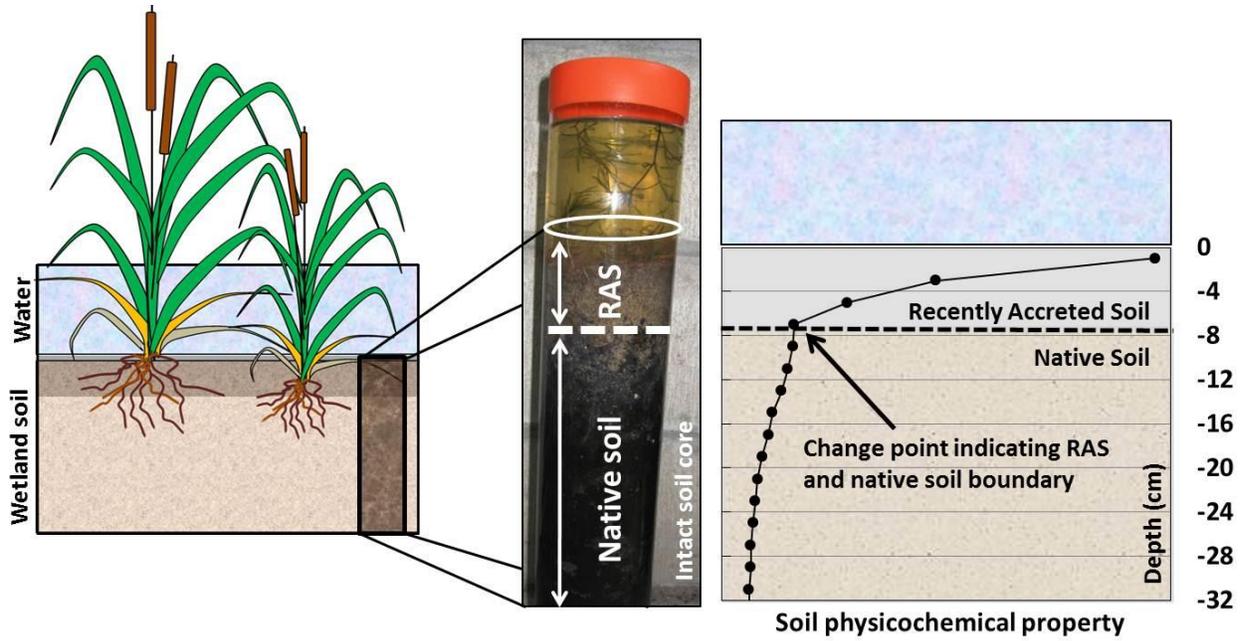


Figure 3-2. A cross-section view of a typical free water surface treatment wetland and schematic depiction of a boundary between recently accreted soil (RAS) and native soils, which is identifiable as a change-point using stratigraphic characteristics of the soil profile.

Change-point depth obtained from SegReg using soil profile parameters from site 51-A, STA-2

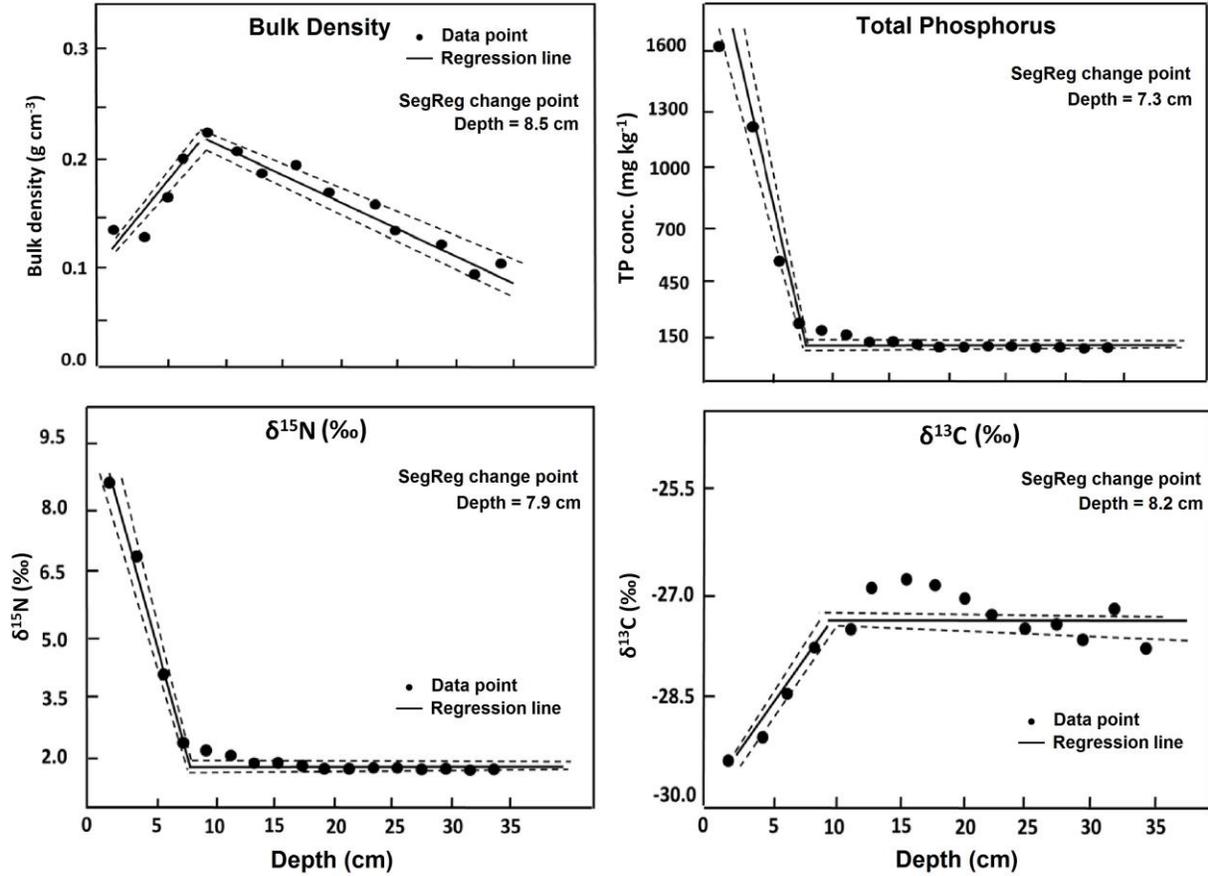


Figure 3-3. SegReg output using bulk density (g cm⁻³), total phosphorus content (mg P kg⁻¹), and stable isotopic ratios of C and N [δ¹³C (‰) and δ¹⁵N (‰), respectively] in a representative soil profile from a site in STA-2. The change-point is identified with a 90% confidence interval. Each data point represents a 2-cm soil core section.

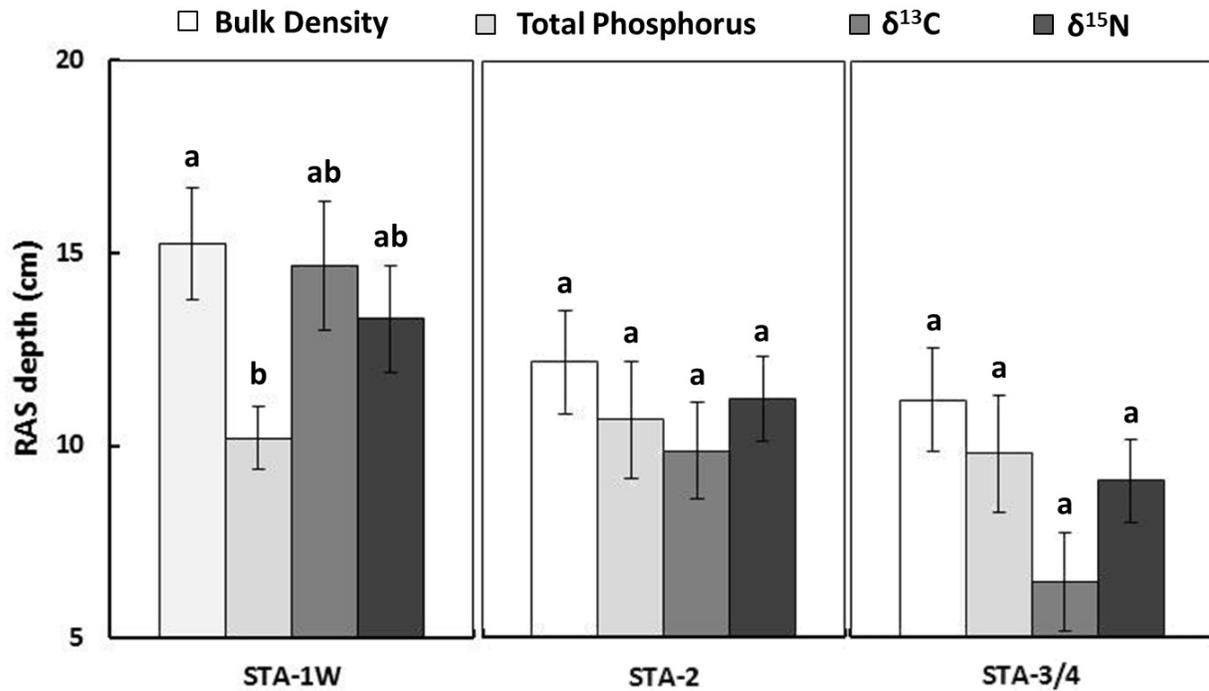


Figure 3-4. Depth of RAS for STA-1W, STA-2, and STA-3/4 as determined by SegReg change-points using four variables (bulk density, total phosphorus, isotope ratio of C and N [$\delta^{13}\text{C}$ (‰) and $\delta^{15}\text{N}$ (‰) respectively]). Only significant difference in RAS depths between bulk density and TP in STA-1W (each STA tested separately using Tukey-Kramer HSD test, $p < 0.05$). Error bars represent standard error of the mean. The total number of soil cores (n) used in this analysis was 40, 29 and 58 for STA-1W, STA-2, and STA-3/4 respectively.

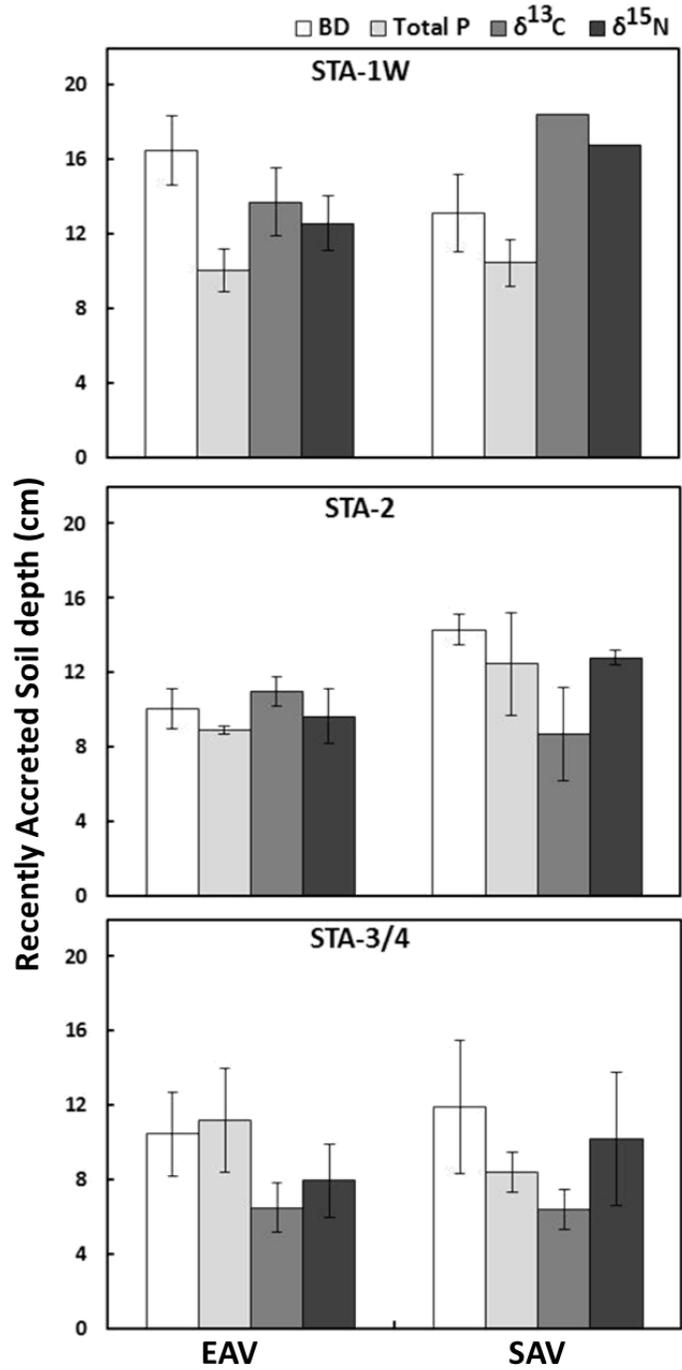


Figure 3-5. Variation in RAS depth between two dominant vegetation types – Emergent Aquatic Vegetation (EAV) and submerged aquatic vegetation (SAV) for four parameters - bulk density (g cm^{-3}), total phosphorus (mg P kg^{-1}), stable isotope ratio of C and N [$\delta^{13}\text{C}$ (‰) and $\delta^{15}\text{N}$ (‰) respectively]. No significant differences observed (each STA tested separately using Tukey-Kramer HSD test, $p < 0.05$). Error bars represent standard error of the mean.

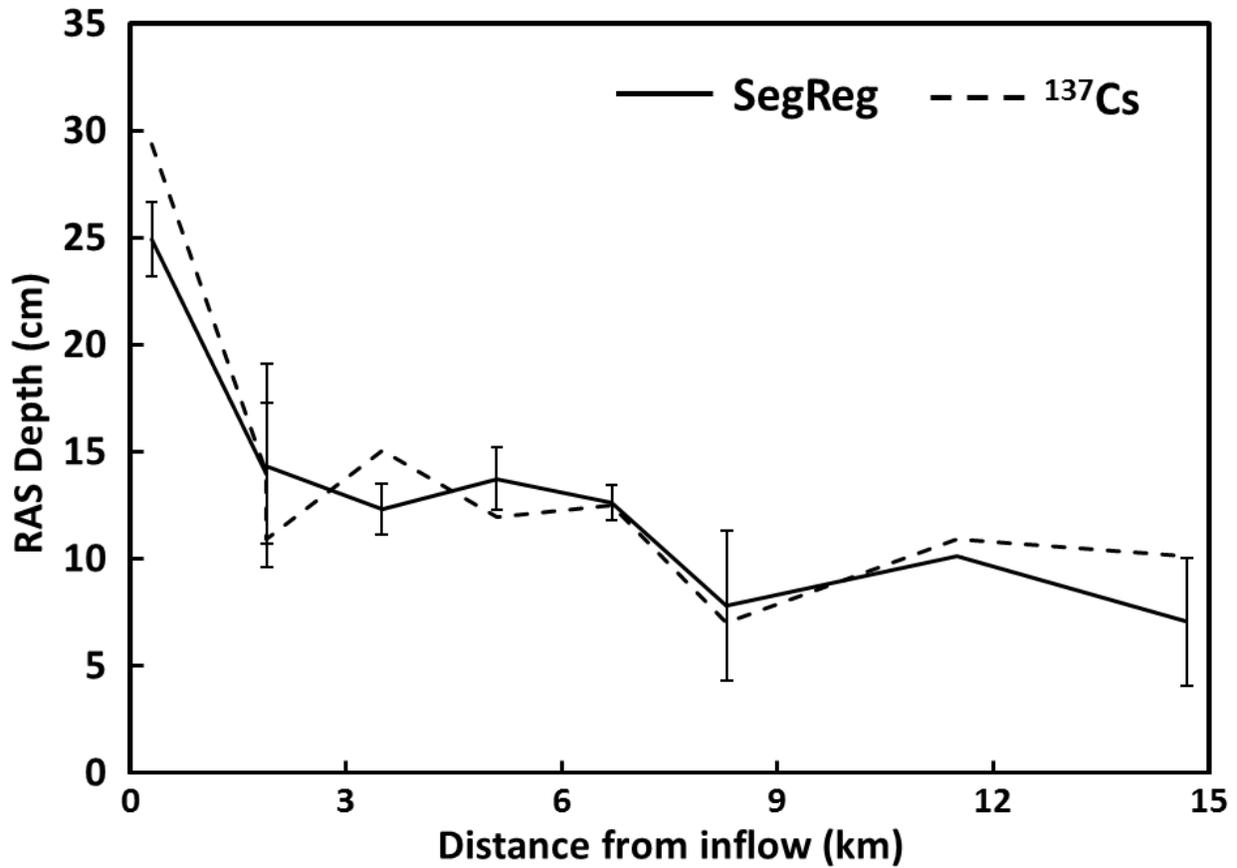


Figure 3-6. Comparison of RAS depth obtained by using SegReg program and ¹³⁷Cs peaks from Everglades Water Conservation Area-2. Three soil profile characteristics – bulk-density (g cm^{-3}), total phosphorus (mg P kg^{-1}) and ¹³⁷Cs activity (pCi section^{-1}) were used for SegReg CP determination. No significant difference between RAS depth obtained by two techniques ($p=0.26$, $\alpha=0.05$, paired t-test). Error bars represent standard deviation in SegReg CP depths.

CHAPTER 4
SOIL AND NUTRIENT ACCRETION RATES IN TREATMENT WETLANDS
OF THE EVERGLADES BASIN

Background

Constructed treatment wetlands are dynamic ecosystems characterized by unique hydrology, soils, vegetation and high net primary productivity. These ecosystems are used worldwide to remove water-borne contaminants. Influent chemicals are either assimilated internally or transformed into benign products that are exported from the system (Kadlec and Wallace, 2009). Internal assimilation can occur by physical settling of suspended organic and inorganic constituents or may involve complex processes leading to the eventual incorporation of influent chemicals into plant biomass. The release of contaminants back into the water column after vegetation senescence is inhibited by the reducing conditions present in the wetland environment. Consequently, two processes in wetlands - high rates of net primary productivity and suppressed rates of decomposition, result in the buildup of material at the soil-water interface (DeBusk and Reddy, 1998), which provides a long-term sink for influent constituents (e.g., nutrients). Soil accretion is a sustainable pathway in treatment wetlands for sequestering non-volatile contaminants that cannot be easily transformed into ecologically benign products.

Constructed wetlands exhibit a wide range of treatment efficiencies, depending on the 'contaminant' to be removed (i.e., target substance or attribute), and the prevailing biogeochemical conditions within the wetland over its period of operation. For example, treatment efficiencies for total suspended solids (TSS), biochemical oxygen demand (BOD), and pathogens (bacteria and viruses) have been reported as high as 70% (Kadlec and Wallace, 2009) and range from 40–50% and 40–90% for N and P,

respectively (Andersson and others, 2005; Chen, 2011; Germain and Pietro, 2011; Vymazal, 2007). The treatment capability of constructed wetlands is a consequence of complex biogeochemical processes taking place simultaneously within the water column, the soil profile, in wetland vegetation and microorganisms, and at the soil–water–vegetation interface. The factors that affect these biogeochemical processes in turn affect the treatment efficiency of constructed wetlands.

Previous reviews of treatment wetland performance for specific constituents have attempted to understand the complex pathways and underlying biogeochemical processes that result in treatment. Most notably, studies on C, N and P processing in natural and constructed wetlands (Brix, 1994; Craft and Richardson, 1993a; D'Angelo and Reddy, 1999; Kayranli and others, 2010; McLatchey and Reddy, 1998; Reddy and Debusk, 1985; Reddy and others, 1999a; Saunders and Kalff, 2001; Vymazal, 2007) have provided insights to help optimize treatment performance and extend the functional life of constructed wetland systems (Kadlec and Wallace, 2009; Vymazal, 2011). This chapter is an attempt to understand the key processes regulating long-term P removal by treatment wetlands. The study was undertaken on a small subset of treatment wetlands, which are characterized by having exceptionally large treatment areas, receive agricultural drainage water as inflows and have an extremely low outflow P concentration target. These large treatment wetlands are referred to as the Everglades Stormwater Treatment Areas (STAs), and the target outflow P concentration falls within the range of 13-19 $\mu\text{g P L}^{-1}$.

Removal of P in treatment wetlands takes place via two distinct pathways: sorption and burial (Reddy and others, 1999a). The P burial involves biotic components

in whereby a fraction (10-20%) of P contained in microbial and plant biomass avoids decomposition and recycling within the wetland (Reddy and others, 1993; Rybczyk and others, 2002). Continued burial of residual biotic detritus results in accumulation of organic soil that provides a sustainable mechanism of P removal in treatment wetlands (Reddy and others, 1999a). The effectiveness of P removal in treatment wetlands is influenced by factors such as hydraulic loading rate (HLR), inflow P concentration, substrate type, biomass growth rate and soil P concentration (Gu and others, 2001; Kadlec, 2005). Although creation of soil and associated sequestration of P is the only sustainable mechanism for P removal in wetlands, it remains one of the least explored aspects of P retention in these systems [pp 364, (Kadlec and Wallace, 2009)]. The soil and P accretion rates in free surface wetlands have been quantified in only few instances (Craft and Richardson, 1993b; DeLaune and others, 1989; Reddy and others, 1993; Rybczyk and others, 2002). This chapter presents the results of research conducted to address the existing knowledge gap in terms of soil accretion in wetlands by using the STAs as a case study.

Information on soil accretion rates in wetlands allows an accurate determination of nutrient retention in the system over the period of record (POR). Insights into the rate of soil build up and nutrient concentrations in RAS are important for two reasons. First, P concentrations and forms in RAS dictate P exchange rates between soil and the water column, which can reduce the efficiency of a treatment wetland (Reddy and others, 2002). Earlier studies carried out in Water Conservation Area (WCA)-2A showed decreases in P uptake from the overlying water column with P enrichment of the floc and surface soil (Fisher and Reddy, 2001; Richardson and Vaithyanathan, 1995).

Second, knowledge of accretion rates is necessary for optimizing design criteria and to estimate the functional life of a treatment wetland before soil build-up reduces storage capacity and water residence time, necessitating extensive engineering interventions. This could have serious implications in terms of the functional life of treatment wetlands before expensive rehabilitation (e.g., dredging) is required.

In the absence of a clear visual boundary between RAS and antecedent soils in the STAs, it was not possible to discern RAS depth accurately by visual inspection. This challenge, however, was addressed by using stratigraphic characteristics of accreted soil to determine RAS depth in the STAs (Chapter 3) and subsequently determining accretion rates in these treatment wetlands (this chapter).

Objectives and Hypotheses

The first objective of this study was to explore the relationship between soil accretion rates and operational age of the STAs. The operating hypothesis was that most P retained from the water column in the STAs is stored in RAS, which acts as a nutrient enriched repository and generally has higher P concentrations than pre-STA soil. Furthermore, with increasing age, the rate of soil and P accretion would decline, resulting in a higher outflow P concentration.

The second objective was to develop a refined P mass budgets using information on soil P storages in RAS and pre-STA soil and total P removed from the water column. This mass balance approach was an advancement from the one presented in Chapter 2, because it utilized actual depth of RAS instead of a fix 0-10 cm surface soil depth for P storage calculations. The operating hypothesis was that distribution of P within RAS and pre-STA soil is mediated by vegetation, thus vegetation plays a crucial role in controlling whether the STAs function as a nutrient sources or sinks.

Methods

Site Description

Three large constructed wetlands (STA-1W, STA-2 and STA-3/4; Appendix B) in south Florida were chosen for this study (Figure 4-1). At the time of this study, the operational age of selected STAs ranged from 6-16 years. All STAs were constructed with a similar internal configuration, i.e., a number of parallel flow-ways each having one or more treatment cells, with each cell managed for one dominant vegetation community – emergent aquatic vegetation (EAV), or submerged and floating aquatic vegetation (SAV/FAV) (Goforth, 2005). Intact soil cores were collected along a transect parallel to the direction of flow in each cell. The number and location of sampling sites was determined based on the size and shape of each cell. Existing quarter-mile-grid sampling maps obtained from the SFWMD were utilized to identify the sampling locations in this study. Detailed information about three STAs (Appendix B) and sample collection maps (Appendix C) and sampling sites is presented in Appendix D (Tables D-1, D-2 and D-3)

STA-1W: As a part of the long-term management goals of STA-1W, rehabilitation activities were carried out during WY2007-08, including tilling and demucking in Cell 2B and Cell 4 and efforts to convert from EAV to SAV in Cell 1B and Cell 3. Cell 1B and Cell 3 were converted to SAV from EAV and were classified as EAV conversion cells, however for the purpose of analysis those cells were designated as SAV cells. Soil samples collected from these cells were not subjected to isotopic ratio analysis, but all other analyses were carried out. Soil sampling took place in July 2009. A total of 41 soil cores were collected (Appendix C, Figure C-1). Triplicate samples were collected from eight sites.

STA-2: Soil sampling was carried out in October 2009. A total of 29 intact soil cores were collected (Appendix C, Figure C-2). Triplicate samples were collected from five sites.

STA-3/4: As of 2008, Cells 1A, 1B, 2A and 3A were designated as EAV and were managed as such. Cells 2B and 3B were designated SAV. However, Cells 1B and 2B were converted to SAV in WY2009, and were considered as SAV for this study. Soil cores were collected in January and February 2010. A total of 58 soil cores collected from EAV and SAV cells (Appendix C, Figure C-3). Triplicate samples were collected from nine sites.

Soil Sampling and Processing

Soil cores (n=128) were collected using a stainless steel tube (10.2-cm internal diameter [ID], 0.2-cm wall thickness [WT]). Depth of soil cores ranged from 10 - 40 cm, as limited by the depth of bedrock from the wetland soil surface. Soil cores were transferred into clear cellulose acetyl butyrate tubes (10.2-cm ID, 0.16-cm WT) in the field and transported to the laboratory for storage at 4°C until they were analyzed.

Thickness of the unconsolidated surface detrital layer (floc) was measured before removing this material from the soil core. The remaining soil core was then sectioned at 2-cm intervals along its entire length. The total number of such sections were 733 (STA-1W), 505 (STA-2) and 573 (STA-3/4) [For details see Tables C-1, C-2 and C-3 (Appendix C)]. Surface material (floc) and 2-cm soil sections were dried at 70°C for bulk density determination. Dried samples were finely ground using a ball mill and passed through a 2-mm mesh before chemical analysis.

Total P was determined by the ashing and HCl digestion (Andersen, 1976), using standard molybdate colorimetry for analysis (U.S. Environmental Protection Agency,

1993). Total nitrogen (TN) and total carbon (TC) were determined using a Costech Elemental Analyzer (Model 4010, Costech Analytical Industries, Inc., Valencia, CA) coupled to a Finnigan MAT Delta^{Plus} XL Isotope Ratio Mass Spectrometer (CF-IRMS, Thermo Finnigan, San Jose, CA) via a Finnigan Conflo II interface. Elemental calibration was accomplished using peach leaves (2.93% N, 44.65% C).

Data Analysis

Phosphorus storage (g P m^{-2}) in floc, RAS and pre-STA soil were calculated using Equation 2-1 and 2-2 (Chapter 2) for STA-1W, STA-2 and STA-3/4. In this study, however, bulk-density, TP concentrations, and depth of soil cores were determined on the soil cores collected in WY2010, (Chapter 3). The change-point depth obtained by the CPT was used to differentiate the boundary between RAS and pre-STA soil. The mass of P in RAS and pre-STA soil was obtained by calculating P storage for each 2-cm soil section and then summing P storage over all sections within each soil layer. Maximum soil core depth considered for this analysis was 30 cm, hence each STA had different pre-STA soil depth depending on the mean RAS depth, as determined by subtracting RAS depth from the total soil core depth (30 cm). As a result, P storage in the pre-STA soil fraction of STA-1W, STA-2 and STA-3/4 represented 17, 19 and 20 cm deep sections, respectively.

RAS depths for all soil cores from within a cell were averaged to obtain the mean RAS depth for that cell. The mean RAS depths for all cells within each STA were used to calculate mean RAS depth for the whole STA. Soil accretion rates (cm yr^{-1}) were calculated using average RAS depths and the operational age of 16, 10, and 6 years for STA-1W, STA-2 and STA-3/4, respectively. Phosphorus accretion rates ($\text{g m}^{-2} \text{yr}^{-1}$) were determined using total P storage in RAS over the operational age of each STA

corrected to a unit surface area. Comparison of differences in RAS depths among different cells within each STA were tested with one-way ANOVAs followed by the Tukey-Kramer HSD tests ($p < 0.05$) using JMP (Version 7; SAS Institute Inc., Cary, NC, 1989-2007).

Mass Balances

Phosphorus mass balances were calculated using TP retained from the water column over the POR and P mass storage (g P m^{-2}) in floc, RAS and pre-STA soil for each STA. Total P retained from the water column was obtained from the 2010 South Florida Environmental Report (Pietro and others, 2010). It was assumed that floc P storage (FPS) at any given time reflected the fraction of P supplied from the water column (P_{Wc}) as well as any P moved upwards from RAS. If FPS was smaller than P_{Wc} , it was assumed that P had moved from floc into the RAS ($P_{flux F}$; -ve). Total P stored in RAS (RAS PS; g P m^{-2}) indicated net P derived from floc ($P_{flux F}$) as well as any P from pre-STA soil ($P_{flux PSS}$). When RAS PS was '+ve', it indicated movement of P from pre-STA soil ($P_{flux PSS}$, +ve). These calculations are illustrated in Figure 4-2. The arrows indicate direction of P flux from one compartment to other.

For all practical purposes, soils represent the sole long-term nutrient storage pool in wetlands, whereas nutrients in live vegetation serve as a transient pool (Howard-Williams, 1985), hence P present in vegetation was not considered in P mass-balance calculations. Critical assumptions made for developing P mass balances are listed below –

- The total mass of TP retained from the water column (P_{Wc}) initially resides as floc, therefore floc P storage (FPS) at any given time reflects the fraction of TP incorporated from the water column as well as contribution from vegetative detrital matter (physical settlement of particulate forms, adsorption-absorption of soluble forms, biological immobilization by microbial communities).

- Floc P contributed by vegetative detrital matter deposition may represent a fraction that could be obtained from underlying soils by rooted plants (EAV) or directly from the water column by submerged and floating plants (SAV/FAV). For comparisons at STA level, both EAV and SAV/FAV cells within one STA were averaged to obtain FPS for that STA.
- Floc becomes soil over time, so with a long observation period some of the water-column TP have passed through the floc and into the surface soil.
- Flux of P from pre-STA soil ($P_{\text{flux PSS}}$) to overlying soil or floc is regulated by redox conditions and the equilibrium P concentration (EPCo).
- Phosphorus in live vegetation biomass at a given time (i.e., plant standing stock) accounts for only a tiny fraction of TP in the STAs and represents a transient pool which ultimately gets transformed into floc and soil after plant senescence, following the decay continuum pathway.

Results

Comparison of EAV and SAV bulk density and TP depth profiles for STA-1W, STA-2 and STA-3/4 is presented in Figure 4-3. Bulk density of EAV cells was lower than SAV cells until a depth of -14 cm in STA-1W and at all depths in STA-2. In STA-3/4 no differences were seen between EAV and SAV until top 8 cm, however deeper sections showed higher bulk density in EAV cells. In general, bulk-density was higher in STA-3/4 than in the other STAs. Total P concentration was higher in surface soils of EAV cells (-5 to -16 cm) compared to SAV cells in all STAs. Total P concentration decreased with depth, with most pronounced decrease observed until -12 to -14 cm in both EAV and SAV cells in all STAs. There is little change in the deeper strata corresponding to the surface soil.

Comparison of EAV and SAV $\delta^{15}\text{N}$ (‰) and $\delta^{13}\text{C}$ (‰) depth profile for all three STAs are presented in Figure 4-4. Higher $\delta^{15}\text{N}$ (‰) values suggest nutrient enrichment in the top soil layers in comparison to the deeper sections. The trend for $\delta^{15}\text{N}$ (‰) and $\delta^{13}\text{C}$ (‰) between EAV and SAV cells was similar to the other parameters, i.e., there

was a marked difference in enrichment between EAV and SAV cells in the top soil layers. The soil $\delta^{13}\text{C}$ (‰) profile for STA-3/4 was dissimilar from the other two STAs, such that the depth profile of EAV cell exhibited less negative values of $\delta^{13}\text{C}$ (‰) in the surface layer of EAV cells in comparison to SAV cell. This indicated enrichment (or evidence of non-discrimination against heavier C isotope) by the surface layer of EAV cells in STA-3/4 whereas in STA-1W and STA-2 this property was exhibited by SAV cells.

The C:N and N:P ratios in soil profiles between EAV and SAV cells for all three STAs are presented in Figure 4-5. The C:N ratio did not show much difference between EAV and SAV cells in STA-1W and STA-3/4; the EAV and SAV C:N ratios across most of the soil profile appeared highly correlated. The N:P ratios showed a steady increase with depth and were similar for both EAV and SAV cells of STA-1W and STA-3/4 however STA-2 showed marked difference between EAV and SAV cells below 5 cm depth. In most of the STAs, P in the water column is depleted progressively as water flows from EAV to SAV cells, which resulted in higher soil profile N:P ratios in SAV cells compared EAV cells. This was not the case for STA-2, probably because the P loading rates for EAV and SAV cells were similar. Also, EAV and SAV cells in STA-2 are arranged as parallel one-cell flow-ways, and unlike the other STAs where outflow from EAV cells is the inflow to SAV cells, receive water without any pre-treatment by an EAV cells. Inter-cell variability in soil physico-chemical characteristics for each cell of the three STAs is presented in Appendix D (Figures D-1, D-2 and D-3).

Soil and Phosphorus Accretion Rates

The depth of RAS was determined by identifying the change-point (CP) in each soil core independently utilizing four variables: bulk density, total P content, $\delta^{15}\text{N}$ and

$\delta^{13}\text{C}$ (see detailed methodology in Chapter 3). Nutrient mass ratios (C:N and N:P) were also examined, but the absence of a well-defined CP in the soil profiles precluded their use in the analysis. The mean depth of RAS as determined by CP technique (CPT) was 14.7 ± 5.1 , 11 ± 3.3 and 10 ± 4.6 cm in STA-1W, STA-2 and STA -3/4, respectively (Figure 4-6). RAS depth was significantly different between STA-1W and STA-3/4.

Average RAS depths were used to calculate soil (cm yr^{-1}) and P ($\text{g m}^{-2} \text{yr}^{-1}$) accretion rates for each cell in the STAs (Table 4-1). The mean values presented in this table are averages of each cell. The relationship between soil and P accretion rates suggested a declining trend in P and soil accretion with time in the STAs (Figures 4-7 and 4-8).

Phosphorus Mass Balance

Phosphorus mass balances were calculated for the STAs using CP depths (Table 4-1) as a boundary indicator between RAS and pre-STA soil. Phosphorus retained over the POR in STA-1W, STA-2 and STA-3/4 was 14.8 , 7.0 and 4.6 g P m^{-2} , respectively. Phosphorus mass balances for all three STAs is presented in Figure 4-9. Large variability was observed in the flux of P from pre-STA soil to RAS. All three STAs experienced positive P flux from pre-STA soil to RAS. This flux was highest in STA-3/4 with the shortest operational age (7 years) and lowest POR P retention. Floc P storage was highest in STA-2.

Discussion

Considerable variability was found in the physico-chemical properties along soil profiles of STAs. The RAS serves as long-term integrator of existing conditions in wetlands (Inglett and Reddy, 2006; Reddy and DeLaune, 2008; Smol, 1992) and the observed variability in STA soil characteristics could be attributed to diverse conditions

in these wetlands during their operational history. Differences observed in soil characteristics between EAV and SAV cells varied from one STA to other, and insufficiently robust to conclude if these differences were due to vegetation or other confounding factors (Figures D-1, D-2 and D-3; Appendix D).

Soil Physico-Chemical Properties

High P concentrations in the surface soil of both EAV and SAV cells reflected high P loading and incorporation of influent P into RAS. As STA age increased, the amount of P stored in newly created soils was increasingly derived from P retained from the water column. This relationship was established in Chapter 2 (Figure 2-2), and evidence of P enrichment in STA surface soil was further observed when cells with different vegetation type were compared (Figure 4-3). STA-1W with longest operational history (16 years) showed relatively higher P concentrations until a depth of -12 to -13 cm, whereas in STA-2 and STA-3/4 this depth was at -8 to -10 cm (Figure 4-3). Higher bulk densities in those soil fractions resulted in higher P storages in RAS compared to pre-STA soil.

Soil $\delta^{15}\text{N}$ (‰) and $\delta^{13}\text{C}$ (‰) displayed generally larger values in the top layers in comparison to the deeper core sections. These results are an evidence of increased nutrient inflows and reduced organic matter decomposition under saturated conditions after STA establishment and was attributed to increased uptake (or decreased discrimination) of isotopically 'heavy' N and C from the inflow water and subsequent diagenesis of dead plant matter, whose isotopically 'lighter' fractions were preferentially mineralized and lost from the system. The marked difference in the heavier isotope enrichment between EAV and SAV cells was attributed to higher P loading to EAV cells in comparison to the SAV cells. Soil $\delta^{15}\text{N}$ (‰) suggested increased incorporation of

heavier N isotope in EAV cells while $\delta^{13}\text{C}$ (‰) suggested enhanced incorporation of heavier C isotope in SAV cells (smaller ‘-ve’ numbers) in STA-1W and STA-2, commensurate with the existing literature (Inglett and Reddy, 2006). In STA-3/4, surface layers of EAV cells, however, displayed greater values of $\delta^{13}\text{C}$ (‰) than SAV cells. The abundance of P could have triggered higher biotic productivity in the EAV cells of STAs where rapid emergent macrophyte growth constrained discrimination against heavier isotopes as EAV accessed atmospheric CO_2 (-8‰) resulting in increase in $\delta^{13}\text{C}$ (‰) values of surface soil. This reversed pattern in STA-3/4 could also be attributed to the effects of vegetation conversion, where prior EAV cells were converted into SAV cells. The soils in the converted cells may still have exhibited characteristics that were indicative of their past vegetation community.

Soil and Phosphorus Accretion Rates

Soil accretion has been established as the long-term sustainable P removal mechanism in wetlands (Kadlec, 2009; Reddy and others, 1999a). A detailed listing of methods and measured soil accretion rates from a range of freshwater and coastal wetland systems is presented in Table 3-1 (Chapter 3). The lowest soil accretion rates ($< 0.1 \text{ cm yr}^{-1}$) were reported for bogs that received inputs from rainfall rather than surface runoff (Cameron, 1970; Glaser and others, 1997; Moore and Bellamy, 1974). Accretion rates in productive wetland systems such as the northern region of Everglades (WCAs) have been reported as high as 1 cm or more per year (Craft and Richardson, 1993b; Reddy and others, 1993). Studies conducted on treatment wetlands suggest soil accretion rates ranging from 0.2 to 13.7 cm yr^{-1} (CH2M.HILL, 2003; Coveney and others, 2002; Keller and Knight, 2004). Phosphorus accretion rates from these systems varied from 0.01 to 2.0 $\text{g P m}^{-2} \text{ yr}^{-1}$. White and others, (2001) reported

average soil accumulation of 0.6 cm yr^{-1} for the Orlando Easterly Wetland, with an average P accretion rate of $0.66 \text{ g P m}^{-2} \text{ yr}^{-1}$. The Houghton Lake marsh is one of the longest running surface-flow treatment wetlands (30+ years), and the results of a long-term accretion study suggested sediment and P accretion rates of 1.33 cm yr^{-1} and $1.5 \text{ g P m}^{-2} \text{ yr}^{-1}$, respectively (Kadlec, 2009). Phosphorus accretion increases with P loading to a wetland (Reddy and others, 1993), however, an increase in accretion does not necessarily result into low surface water outflow P concentrations, especially for intermittently flooded wetlands like the STAs where decomposition of organic detritus during periods of dryout can release labile P back to the water column (Newman and Pietro, 2001).

Studies conducted in the Everglades system have illustrated the role of calcium (Ca) in P sequestration in these wetlands (Porter and Sanchez, 1992; Richardson and Vaithyanathan, 1995). Soil fractionation studies have shown Ca-bound P to be the major form of Pi in WCA-2 soils (Koch and Reddy, 1992; Qualls and Richardson, 1995). Phosphorus co-precipitation with CaCO_3 as an important mechanism for P removal has been proposed in a variety of wetland systems (Scinto, 1997). In the context of the STAs, it has been proposed that SAV is better suited for P removal than EAV, a hypothesis supported by studies at the mesocosm (Dierberg and others, 2002b), STA prototype (Nungesser and Chimney, 2001) and field scales (Juston and DeBusk, 2006). Soil accretion in SAV systems could therefore be a result of both Ca-P co-precipitation and uptake by macrophytes. The cycle of flooded-drained conditions in the STAs may not provide an opportunity for amorphous co-precipitated Ca-P to be converted into stable crystalline forms. This may eventually impact the long-term stability of

sequestered P in the STAs as Ca-associated P will be prone to dissolution following redox and pH changes. Dryout conditions also promote oxygen availability in soils, resulting in enhanced mineralization rates and subsequent release of P (McLatchey and Reddy, 1998). These processes are integrated into the soil accretion rates determined for the STAs in this study, and could be one explanation for decreasing accretion rate over time as the STAs underwent multiple dry-rewetting cycles, resulting in soil oxidation and loss of labile P forms.

Another explanation for the declining trend of soil and P accretion rates with increasing STA age (Figures 4-7 and 4-8) could be compaction of old soils as new soils accrued on the surface of previously accumulated surface. This suggests that although new soil is consistently accumulating, the proportional increase in thickness of soil layers may be non-linear. This was supported by an experimental study conducted within the STAs, where soil accretion rates were large in the short-term, but declined over time (Chimney and others, 2000). Secondly, two of the older cells in STA-1W (Cell 1B and Cell 4) were rehabilitated in 2005 to -2007 when approximately 180,000 cubic yards of P-enriched floc and subsurface soil, including 19 mt of P, were removed. The loss of this soil and associated P could have been reflected as a decrease in P and sediment accretion rates for STA-1W.

Phosphorus Mass Balance

The P mass balance developed after ascertaining the boundary between RAS and pre-STA soil was an improvement from the preliminary mass-balance analysis (Chapter 2) in that the former analysis accounted for P storages within RAS instead of a fixed 0-10 cm surface soil section. The preliminary P mass balance (Chapter 2) utilized P storages in 0-10 cm of surface soil, which could have misrepresented P movement to

or from soils to the water column and distorted the actual amount of P that was retained from the water column and the portion that was derived from pre-STA soil.

The ability to differentiate between RAS and pre-STA soil P storage allowed calculation of total P flux from pre-STA soil to RAS. At any given time, the vegetation biomass represents only a small proportion of P present in wetland storage compartments (Faulkner and Richardson, 1989), hence it was not included in P mass balance calculations for the STAs. The P flux from pre-STA soil to RAS was indicative of the mining subsurface P by vegetation and deposition on the surface through detrital accumulation which eventually became part of RAS (Reddy and DeLaune, 2008; Reddy and others, 2002). This P flux redistributed P within the soil profile where P from deeper soil was brought to the surface layer. The movement of P from pre-STA to RAS involves a series of complex biological processes involving wetland vegetation and microbial assemblages.

Summary

Phosphorus retention in the STAs does not seem to be a simple straightforward process of P removal by biotic and abiotic processes, but instead is a complex interplay where redistribution and mobilization of P stocks take place within the soil profile. Wetland vegetation play a crucial role in this redistribution of P, however clear differences on the basis of vegetation types (EAV and SAV/FAV) were not clearly observed from this experimental study. Different functional forms of P undergo considerable transformation as P is cycled through various compartments within wetlands (Qualls and Richardson, 2003; Reddy and others, 1999a). Such changes have a great influence on the stability of accreted P and subsequently, the overall effectiveness of the STAs. This is why characterization of P stability in RAS was carried

out using an operationally defined P fractionation scheme, details of which are presented in the next chapter (Chapter 5).

Table 4-1. Soil (cm yr⁻¹) and phosphorus (g m⁻² yr⁻¹) accretion rates in STA-1W, STA-2 and STA-3/4 (mean ± sd).

Vegetation	STA	Recently Accreted Soil depth [†] (cm)	Soil accretion (cm yr ⁻¹)	P accretion (g m ⁻² yr ⁻¹)
	STA-1W	14.7 ± 5.1(n=28)	0.9 ± 0.3	1.3 ± 0.6
EAV	Cell 1A	19.3	1.2 ± 0.46	1.6 ± 0.88
EAV	Cell 2A	16.1	1.0 ± 0.1	2.0 ± 0.21
SAV	Cell 1B	13.5	0.8 ± 0.17	0.8 ± 0.46
SAV	Cell 2B	15.9	1.0 ± 0.34	1.7 ± 0.66
SAV	Cell 3	12.9	0.9 ± 0.3	1.2 ± 0.5
SAV	Cell 4	10.8	0.7 ± 0.22	0.7 ± 0.22
	STA-1W Cell 5	12 ± 5.5 (n=12)	1.2 ± 0.55	2.0 ± 1.2
EAV	Cell 5A [#]	10.4	1.0 ± 0.42	2.0 ± 1.37
SAV	Cell 5B [#]	12.6	1.2 ± 0.65	2.1 ± 1.1
	STA-2	11 ± 3.3 (n=29)	1.1 ± 0.3	1.9 ± 0.9
EAV	Cell 1	8.9	1.0 ± 0.26	1.0 ± 0.13
EAV	Cell 2	10.5	1.0 ± 0.26	1.6 ± 0.41
SAV	Cell 3	12.5	1.2 ± 0.4	2.5 ± 1
SAV	Cell 4	12.9	1.3 ± 0.94	2.7 ± 0.94
	STA-3/4	10 ± 4.6 (n=39)	1.7 ± 0.77	3.3 ± 2
EAV	Cell 1A	8.2	1.4 ± 0.48	2.7 ± 0.9
EAV	Cell 2A	12.1	2.0 ± 1.1	5.5 ± 4.2
SAV	Cell 1B	11.9	2.0 ± 0.83	2.4 ± 0.97
SAV	Cell 2B	8.5	1.5 ± 0.46	3.8 ± 1.5

[#] Cell 5A and cell 5B came online in WY2000, much later than the rest of the STA (WY1994).

[†]Number of soil cores analyzed are in parentheses.

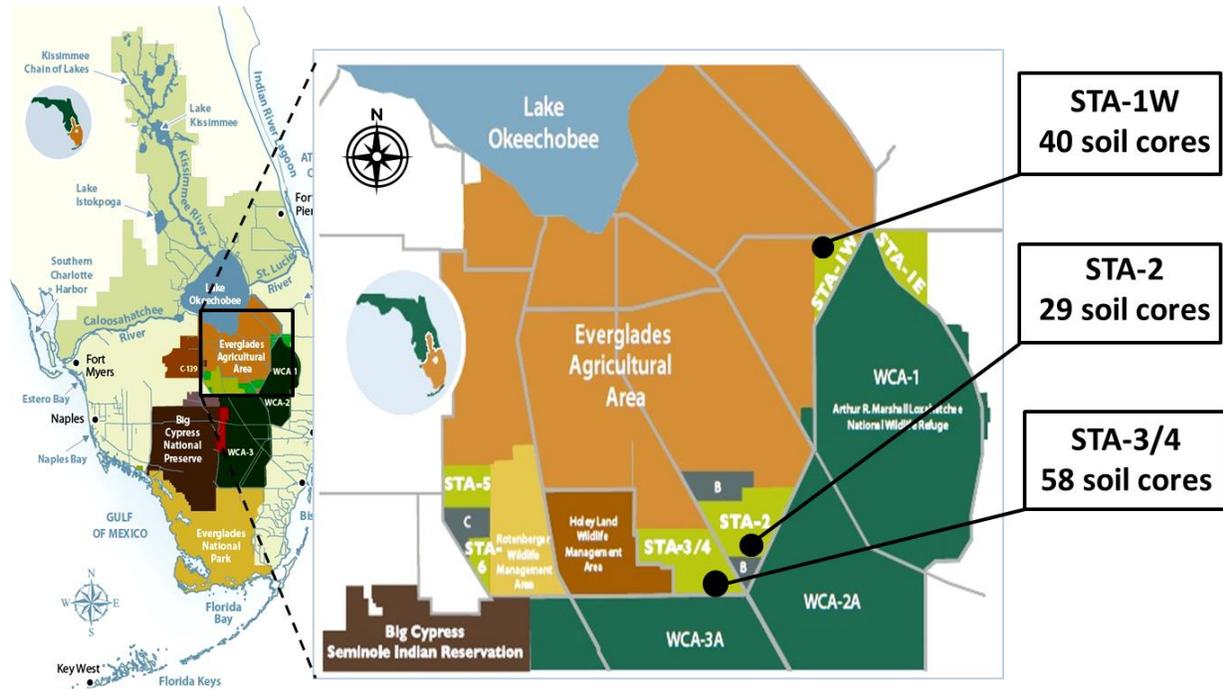
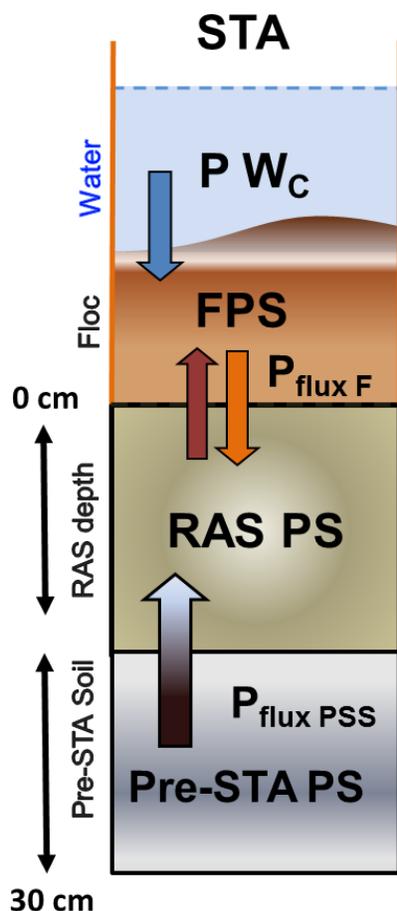


Figure 4-1. Location of the three treatment wetlands used in this study, the Stormwater Treatment Areas: STA-1W, STA-2 and STA-3/4 and the number of soil cores collected from each STA.

Phosphorus mass balance for STAs



All values expressed in g P m^{-2}

PW_c = P retained from water column
[Inflow TP conc. – Outflow TP conc.]

FPS = Floc P storage
[WY2010]

$P_{\text{flux F}}$ = Floc and soil interface P flux
[$P_{\text{flux F}} = \text{FPS} - PW_c$]

RAS PS = Recently Accreted Soil P
storage [WY2010]

Pre-STA PS = Pre-STA soil P storage

$P_{\text{flux PSS}}$ = P flux from Pre-STA soil
[$P_{\text{flux PSS}} = \text{RAS PS} - P_{\text{flux F}}$]

Figure 4-2. Phosphorus mass balance calculations for soil P storage with respect to net P retained from the water column. All values are in g P m^{-2} . Arrows indicate flux of P between compartments. Top arrow indicates P movement from the water column to floc. Middle row arrows show P movement between floc and RAS. Lower row arrows indicate P movement from pre-STA soil to RAS.

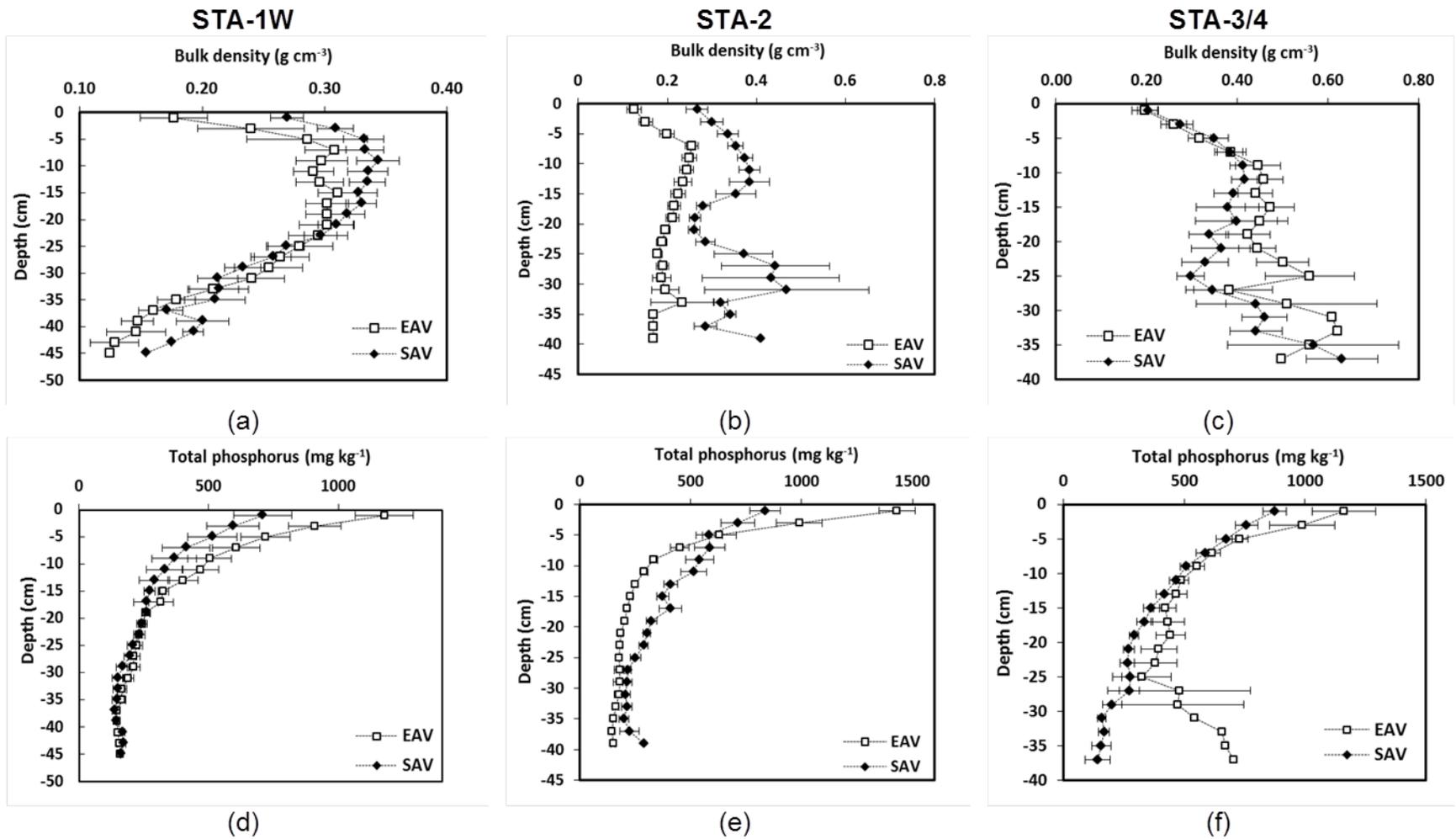


Figure 4-3. Differences in soil profile bulk density and total phosphorus content between two vegetation communities, EAV and SAV, in STA-1W, STA-2 and STA-3/4. Symbols represent mean values for each parameter. Error bars represent one standard error of the mean.

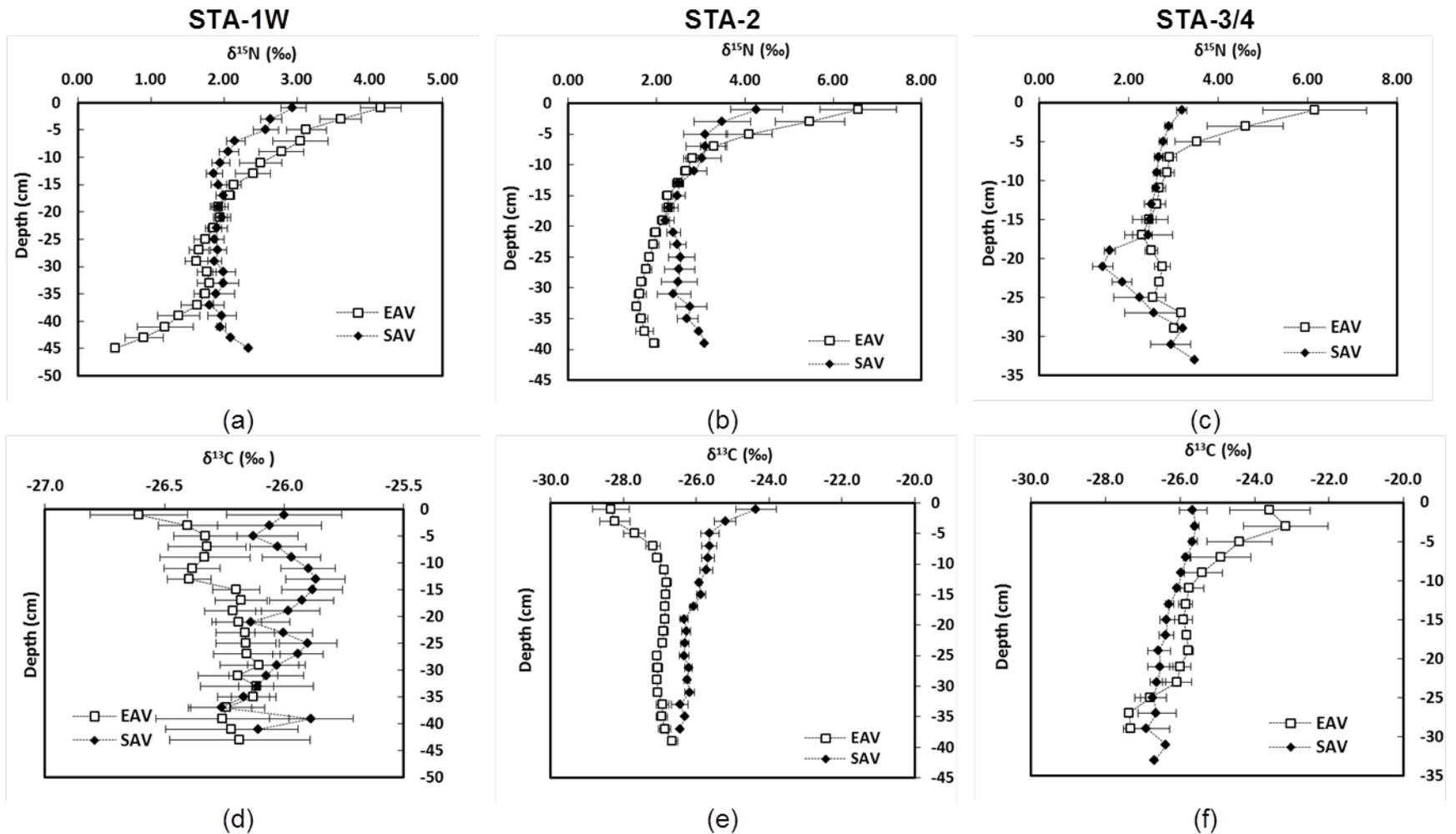


Figure 4-4. Differences in soil profile $\delta^{15}\text{N}$ (‰) and $\delta^{13}\text{C}$ (‰) between two vegetation communities, EAV and SAV, in STA-1W, STA-2 and STA-3/4. Symbols represent mean values for each parameter. Error bars represent one standard error of the mean.

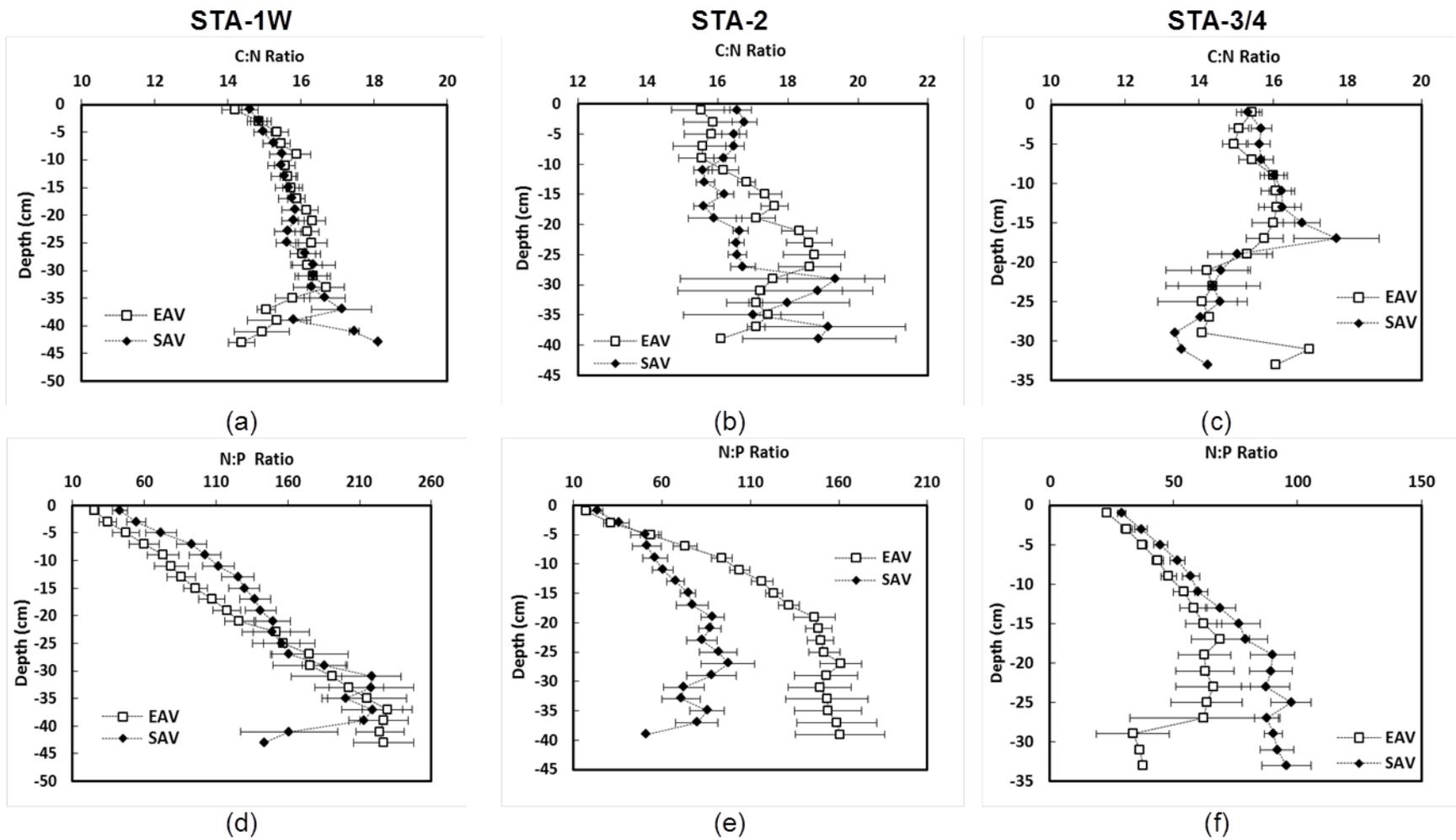


Figure 4-5. Differences in soil profile C:N ratio and N:P ratio between two vegetation communities, EAV and SAV, in STA-1W, STA-2 and STA-3/4. Symbols represent mean values for each parameter. Error bars represent one standard error of the mean.

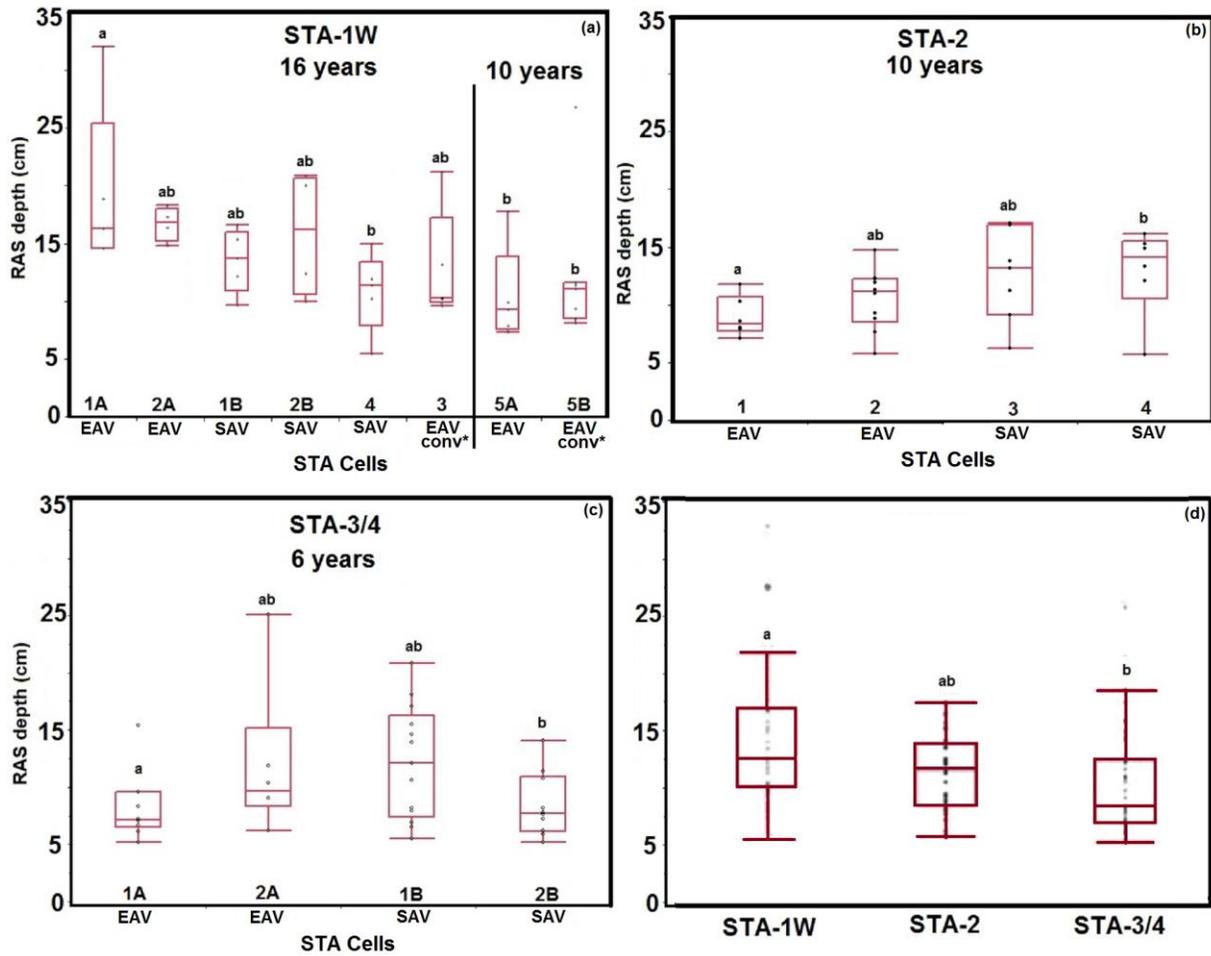


Figure 4-6. RAS depth as determined using change-point analyses for different cells of STA-1W (a), STA-2 (b), STA-3/4 (c) and for entire STA (d). Horizontal lines within boxes represent median values. Test of significance between RAS depths determined for each STA cell using a Tukey-Kramer HSD test ($p < 0.05$).

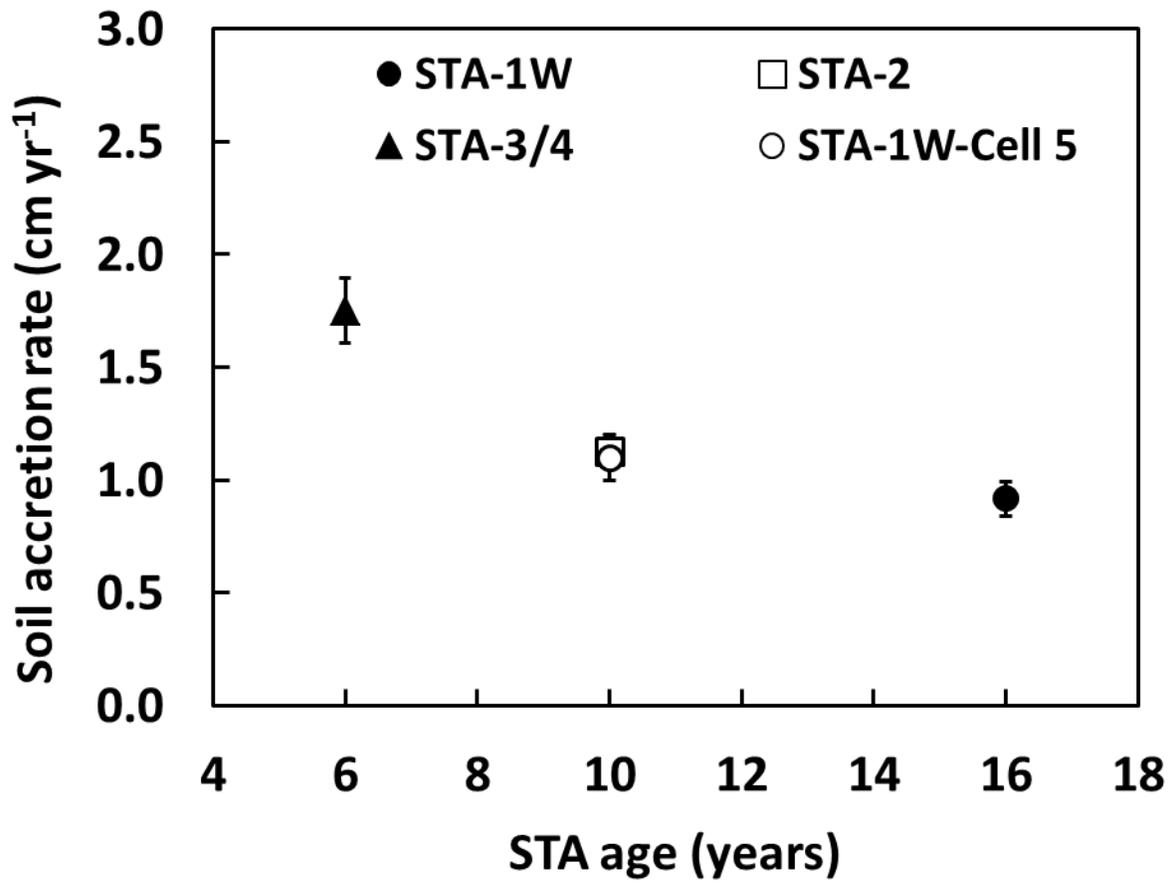


Figure 4-7. Soil accretion rate (cm yr⁻¹) as a function of STA age for STA-1W, STA-2 and STA-3/4. Error bars represent one standard error of the mean.

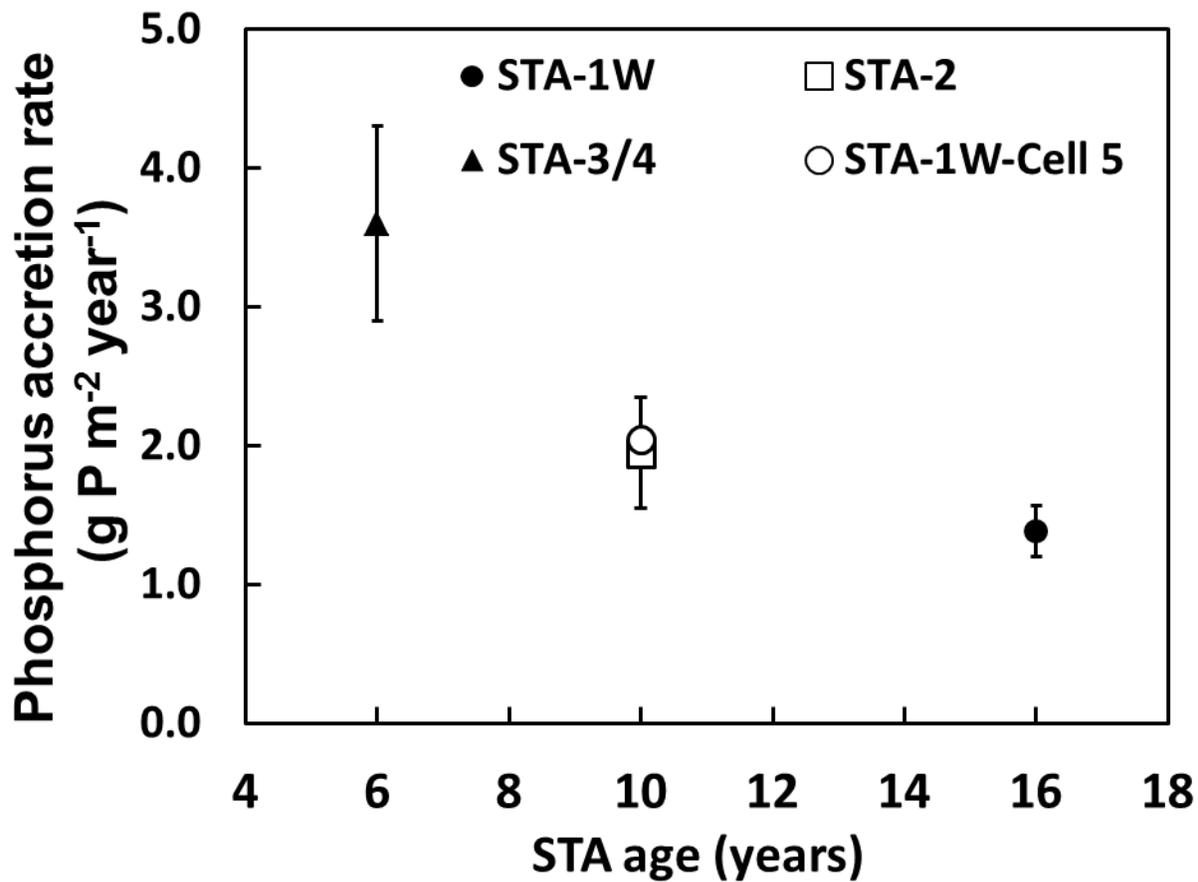
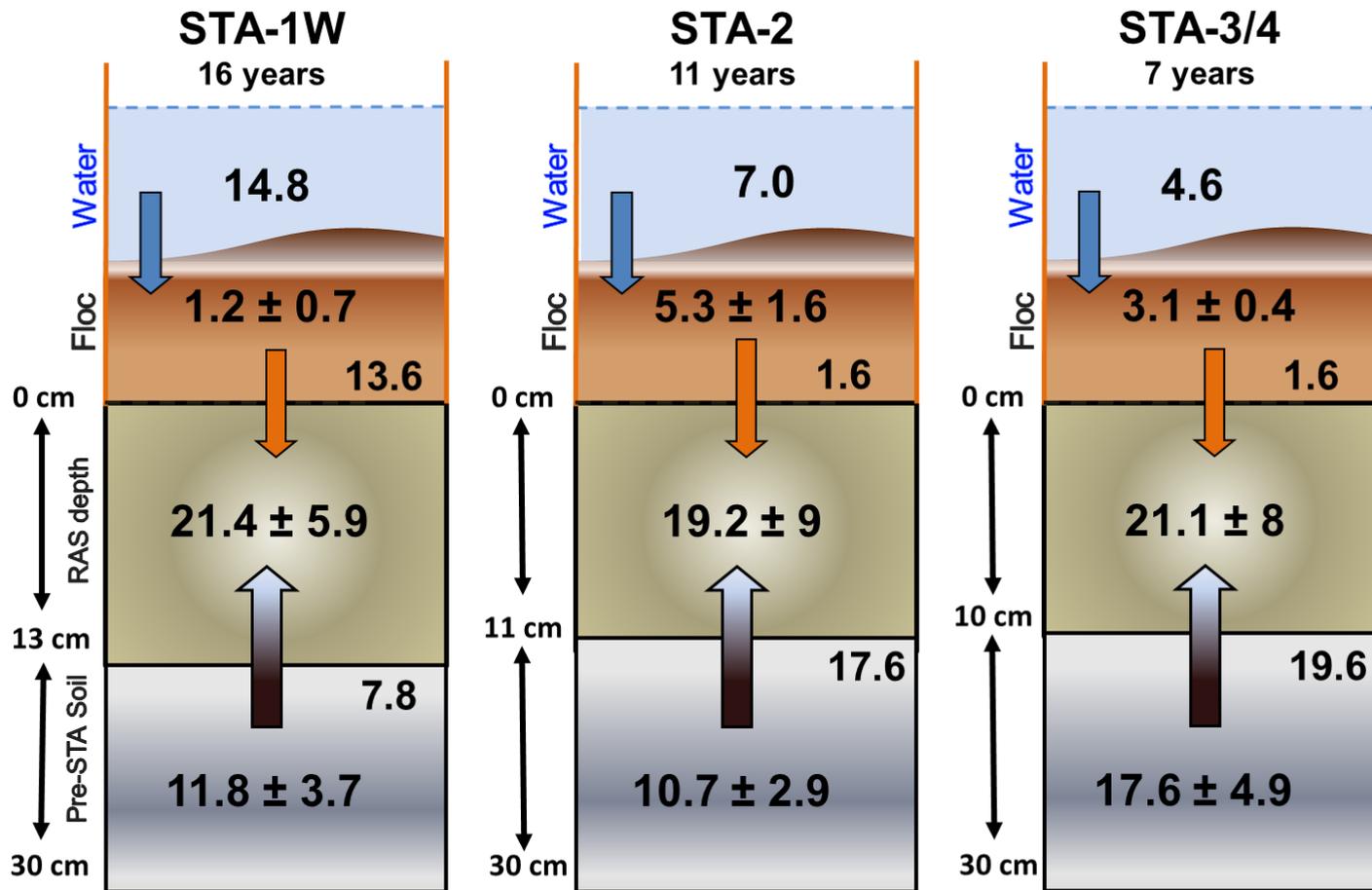


Figure 4-8. Phosphorus accretion rate ($\text{g P m}^{-2} \text{ yr}^{-1}$) as a function of STA age for STA-1W, STA-2 and STA-3/4. Error bars represent one standard error of the mean.



All values expressed in g P m^{-2}

Figure 4-9. Phosphorus mass balance calculations for soil P storage with respect to net P retained from the water column. All values are in g P m^{-2} . Arrows indicate flux of P between storage compartments. Top arrow indicates P movement from the water column to floc. Middle row arrows show P movement between floc and RAS. Lower row arrows indicate P movement from pre-STA soil to RAS.

CHAPTER 5 STABILITY OF PHOSPHORUS IN RECENTLY ACCRETED SOILS: ASSOCIATED VEGETATION EFFECTS

Background

Constructed wetlands have biogeochemical processes that result in the transformation and assimilation of pollutants. Accumulation of organic matter that forms recently accreted soil (RAS) is an example of one such assimilatory process which provides a sink for influent constituents (Rogers, 1984). Characteristics of RAS in constructed wetlands are often dissimilar from antecedent soils (White and others, 2001). These differences usually arise because of the existing wetland vegetation, hydrologic regime, nutrient and sediment loading, environmental disturbance, and management intervention (Kadlec, 2009; White and others, 2001). As such, interplay of these factors regulates how sequestered nutrients are distributed into pools of varying chemical stability and the extent of their recalcitrance determines constructed wetland's treatment performance (Fisher and Reddy, 2010). Characterization of the relative stability of sequestered nutrients in constructed wetlands is important for understanding the risk of releasing these nutrients back to the water column in response to changing environmental conditions. This information is also crucial for planning interventions aimed at maintaining a constructed wetland's role as a pollutant sink for an extended period (Newman and Pietro, 2001; Olila and others, 1997).

The Everglades Stormwater Treatment Areas (STAs) provide a representative example of large-scale constructed wetlands that were established to remove excess phosphorus (P) from agricultural drainage waters originating in the Everglades Agricultural Area (EAA) (Chimney and others, 2006). The long-term functioning of the STAs as sinks for P is based on sustained incorporation of P in accreted soil (Kadlec,

2009; Reddy and others, 1999a; Walker and Kadlec, 2011). This requires the continuous accrual of P in stable fractions that are resistant to release in response to changes in environmental conditions, including fluctuation in redox conditions, pH and temperature, the availability of electron acceptors, microbial activity, and anthropogenic disturbances (Fisher and Reddy, 2001; Pant and Reddy, 2001). The mobility and reactivity of sequestered P in the STAs are controlled by the chemical composition of P in soil and water, the relative sizes of various P pools in the soil, interactions of soluble P fractions with solid soil phases, and decomposition of soil organic matter (Moore and others, 1998).

Both organic and inorganic forms of P are found in wetland soils; however, the relative proportion of each of these forms depends on soil type - mineral or organic, and the forms of any P added to the system. Organic P usually constitutes more than half of soil total P (TP) in wetlands (Moore and others, 1998). Organic P forms extracted from mineral wetland soils include inositol phosphates, phospholipids, and nucleic acids (Turner and others, 2006) whereas a significant proportion of organic P occurs as phosphodiester or products of phosphodiester hydrolysis in organic soils (Turner and Newman, 2005). As much as one third of inositol P can be complexed with humic and fulvic acids, thereby reducing the bioavailability of this soil P fraction. The reactivity of organic P forms determines their movement and potential availability, and has significant implications for long-term storage of P in accreted soils in treatment wetlands.

Quantification of reactive and non-reactive P pools in the STAs is useful for determining the potential P flux from RAS to the overlying water column under normal

operating conditions as well as for estimating potential P loss during changes in hydrologic condition, such as drought (Fisher and Reddy, 2001). Estimates of the relative proportion of reactive and non-reactive pools in accreted P are useful in predicting sustainable P removal in the STAs and for achieving long-term goals for the Everglades restoration.

Soil and P accretion rates for the Everglades STAs, and related P storage in floc, RAS and pre-STA soil were determined in previous studies (see Chapter 2 and Chapter 4). These studies showed that treatment performance across the STAs have been variable although these systems have consistently removed P from the water column. The removed P has been sequestered in RAS, which forms the top 10-14 cm of P enriched surface soil in the studied STAs (STA-1W, STA-2 and STA-3/4).

Objectives and Hypotheses

The main objectives of this study were to determine the relative proportion of reactive and non-reactive P fractions in Everglades STA soils and assess the influence of wetland vegetation - emergent aquatic vegetation (EAV) and submerged and floating aquatic vegetation (SAV/FAV) on the reactivity of these P fractions. The operating hypothesis was that the differences in vegetation will have a pronounced effect on P processing and will actively influence the quantity of P forms in RAS. The quality and consequently the reactivity of accreted P in RAS will determine its potential mobility and impact treatment efficiency of STAs.

Methods

Site Description

Two STAs with different operational age were selected for this study: STA-1W = 16 or 10 years (depending on the cell) and STA-2 = 10 years (Figure 5-1). In STA-1W,

soil samples were collected from two EAV cells - Cells 3 and 5A and one SAV cell – Cell 5B. Cells 5A and 5B were constructed later than the other cells in STA-1W and only had an operational age of 10 years. Cell 3 underwent conversion from an EAV dominated cell to a SAV cell, but was classified as an EAV cell in this study. In STA-2, Cells 1 and 2 were EAV while Cells 3 and 4 were SAV for the entire period of record.

Soil and Chemical Analysis

Intact soil cores (n =44) were collected during April to June, 2011, using a stainless steel tube (10.2-cm internal diameter [ID]; and 0.2-cm wall thickness [WT]). The depth of soil cores ranged from 10 - 40 cm as limited by the depth of the bedrock from the soil surface. Soil cores were transferred into clear cellulose acetyl butyrate tubes (10.2-cm ID, 0.16 cm WT) in the field and transported to the laboratory for storage at 4°C until they were analyzed.

Initial processing involved sectioning of all cores into three layers – floc, RAS and pre-STA soil. Floc was collected separately after recording its depth. The remainder of each soil core was divided into RAS and pre-STA soil. The depth of RAS was the same as calculated earlier (Chapter 3) using the change-point technique. Mean RAS depths in soil cores from STA-1W and STA-2 are presented in Table D-4 in Appendix D. RAS was further divided into sections of 4 cm each (there were 2-3 4-cm sections in each soil core depending on RAS depth). The remainder of the soil core below RAS was designated as pre-STA soil (antecedent native soil). Floc and soil samples were dried at 70° C for bulk density determination. Dried samples were finely ground using a ball mill and passed through a 2-mm sieve before chemical analysis.

Total P was determined with the ashing and HCl digestion method (Andersen, 1976) using standard molybdate colorimetry for analysis (U.S. Environmental Protection

Agency, 1993). Total nitrogen (TN) and total carbon (TC) were determined using a Costech Elemental Analyzer (Model 4010, Costech Analytical Industries, Inc., Valencia, CA). Elemental calibration was accomplished using peach leaves (2.93% N, 44.65% C).

Metals such as calcium (Ca), magnesium (Mg), iron (Fe) and aluminum (Al) were determined in the soil extract obtained by treating flocc and soil samples with 1M HCl fraction by inductively coupled plasma (ICP) mass spectrometry.

Soil Phosphorus Fractionation

Soil P fractions were measured using the simplified chemical P fractionation scheme described in Figure 5-2 (Ivanoff and others, 1998). The procedure involved sequential chemical extraction of a 1:50 dry sediment-to-solution mixture with: a) 1M HCl representing inorganic P (labile P bound to Ca, Mg, Fe, and Al [Pi]), and b) 0.5M NaOH representing organic P associated with fulvic and humic fractions (moderately to highly resistant organic P [Po]). Soil P extracted with acid and alkali are defined as the reactive P pool. Phosphorus remaining in soil after the sequential extractions (residual P [Pr]) was measured by ignition and defined as non-reactive P that included both organic and inorganic compounds, although little is known about the structure and chemical composition of this P fraction.

Extracts from P fraction were centrifuged at 6000 rpm for 10 min, filtered through a 0.45 µm filter and analyzed for soluble reactive P (SRP) or digested with sulfuric acid and potassium persulfate and analyzed for TP. Solutions were analyzed by colorimetry, determined by reaction with molybdate using a Technicon AAll autoanalyzer (Murphy and Riley, 1962; U.S. EPA, 1993). Residual P was determined using an ignition method (Andersen, 1976) and analyzed as described above for TP.

Data Analysis

The purpose of sub-dividing RAS into 4-cm sections was to explore the changes in P pools at a finer depth resolution and capture the age effect manifested in deeper sediments. Hence, in a 12-cm RAS layer for example, soil characteristics close to the boundary between accreted and pre-STA soil would be different from RAS closer to the surface floc. Homogenizing the entire RAS layer for analysis could lose any depth information, and fail to capture any gradients in the various P fractions.

The mass of TP for each RAS section was added to produce one overall value for entire RAS section. Ultimately, for data analysis, interpretation and synthesis, each site contributed a maximum of three sample points – floc, RAS and pre-STA soil. For sites with no floc, only two soil layers (RAS and pre-STA soil) were used. For pre-STA soil, P storages were calculated for a layer 15 cm deep, while measured soil depth was used in P storage calculations for the floc and RAS fractions.

Statistical analysis was performed to compare means of soil nutrients pools (TP, total nitrogen [TN], and total carbon [TC]) from STA-1W and STA-2 separately for comparisons of vegetation treatment effect. Similar comparisons were performed separately for EAV and SAV cells for each P fraction – P_i , P_o and P_r in floc, RAS and pre-STA soil using student's t tests assuming equal variances with a level of significance (α) = 0.05. These analyses were carried out to explore differences in P fractions due to vegetation affects.

Results

Soil Physico-Chemical Properties

The soil physical and chemical characteristics showed differences between two vegetation type (EAV or SAV) as well as among different soil core sections (floc, RAS and pre-STA) when compared independently for each STA.

Bulk density

The bulk density of floc in SAV cells of STA-1W was significantly greater than that of EAV cells, whereas in STA-2, floc, RAS and pre-STA sections displayed higher bulk density in SAV cells as compared to EAV cells (Table 5-1).

Loss on Ignition

The LOI in floc fraction of STA-1W showed a significant difference between EAV and SAV cells (Table 5-2). In STA-2, LOI in EAV and SAV cells was significantly different for all soil sections. Floc samples from the SAV cell had a low mean LOI compared to the other soil sections suggesting a higher mineral fraction in floc.

Total Phosphorus

No significant differences in TP content were detected between STA-1W EAV and SAV cells for all soil sections (Table 5-3). In STA-2, TP content in EAV and SAV cells was significantly different for all three sections. Floc TP concentration was lower in SAV cells whereas it was higher for RAS and pre-STA soil sections when compared to EAV cells of STA-2. Total P storage pools for each soil fraction in STA-1W and STA-2 are presented in Table 5-4.

Total P content and TP storages in samples from each cell of STA-1W and STA-2 are presented in Appendix E (Tables E-4 and E-5).

Total Nitrogen

Results for TN in STA-1W showed a significant difference between EAV and SAV cells for floc but no differences in RAS or pre-STA soil (Table 5-5). Total N content in floc and RAS was significantly different between EAV and SAV cells in STA-2 but there was no difference for pre-STA soil. SAV cells had lower TN concentrations in floc and RAS compared to EAV cells in both STA-1W and STA-2. Total N storage pools for each soil fraction for STA-1W and STA-2 are presented in Table 5-6.

Average TN content and TN storages in samples from each cell of STA-1W and STA-2 are presented in Appendix E (Tables E-6 and E-7).

Total Carbon

Results for STA-1W showed significant differences in TC content between EAV and SAV cells for floc but no differences in RAS or pre-STA soil in EAV and SAV cells (Table 5-7). Total C content in floc, RAS and pre-STA soil in STA-2 were significantly different between EAV and SAV cells. Floc TC content was lower in SAV cells compared to EAV cells of STA-1W while TC content in floc, RAS and pre-STA soil of SAV cells was lower than in EAV cells of STA-2. Total C storage pools for each soil fraction for the STA-1W and STA-2 are presented in Table 5-8.

Average total C and mass C storages in the samples from each cell of STA-1W and STA-2 are presented in Appendix E (Tables E-8 and E-9).

Metals

Comparisons between the metals content in EAV and SAV cells of STA-1W and STA-2 in all soil fractions are presented in Table 5-9 for Ca, Table 5-10 for Mg, Table 5-11 for Fe and Table 5-12 for Al. The Ca content in floc samples was significantly higher in SAV cells than in EAV cells for both STAs. The Mg content in RAS fraction of SAV

cells was significantly higher than EAV cells of STA-2. The Fe content in pre-STA samples was significantly higher in SAV cells than in EAV cells for STA-1W. Significant differences in Al were observed for RAS and pre-STA soil between EAV and SAV cells of both STAs.

Phosphorus Fractions

The relative size of the P fractions (Po, Pi and Pr) varied from one cell to another, but showed a similar pattern for floc, RAS and pre-STA soil: Pi ranged from 15 - 45% of TP, whereas Po was 35 - 50% and Pr was 20 - 35% of TP, respectively. These results from STA-1W and STA-2 are shown in Figures 5-3 (A) and 5-4 (A), respectively and relative proportions are presented in Figures 5-3 (B) and 5-4 (B).

In STA-1W, Pi content was highest in floc for the SAV cell - Cell 5B whereas it was slightly lower in floc in the EAV cell - Cell 5A. Cell 3 had lower Pi content in comparison to the other two cells (Figure 5-3). The relative proportion of Po was mostly constant in floc, RAS and pre-STA soil. Residual P was highest in RAS and pre-STA soil of SAV cells (Cell 3 and Cell 5B). In STA-1W (both EAV and SAV cells combined), Pi in floc samples was 30% of TP while both RAS and pre-STA soil was 27% of TP as Pi. Organic P in floc was 41%, and 37% and 40% of TP in RAS and pre-STA soil, respectively.

In STA-2, the relative proportion of Pi was highest in floc for the SAV cells - Cell 3, whereas it was lower for floc in EAV cells (Cell 1 and Cell 2) (Figure 5-4). The relative proportion of Po was higher in floc, RAS and pre-STA soil of EAV cells compared to SAV cells. Residual P was in the same range for floc, RAS and pre-STA soil. In STA-2s (both EAV and SAV cells combined), the Pi in floc samples was 30% of the TP. RAS

and pre-STA soil had 26% and 25% of TP respectively. Organic P in floc was 40% of TP, and 40% and 52% of TP in RAS and pre-STA soil, respectively.

Vegetation Effects

Significant differences were observed between EAV and SAV cells when both STAs were analyzed together, such that EAV floc (Po) was greater than SAV floc, SAV RAS (Pi) was greater than EAV RAS and SAV pre-STA (Po and Pr) was greater than EAV pre-STA fraction (Table 5-13). Individually, STA-1W showed higher Po content in EAV floc in comparison to SAV floc, and higher Po content in SAV pre-STA sections (Tables 5-14). The relative proportion of Pr was lower for EAV cells in STA-1W in comparison to SAV cells. In STA-2, floc Po was higher in EAV cells in comparison to SAV floc Po (Table 5-15). For RAS fraction, Pi content was significantly higher in SAV cells. Pre-STA soil had significantly higher Pi, Po and Pr fractions in SAV cells compared to EAV cells. Residual P was found to be almost equal in both EAV and SAV cells of both STAs except for pre-STA soil section of STA-2. (Table 5-15).

To assess the influence of SAV and EAV on partitioning P into various fractions, Pi and Po content was plotted against TP concentration for all soil sections pooled over both STAs by vegetation type (Figures 5-5 and 5-6). No clear difference between SAV and EAV cells was detected in either STA. However, the Pearson correlation coefficient, calculated separately for EAV and SAV cells using pooled data from both STAs, showed that Pi is strongly correlated with TP in SAV cells while Po is strongly correlated with TP in EAV cells. The reactive P constituted 75% of TP in floc sections of EAV cells and 62% of TP in SAV cells (Figure 5-7). In RAS, reactive P was 64% of TP for EAV and 67% of TP for SAV cells. However, floc and RAS sections of EAV cells showed higher Po fractions (50% and 40% of TP, respectively) compared to SAV (23% and 37%

of TP, respectively). Pre-STA soil was similar for EAV and SAV cells, with a higher proportion of reactive P fractions distributed as organic P (65% and 78%, respectively).

Correlations Among Soil Properties

Correlations among various soil parameters for all soil fractions from both STA-1W and STA-2 are shown in Table 5-16. Positive correlations were observed between Pi and Ca ($r = 0.54$) and Mg ($r = 0.31$) whereas negative correlations were found between Pi and Fe ($r = -0.37$) and Al ($r = -0.20$). Iron and Al were negatively correlated with TP, Pi and Po. Total P and Pr had low but significant correlations with Ca. Inorganic P was significantly correlated with more STA soil parameters compared to Po.

EAV Cells: Correlations among various soil parameters for all soil fractions from EAV cells of both STA-1W and STA-2 are shown in Table 5-17. High positive correlation were observed between TP and Po ($r = 0.90$) whereas no correlation was found between Ca and Po. Negative correlations were found between TP and Fe ($r = -0.58$) and Al ($r = -0.46$).

SAV Cells: Correlations among various soil parameters for all soil fractions from SAV cells of both STA-1W and STA-2 are shown in Table 5-18. High positive correlation were observed between TP and Pi ($r = 0.80$) and Ca and Pi ($r = 0.69$). Negative correlations were found between TP and Fe ($r = -0.56$) and Al ($r = -0.39$).

STA-1W: Correlations among various soil parameters for STA-1W are shown in Table 5-19. Positive correlations were observed between Pi and Ca ($r = 0.58$) and Mg ($r = 0.44$). Negative correlations were found between TP and Fe ($r = -0.68$) and Al ($r = -0.57$). A negative correlation was also observed between Pi and Al ($r = -0.36$). Total P was significantly correlated with Ca ($r = 0.46$) and Mg ($r = 0.26$). Iron and Al were

positively inter-correlated. No correlation was found between Po with Ca or Mg. No significant correlation was found between TP and TN. Correlation matrices elucidating relationships within SAV and EAV cells in STA-1W are presented in Tables E-16 and E-17 (Appendix E).

STA-2: Correlations among various soil parameters for STA-2 are shown in Table 5-20. The highest correlations were between Pi and Ca ($r = 0.61$) and Mg ($r = 0.36$). Negative correlations were found between TP and Fe ($r = -0.51$) and Al ($r = -0.40$). There was no correlation between Pi and Al; however, Pi and Fe were negatively correlated ($r = 0.33$). Iron and Al were positively inter-correlated. Total P was significantly correlated with Ca ($r = 0.30$) but not with Mg. Organic P was negatively correlated with Mg ($r = -0.37$) but no correlation was observed for Po with Ca. Negative correlations were found between TP and TN ($r = -0.31$) and TC ($r = -0.51$). Correlation matrices elucidating relationships within SAV and EAV cells in STA-2 are presented in Tables E-18 and E-19 (Appendix E).

Discussion

About thirty percent of TP is present in non-reactive P fraction for different soil sections (floc, RAS and pre-STA soil; Figure 5-18). Data range is limited in pre-STA soil, and showed no difference between two vegetation types (EAV and SAV). Floc and RAS fractions were, however, more variable and exhibited a greater range of TP values. The high concentration of Pi in the near-surface soil suggests that Pi may be loosely bound to organic matter, bound to solid phases such as CaCO_3 , or present as recently precipitated, amorphous, mono-calcium phosphate.

Given the important role Ca plays in the retention of P in wetlands with alkaline soils, the relationship between Ca and TP in floc, RAS and pre-STA soil was explored for STA-1W in Figure 5-9 (n=50) and for STA-2 in Figure 5-10 (n=75). Pre-STA soil showed no difference between SAV and EAV cells and were clustered together for both STAs (Figures 5-9 and 5-10). RAS samples, from both SAV and EAV cells, were located in the center of graphs with intermediate TP and Ca values. Floc samples exhibited greatest dissimilarity between SAV and EAV cells and the distinct clusters for each vegetation were separated apart in plots for STA-1W and STA-2 (Figures 5-9 and 5-10). SAV Cell 5A (STA-1W) had higher Ca concentration per unit of P, in comparison to EAV cells. However, floc characteristics of SAV Cell 3 (STA-1W), which underwent conversion from EAV to SAV, were similar to EAV cell, possibly due to cell's history as an EAV cell. In STA-2, EAV cells had higher TP content in floc in comparison to SAV cells. SAV cells showed relationship between soil TP and Ca indicating that P movement into floc is controlled by Ca and could be a co-precipitation mechanism induced by epiphyton-periphyton assemblages in open water. It also suggested that SAV cells had a higher proportion of Pi in floc fractions in comparison to EAV cells.

Positive correlation between Pi with Ca and Mg suggest that Pi dynamics in STA soils are governed by Ca and Mg. Earlier P sorption studies conducted in the EAA and WCAs also show positive relationships between P sorption and Ca (Porter and Sanchez, 1992; Richardson and Vaithyanathan, 1995).

When explored separately for each soil section – floc, RAS and pre-STA, the vegetation effects on P fractions for STA-1W were found to be insignificant except for Po in floc and the pre-STA soil. For STA-2, significant differences were observed

between EAV and SAV cells for floc, RAS and pre-STA soil. A significant difference was observed in floc section for Po fractions between EAV and SAV. Organic P was higher in floc of EAV cells. For RAS sections, Pi was significantly higher in SAV cells. Pre-STA soil fractions indicated higher Pi, Po and Pr fractions in SAV cells in comparison to EAV cells. The comparison across two studied STAs is confounded by the fact that these two systems were considerably dissimilar due to different hydraulic and P loading, basin characteristics, vegetation coverage, and management interventions.

Reactions that fix P in wetland soils include precipitation of Fe with hydroxide and phosphate in aerobic pore waters (Fox, 1989), the formation of the ferrous phosphate mineral vivianite in the anaerobic zone (Emerson and Widmer, 1978; Manning and others, 1991; Woodruff and others, 1999), and co-precipitation of phosphate with calcite in hard-water systems (House and Denison, 1997; Koschel and others, 1983; Kuchler-Krischun and Kleiner, 1990). Higher Pi levels in RAS suggest re-mineralization of labile Po, and retention of Pi through adsorption and precipitation. Precipitation of P with Fe^{3+} could be enhanced by a fluctuating water table, which these STAs regularly experienced, except for SAV cells where high water levels are actively managed (although sections of SAV cells also experience dry conditions during severe droughts).

Water-level drawdown and soil drainage are commonly used in treatment wetlands to consolidate flocculated material, accelerate soil accretion, and allow access for maintenance operations (Kadlec and Wallace, 2009). This could result in releasing Pi to the water column upon re-flooding (Newman and Pietro, 2001; Olila and others, 1997). Drying and rewetting can also release Po through microbial cell lysis (Turner and Haygarth, 2001), while redox changes could destabilize Po complexed with Fe. A recent

study, explored four different management options for enhancing SRP removal by treatment wetland soils(Lindstrom and White, 2011). These authors compared physical and chemical treatments such as dry down, surface additions of alum or calcium carbonate (CaCO_3) and physical removal of the accreted organic soil as a potential means to reduce P flux from the soils. The results demonstrated organic soil layer removal and surface alum addition as the most effective options.

Summary

Soil P, not extracted by either acid or alkali, is considered as residual P and operationally defined as nonreactive P. For all practical purposes, nonreactive P is unavailable for biotic or abiotic transformations. Approximately 25-30% of soil TP in the STAs was non-reactive. The stability of this fraction can be attributed to the presence of P associated with highly stable organic materials such as lignin and organometallic complexes. Phosphorus enriched STA soils (floc and RAS) typically contained less TP in the non-reactive pool than did pre-STA soil. In this study, the P_i and P_o fractions in floc and RAS sections together accounted for 65-70% of all TP stored in soil. This P can be classified as reactive, and it is prone to be released into the water column when environmental conditions become favorable. A sizeable pool of reactive P in STA soils, presents a risk for disrupting treatment efficiency of STAs and, if released into the water column it could result in P impacts downstream. The long-term stability of P in treatment wetlands is dependent on the relative proportion of non-reactive P. Exploration of P accretion and partitioning in various fractions as a function of STA age could provide insights on how the stability of P fractions varies over time.

Table 5-1. Summary statistics for bulk density of soil sections in EAV and SAV cells of STA-1W and STA-2 and results of t-tests of differences between vegetation communities.

Bulk Density (g cm ⁻³) Avg ± sd (n)	STA-1W			STA-2		
	EAV#	SAV	P-value	EAV	SAV	P-value
Floc	0.09 ± 0.04 (9)	0.15 ± 0.05 (7)	0.021 *	0.06 ± 0.03 (14)	0.12 ± 0.01 (7)	<0.001 ***
RAS	0.27 ± 0.06 (10)	0.32 ± 0.05 (7)	0.123 ns	0.22 ± 0.07 (14)	0.28 ± 0.07 (13)	0.022 *
Pre-STA soil	0.31 ± 0.05 (10)	0.28 ± 0.04 (7)	0.205 ns	0.17 ± 0.1 (14)	0.29 ± 0.09 (13)	0.004 **

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance)

STA-1W Cell 3 analyzed as EAV cell.

Table 5-2. Summary statistics for loss on ignition of soil sections in EAV and SAV cells of STA-1W and STA-2 and results of t-tests of differences between vegetation communities.

Loss on Ignition (%) Avg ± sd (n)	STA-1W			STA-2		
	EAV#	SAV	P-value	EAV	SAV	P-value
Floc	80 ± 4 (9)	66 ± 6 (7)	<0.001 ***	72 ± 12 (14)	29 ± 6 (7)	<0.001 ***
RAS	83 ± 7 (10)	84 ± 4 (7)	0.891 ns	85 ± 4 (14)	69 ± 13 (13)	<0.001 ***
Pre-STA soil	89 ± 2 (10)	88 ± 4 (7)	0.348 ns	87 ± 1 (14)	75 ± 22 (13)	0.038 *

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance)

STA-1W Cell 3 analyzed as EAV cell

Table 5-3. Summary statistics for total phosphorus content of soil sections in EAV and SAV cells of STA-1W and STA-2 and results of t-tests of differences between vegetation communities.

TP (mg kg ⁻¹) Avg ± sd (n)	STA-1W			STA-2		
	EAV#	SAV	P-value	EAV	SAV	P-value
Floc	1052 ± 361 (9)	924 ± 176 (7)	0.405 ns	1097 ± 248 (14)	766 ± 293 (7)	0.014 *
RAS	561 ± 268 (10)	509 ± 125 (7)	0.645 ns	384 ± 114 (14)	608 ± 175 (13)	0.001 **
Pre-STA soil	294 ± 125 (10)	364 ± 108 (7)	0.247 ns	197 ± 45 (14)	318 ± 114 (13)	0.001 **

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance)

STA-1W Cell 3 analyzed as EAV cell

Table 5-4. Summary statistics for total phosphorus storage pools for each soil fraction in EAV and SAV cells of STA-1W and STA-2.

TP (g P m ⁻²) (Avg ±sd)	STA-1W			STA-2			
	EAV Cell-5A	SAV Cell-3 Cell-5B		EAV Cell 1 Cell 2		SAV Cell 3 Cell 4	
Floc	9.3 ± 2.2	5.8 ± 1.8	8.1 ± 3.9	6.2 ± 2.4	4.7 ± 3.3	7.5 ± 3.9	--
RAS	17.8 ± 13.3	12.8 ± 4.6	15.5 ± 6.6	5.7 ± 2	9.8 ± 3.2	13.5 ± 5.4	18.8 ± 5.4
Pre-STA soil	19.7 ± 7.9	8.7 ± 1.3	15.5 ± 6.5	3.6 ± 0.7	6.8 ± 5.9	11.5 ± 6.6	17.1 ± 9.5

Table 5-5. Summary statistics for total nitrogen content of soil sections in EAV and SAV cells of STA-1W and STA-2 and results of t-tests of differences between vegetation communities.

TN (g N kg ⁻¹) Avg± sd (n)	STA-1W			STA-2		
	EAV	SAV	P-value	EAV	SAV	P-value
Floc	31 ± 3 (9)	28 ± 3 (7)	0.021 *	26 ± 4 (14)	12 ± 2 (7)	<0.001 ***
RAS	32 ± 7 (10)	33 ± 3 (7)	0.900 ns	30 ± 2 (14)	26 ± 5 (13)	0.019 *
Pre-STA soil	32 ± 3 (10)	34 ± 3 (7)	0.254 ns	28 ± 1 (14)	30 ± 5 (13)	0.259 ns

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance)

Table 5-6. Summary statistics for total nitrogen storage pools for each soil fraction in EAV and SAV cells of STA-1W and STA-2.

TN (kg Nm ⁻²) (Avg± sd)	STA-1W			STA-2			
	EAV Cell-5A	SAV Cell-3	SAV Cell-5B	EAV Cell 1	EAV Cell 2	SAV Cell 3	SAV Cell 4
Floc	0.2 ± 0.1	0.3 ± 0.2	0.2 ± 0.1	0.2 ± 0.1	0.1 ± 0.1	0.1 ± 0	--
RAS	0.9 ± 0.5	0.9 ± 0.3	1 ± 0.3	0.5 ± 0.2	0.7 ± 0.2	0.7 ± 0.4	0.8 ± 0.3
Pre-STA soil	1.5 ± 0.2	1.4 ± 0.2	1.4 ± 0.2	0.6 ± 0.1	0.8 ± 0.5	1 ± 0.2	1.5 ± 0.3

Table 5-7. Summary statistics for total carbon content of soil sections in EAV and SAV cells of STA-1W and STA-2 and results of t-tests of differences between vegetation communities.

TC (g/kg) Avg ± sd (n)	STA-1W			STA-2		
	EAV	SAV	P-value	EAV	SAV	P-value
Floc	416 ± 34 (9)	356 ± 37 (7)	0.004 **	369 ± 50 (14)	196 ± 21 (7)	<0.001 ***
RAS	469 ± 78 (10)	454 ± 21 (7)	0.627 ns	447 ± 20 (14)	384 ± 63 (13)	0.001 **
Pre-STA soil	485 ± 15 (10)	477 ± 15 (7)	0.306 ns	472 ± 11 (14)	421 ± 77 (13)	0.020 *

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance).

Table 5-8. Summary statistics for total carbon storage pools for each soil fraction in EAV and SAV cells of STA-1W and STA-2.

TC (kg C m ⁻²) (Avg± sd)	STA-1W			STA-2			
	EAV Cell-5A	SAV Cell-3	SAV Cell-5B	EAV Cell 1	EAV Cell 2	SAV Cell 3	SAV Cell 4
Floc	3 ± 0.6	3.7 ± 2.4	3 ± 1.2	2.2 ± 0.8	1.6 ± 1	1.9 ± 0.5	--
RAS	13.8 ± 5.8	12.6 ± 3.8	13.7 ± 3.7	7.6 ± 2.3	10.4 ± 2.9	10.2 ± 5.3	11.4 ± 4.8
Pre-STA soil	23.6 ± 3.7	21 ± 2.7	19.7 ± 2.9	9.6 ± 1.6	14 ± 9.1	13.7 ± 2	22.1 ± 3.5

Table 5-9. Summary statistics for calcium content of soil sections in EAV and SAV cells of STA-1W and STA-2 and results of t-tests of differences between vegetation communities.

Calcium (g Ca kg ⁻¹) Avg ± sd (n)	STA-1W			STA-2		
	EAV	SAV	P-value	EAV	SAV	P-value
Floc	36.5 ± 9.5 (9)	82.1 ± 13.6 (7)	<0.001 ***	43.5 ± 18 (14)	198.1 ± 38.2 (7)	<0.001 ***
RAS	39.3 ± 15 (10)	43.9 ± 12.3 (7)	0.516 ns	35.6 ± 9.5 (14)	96.6 ± 55.5 (13)	<0.001 ***
Pre-STA soil	29.2 ± 6.6 (10)	36.3 ± 18.7 (7)	0.279 ns	29 ± 5.7 (14)	32.2 ± 10 (13)	0.302 ns

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance).

Table 5-10. Summary statistics for magnesium content of soil sections in EAV and SAV cells of STA-1W and STA-2 and results of t tests of differences between vegetation communities.

Magnesium (g Mg kg ⁻¹) Avg ± sd (n)	STA-1W			STA-2		
	EAV	SAV	P-value	EAV	SAV	P-value
Floc	2.6 ± 0.7 (9)	3.4 ± 1 (7)	0.075 ns	3.1 ± 3.9 (14)	6.2 ± 1.7 (7)	0.054 ns
RAS	3.1 ± 0.6 (10)	2.7 ± 0.4 (7)	0.214 ns	3.5 ± 0.4 (14)	5.5 ± 1.1 (13)	<0.001 ***
Pre-STA soil	2.4 ± 0.5 (10)	2.1 ± 0.8 (7)	0.369 ns	3.1 ± 0.6 (14)	3 ± 0.8 (13)	0.670 ns

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance).

Table 5-11. Summary statistics for iron content of soil sections in EAV and SAV cells of STA-1W and STA-2 and results of t-tests of differences between vegetation communities.

Iron (mg Fe kg ⁻¹) Avg ± sd (n)	STA-1W			STA-2		
	EAV	SAV	P-value	EAV	SAV	P-value
Floc	210 ± 74 (9)	208 ± 92 (7)	0.965 ns	211 ± 219 (14)	128 ± 99 (7)	0.356 ns
RAS	718 ± 357 (10)	1082 ± 424 (7)	0.074 ns	515 ± 222 (14)	471 ± 324 (13)	0.682 ns
Pre-STA soil	1183 ± 308 (10)	1749 ± 417 (7)	0.006 **	748 ± 301 (14)	990 ± 412 (13)	0.092 ns

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance).

Table 5-12. Summary statistics for aluminum content of soil sections in EAV and SAV cells of STA-1W and STA-2 and results of t-tests of differences between vegetation communities.

Aluminum (mg Al kg ⁻¹) Avg ± sd (n)	STA-1W			STA-2		
	EAV	SAV	P-value	EAV	SAV	P-value
Floc	413 ± 147 (9)	604 ± 319 (7)	0.132 ns	279 ± 429 (14)	184 ± 157 (7)	0.581 ns
RAS	754 ± 125 (10)	1167 ± 234 (7)	<0.001 ***	1362 ± 690 (14)	899 ± 412 (13)	0.046 *
Pre-STA	795 ± 135 (10)	1150 ± 238 (7)	0.001 **	723 ± 259 (14)	1815 ± 1181 (13)	0.002 **

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance).

Table 5-13. Summary statistics for phosphorus content in P fractions in floc, RAS and pre-STA soil from EAV and SAV cells in STA-1W and STA-2 and results of t-tests of differences between vegetation communities.

Both STAs (mg kg ⁻¹)	Floc			RAS			Pre-STA soil		
	Avg ± sd (n)	EAV	SAV	P-value	EAV	SAV	P-value	EAV	SAV
Pi	269 ± 151 (23)	332 ± 154 (14)	0.232 ns	104 ± 107 (24)	174 ± 101 (20)	0.033 *	55 ± 73 (24)	94 ± 68 (20)	0.075 ns
Po	528 ± 210 (23)	192 ± 93 (14)	<0.001 ***	186 ± 69 (24)	207 ± 104 (20)	0.425 ns	101 ± 32 (24)	166 ± 46 (20)	<0.001 ***
Residual P	241 ± 94 (23)	214 ± 54 (14)	0.339 ns	146 ± 57 (24)	171 ± 92 (20)	0.285 ns	70 ± 27 (24)	109 ± 45 (20)	0.001 **

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance).

Table 5-14. Summary statistics for phosphorus content in P fractions in floc, RAS and pre-STA soil from EAV and SAV cells in STA-1W and results of t tests of differences between vegetation communities.

STA-1W (mg P kg ⁻¹)	Floc			RAS			Pre-STA soil		
	Avg ± SD (n)	EAV	SAV	P-value	EAV	SAV	P-value	EAV	SAV
Inorganic P (Pi)	287 ± 198 (9)	305 ± 61 (7)	0.817 ns	160 ± 137 (10)	125 ± 49 (7)	0.531 ns	91 ± 100 (10)	80 ± 56 (7)	0.802 ns
Organic P (Po)	539 ± 244 (9)	240 ± 105 (7)	0.009 **	192 ± 89 (10)	204 ± 31 (7)	0.756 ns	98 ± 25 (10)	174 ± 28 (7)	<0.001 ***
Residual P	240 ± 127 (9)	208 ± 69 (7)	0.553 ns	146 ± 70 (8)	130 ± 43 (7)	0.612 ns	69 ± 17 (10)	108 ± 57 (7)	0.058 ns

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance).

Table 5-15. Summary statistics for phosphorus content in P fractions in floc, RAS and pre-STA soil for EAV and SAV cells in STA-2 and results of t tests of differences between vegetation communities.

STA-2 (mg P kg ⁻¹)	Floc			RAS			Pre-STA soil		
	Avg ± SD (n)	EAV	SAV	P-value	EAV	SAV	P-value	EAV	SAV
Inorganic P (Pi)	258 ± 115 (14)	359 ± 198 (7)	0.178 ns	65 ± 54 (14)	200 ± 109 (13)	0.001 **	30 ± 28 (14)	102 ± 72 (13)	0.002 **
Organic P (Po)	521 ± 189 (14)	145 ± 47 (7)	<0.001 ***	182 ± 53 (14)	209 ± 124 (13)	0.470 ns	104 ± 35 (14)	162 ± 51 (13)	0.002 **
Residual P	241 ± 70 (14)	220 ± 37 (7)	0.481 ns	147 ± 47 (14)	193 ± 100 (13)	0.151 ns	71 ± 32 (14)	110 ± 39 (13)	0.012 *

(* for P<0.05, ** for P<0.01 and *** for P<0.001, ns= not significant; two sample t-test, assuming equal variance).

Table 5-16. Pearson correlation coefficients for select parameters measured in all soil fractions in both STA-1W and STA-2. All correlations evaluated at $\alpha=0.05$ (n =125). ns=not significant.

Both-STAs	Bulk density	TP	Ca	Mg	Fe	Al	Pi	TN	TC	Po	LOI
TP	-0.49										
Ca	ns	0.28									
Mg	ns	ns	0.57								
Fe	0.60	-0.53	-0.35	-0.16							
Al	0.50	-0.41	-0.28	ns	0.49						
Pi	-0.22	0.77	0.54	0.31	-0.37	-0.20					
TN	0.18	-0.21	-0.72	-0.56	0.39	ns	-0.49				
TC	0.26	-0.48	-0.76	-0.51	0.47	0.16	-0.66	0.87			
Po	-0.49	0.78	ns	-0.27	-0.38	-0.33	0.37	ns	ns		
LOI	ns	-0.36	-0.79	-0.54	0.38	0.16	-0.58	0.77	0.88	ns	
Pr	-0.42	0.78	0.31	ns	-0.42	-0.28	0.61	-0.22	-0.49	0.59	-0.41

Table 5-17. Pearson correlation coefficients for select parameters measured in all soil fractions in EAV cells from both STA-1W and STA-2. All correlations evaluated at $\alpha=0.05$ (n =56). ns=not significant.

EAV cells (both STAs)	Bulk density	TP	Ca	Mg	Fe	Al	Pi	TN	TC	Po	LOI
TP	-0.46										
Ca	ns	0.39									
Mg	ns	ns	0.56								
Fe	0.53	-0.58	ns	0.24							
Al	0.31	-0.46	ns	0.36	0.41						
Pi	ns	0.76	0.58	ns	ns	-0.23					
TN	ns	-0.23	-0.59	-0.63	ns	ns	-0.34				
TC	0.47	-0.76	-0.70	-0.42	0.44	0.27	-0.68	0.61			
Po	-0.53	0.90	ns	-0.32	-0.63	-0.49	0.53	ns	-0.54		
LOI	0.33	-0.63	-0.80	-0.56	0.27	ns	-0.64	0.67	0.95	-0.37	
Pr	-0.47	0.78	0.37	ns	-0.51	-0.26	0.58	ns	-0.70	0.68	-0.60

Table 5-18. Pearson correlation coefficients for select parameters measured in all soil fractions in SAV cells from both STA-1W and STA-2. All correlations evaluated at $\alpha=0.05$ (n =69). ns=not significant.

SAV cells (both STAs)	Bulk density	TP	Ca	Mg	Fe	Al	Pi	TN	TC	Po	LOI
TP	-0.56										
Ca	-0.33	0.42									
Mg	ns	0.24	0.71								
Fe	0.64	-0.56	-0.53	-0.47							
Al	0.62	-0.39	-0.45	ns	0.50						
Pi	-0.35	0.80	0.69	0.45	-0.50	ns					
TN	0.20	-0.24	-0.80	-0.62	0.46	ns	-0.60				
TC	0.29	-0.43	-0.79	-0.59	0.53	ns	-0.71	0.94			
Po	-0.38	0.59	ns	ns	ns	ns	ns	0.25	ns		
LOI	0.25	-0.35	-0.79	-0.59	0.50	0.22	-0.65	0.83	0.87	ns	
Pr	-0.45	0.80	0.38	0.25	-0.42	-0.32	0.63	-0.27	-0.44	0.57	-0.39

Table 5-19. Pearson correlation coefficients for select parameters measured in all soil fractions from STA-1W. All correlations evaluated at $\alpha=0.05$ (n =50). ns=not significant.

STA-1W	Bulk density	TP	Ca	Mg	Fe	Al	Pi	TN	TC	Po	LOI
TP	-0.70										
Ca	ns	0.46									
Mg	ns	0.26	0.58								
Fe	0.70	-0.68	-0.37	-0.41							
Al	0.62	-0.57	ns	ns	0.73						
Pi	-0.36	0.80	0.58	0.44	-0.51	-0.36					
TN	ns	ns	-0.45	-0.50	0.24	ns	-0.45				
TC	0.35	-0.61	-0.67	-0.38	0.47	0.33	-0.66	0.73			
Po	-0.68	0.80	ns	ns	-0.49	-0.46	0.50	ns	-0.35		
LOI	0.40	-0.73	-0.88	-0.51	0.60	0.40	-0.72	0.44	0.80	-0.30	
Pr	-0.62	0.82	0.31	ns	-0.53	-0.55	0.57	ns	-0.50	0.63	-0.59

Table 5-20. Pearson correlation coefficients for select parameters measured in soil fractions from STA-2. All correlations evaluated at $\alpha=0.05$ (n =75). ns=not significant.

STA-2	Bulk density	TP	Ca	Mg	Fe	Al	Pi	TN	TC	Po	LOI
TP	-0.42										
Ca	ns	0.30									
Mg	ns	ns	0.54								
Fe	0.49	-0.51	-0.39	ns							
Al	0.55	-0.40	-0.32	ns	0.62						
Pi	ns	0.75	0.61	0.36	-0.33	ns					
TN	ns	-0.31	-0.79	-0.51	0.38	0.24	-0.65				
TC	ns	-0.51	-0.78	-0.48	0.43	ns	-0.75	0.90			
Po	-0.41	0.77	ns	-0.37	-0.33	-0.32	0.28	ns	ns		
LOI	ns	-0.34	-0.78	-0.50	0.28	ns	-0.65	0.84	0.89	ns	
Pr	-0.29	0.77	0.35	ns	-0.33	-0.25	0.65	-0.32	-0.51	0.56	-0.40

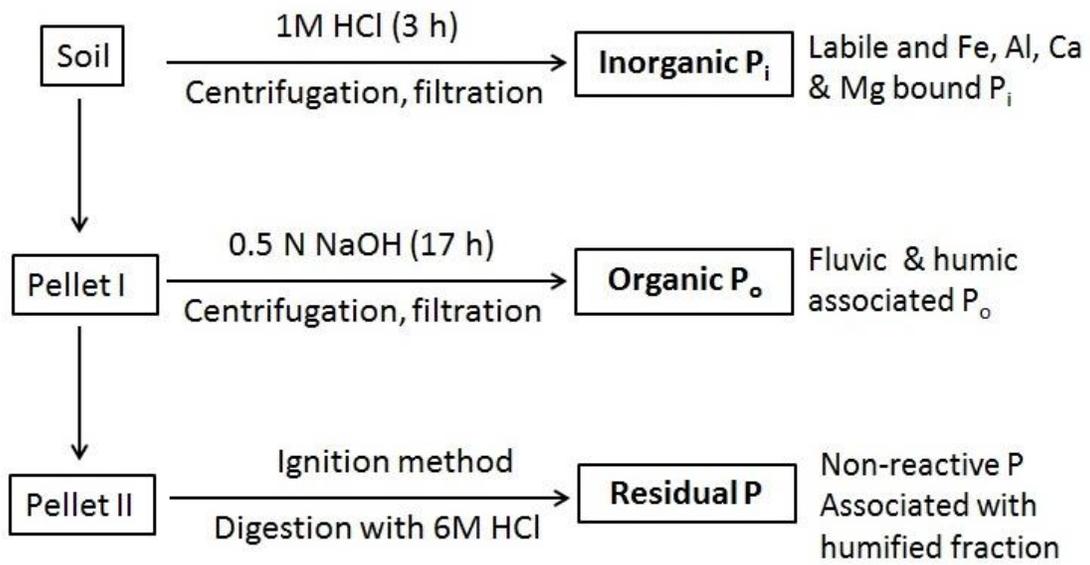
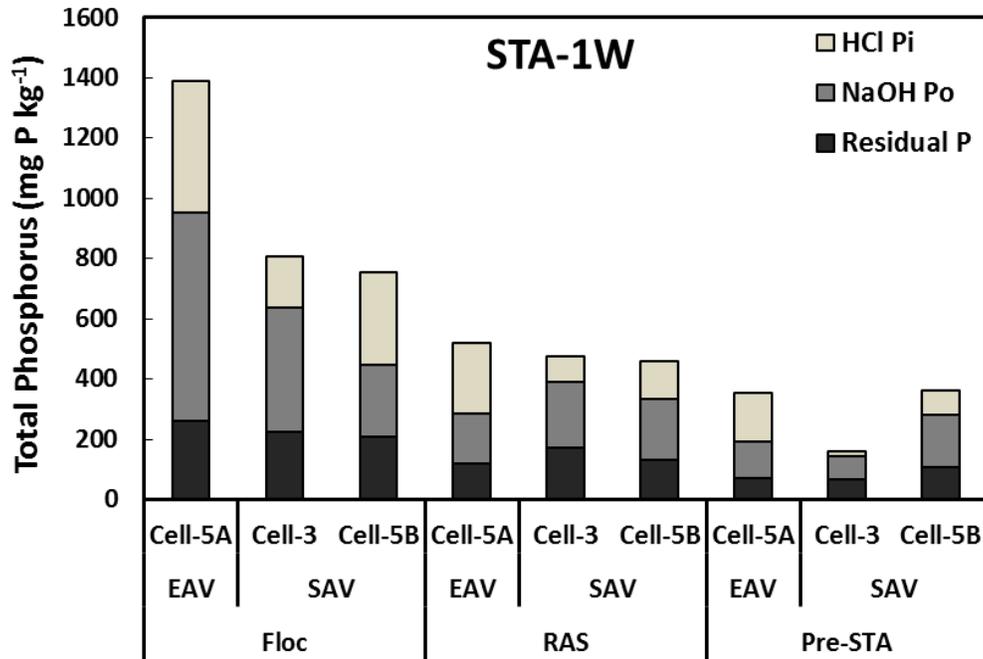
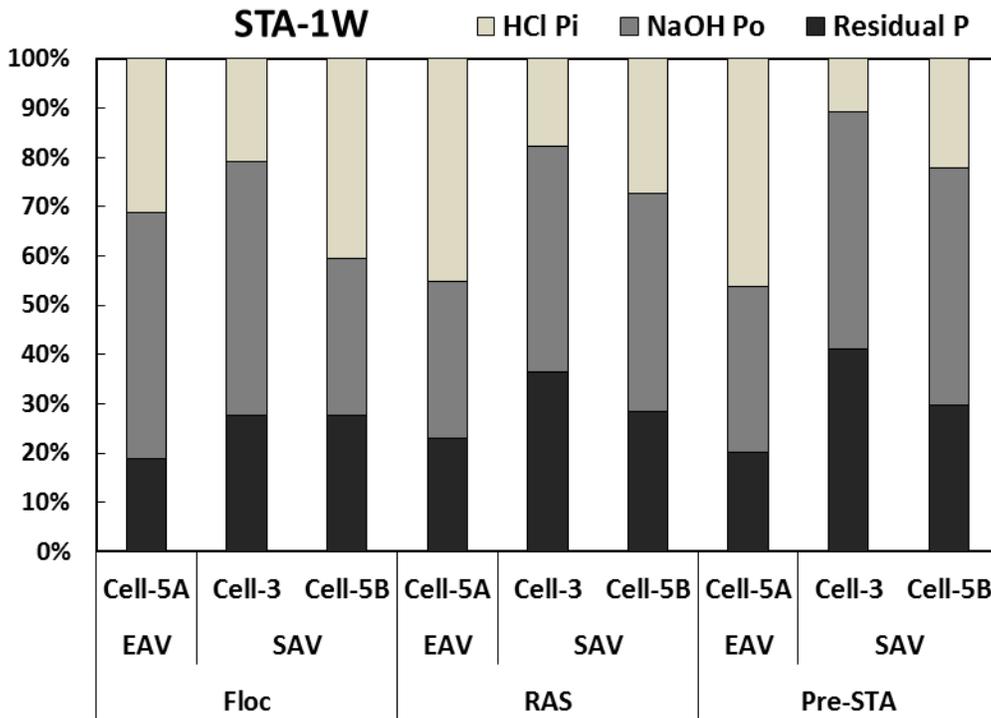


Figure 5-2. Phosphorus fractionation scheme used to characterize P forms in STA soils. Modified from Ivanoff and others, (1998).

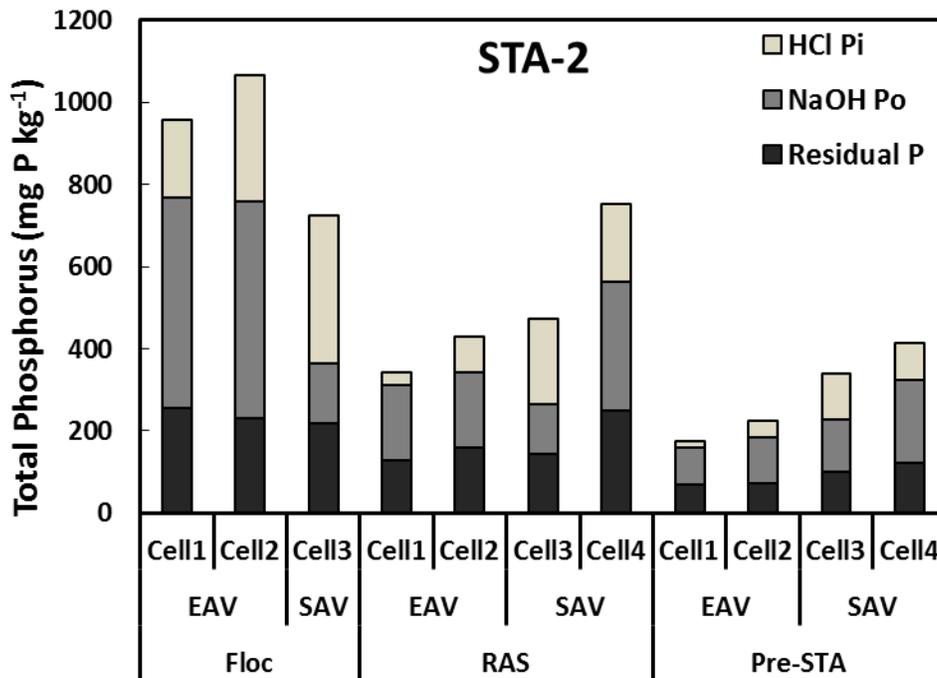


A

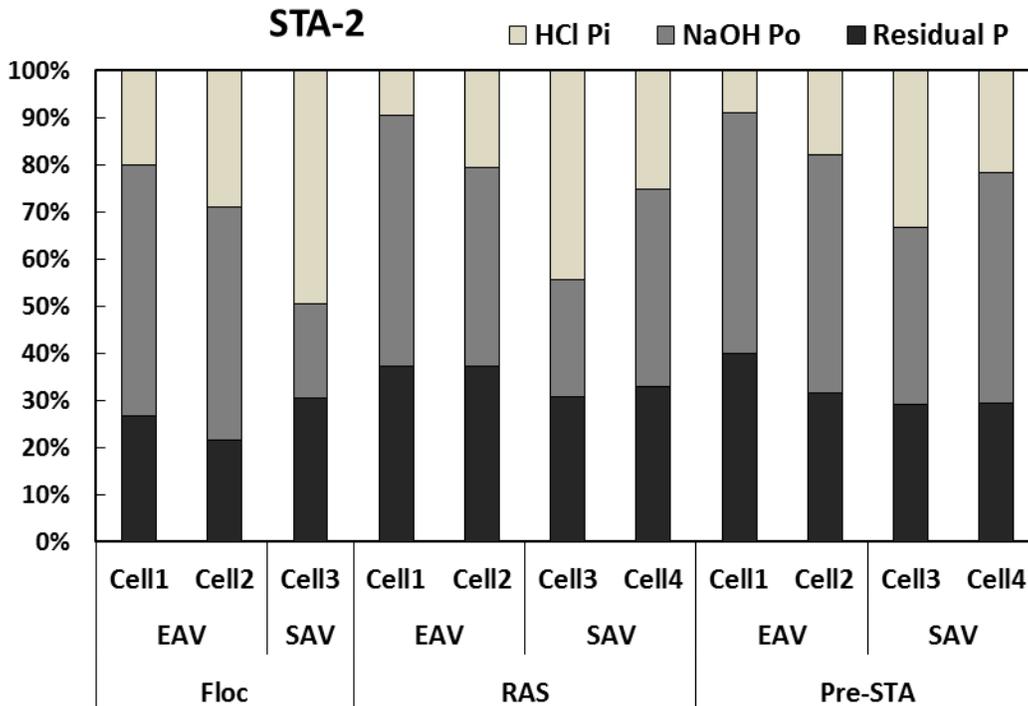


B

Figure 5-3. Phosphorus fractions (organic [Po], inorganic [Pi] and residual P [Pr]) in floc, RAS and pre-STA soil in STA-1W. A) Total P content. B) Relative proportion of P fractions.



A



B

Figure 5-4. Phosphorus fractions (organic [Po], inorganic [Pi] and residual P [Pr]) in floc, RAS and pre-STA soil in STA-2. A) Total P content. B) Relative proportion of P fractions.

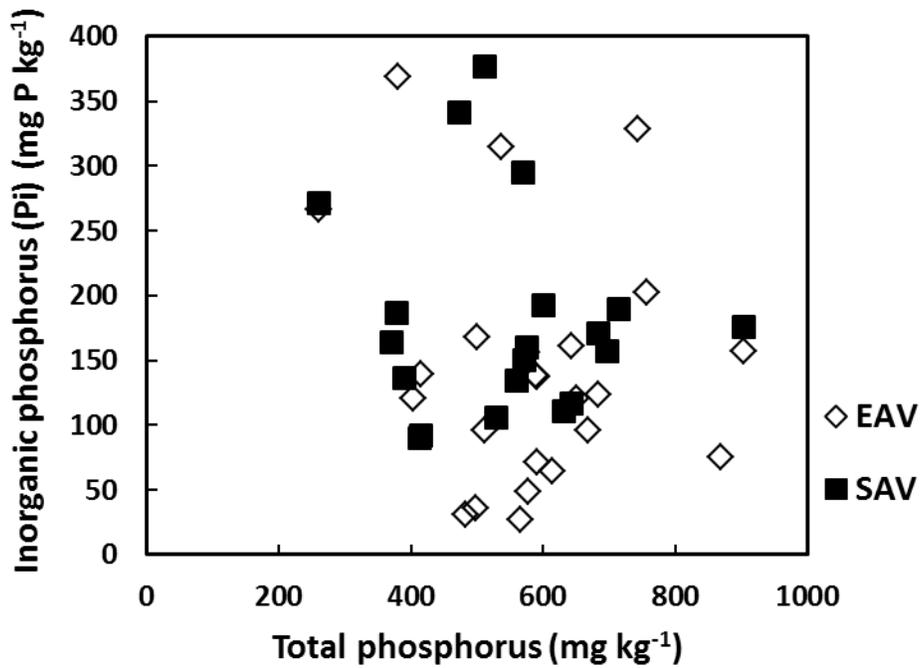


Figure 5-5. Inorganic P [Pi] content plotted against TP for all soil sections in EAV and SAV cells from STA-1W and STA-2.

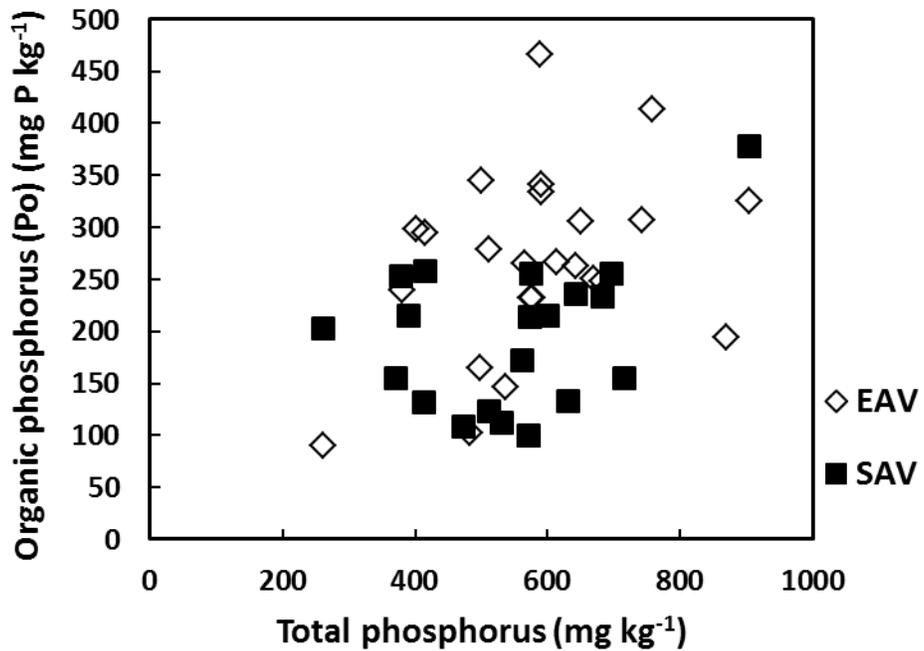


Figure 5-6. Organic P [Po] content plotted against TP in EAV and SAV cells from STA-1W and STA-2.

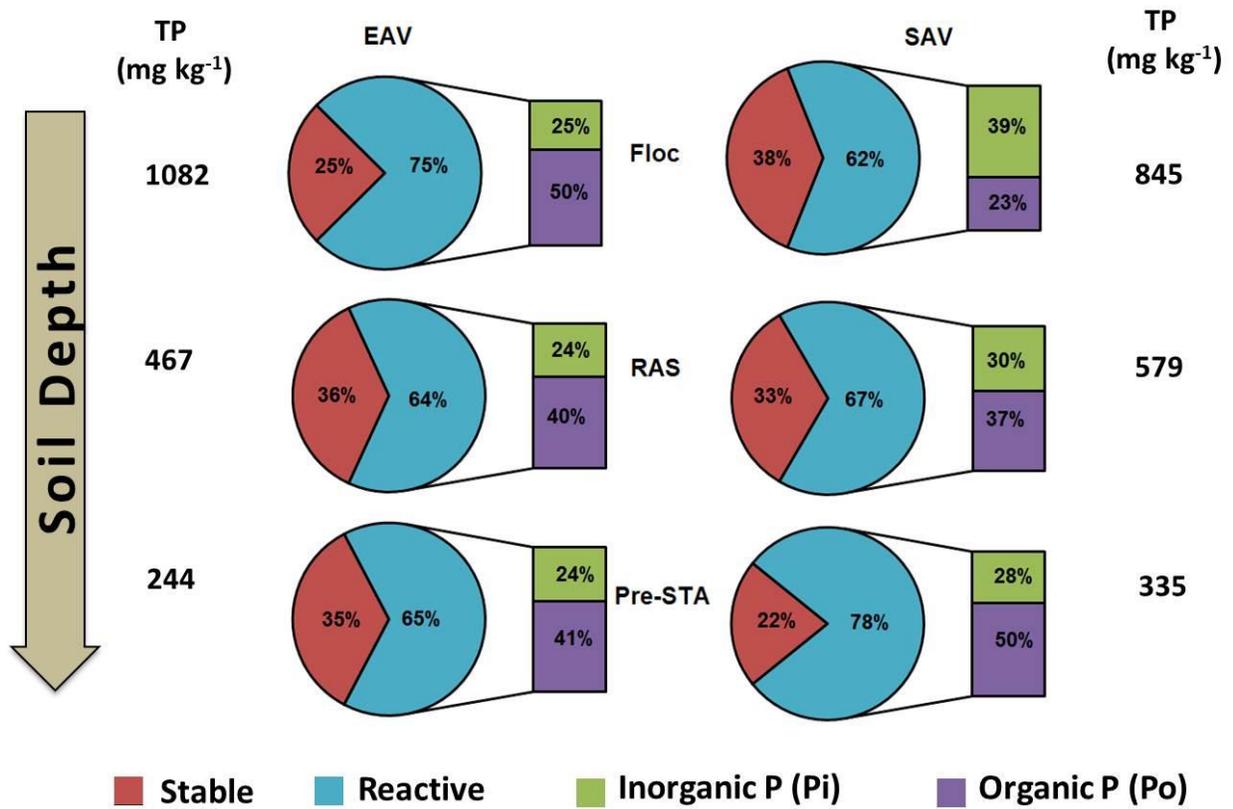


Figure 5-7. Percent composition of stable and reactive phosphorus pools in the floc, RAS and pre-STA soil of EAV and SAV cells pooled over both STA-1W and STA-2.

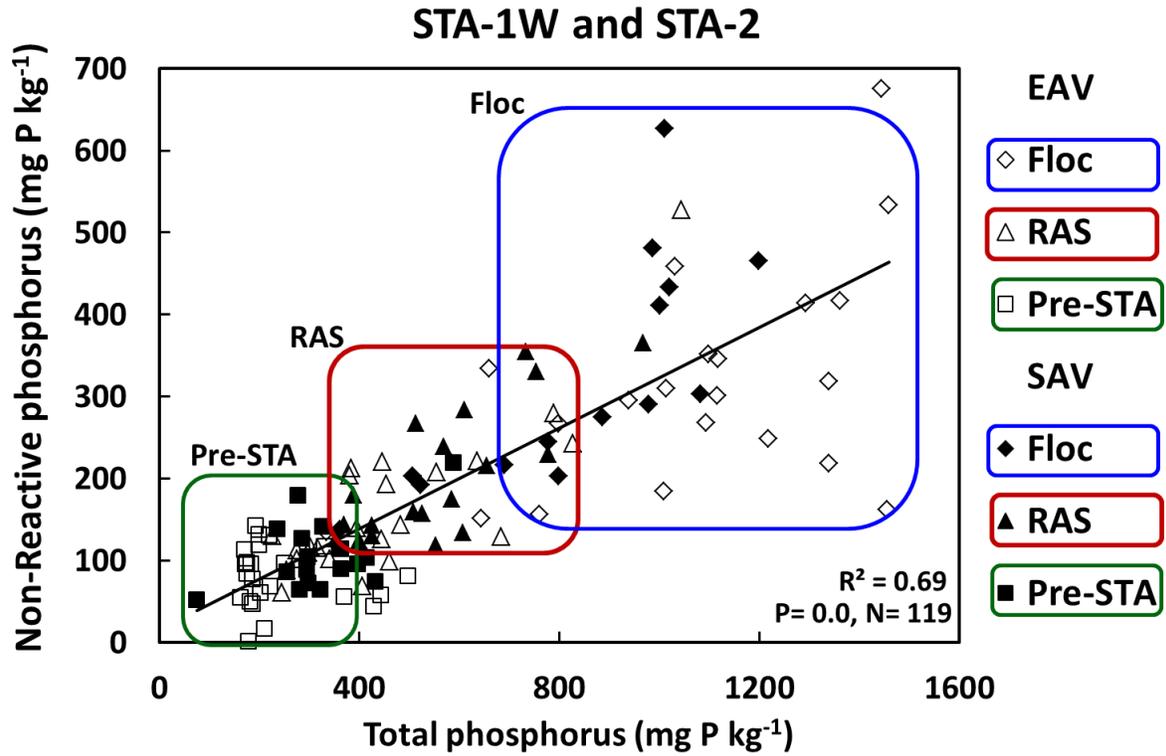


Figure 5-8. Non-reactive phosphorus (stable P) as a fraction of total phosphorus in floc, RAS and pre-STA soil of STA-1W and STA-2.

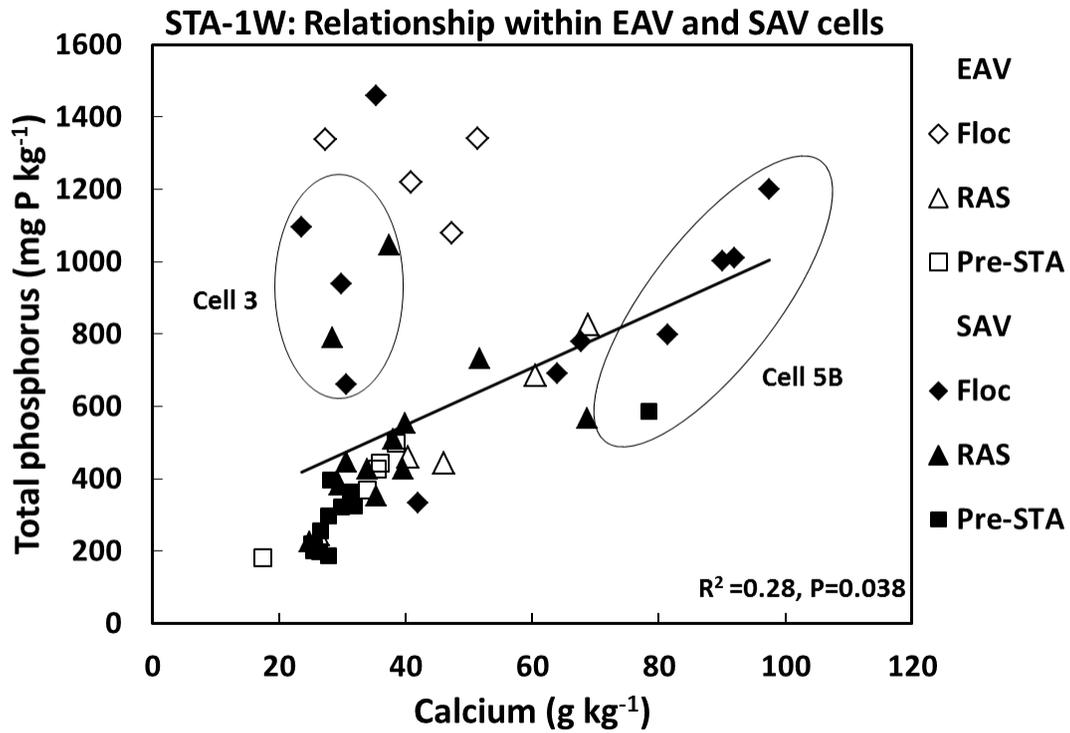


Figure 5-9. Relationship between phosphorus (mg P kg⁻¹) and calcium (g Ca kg⁻¹) in EAV and SAV cells of STA-1W. Open symbols represent EAV cells and closed symbols represent SAV cells. (n=50). For regression line n= 35, P-value < 0.05.

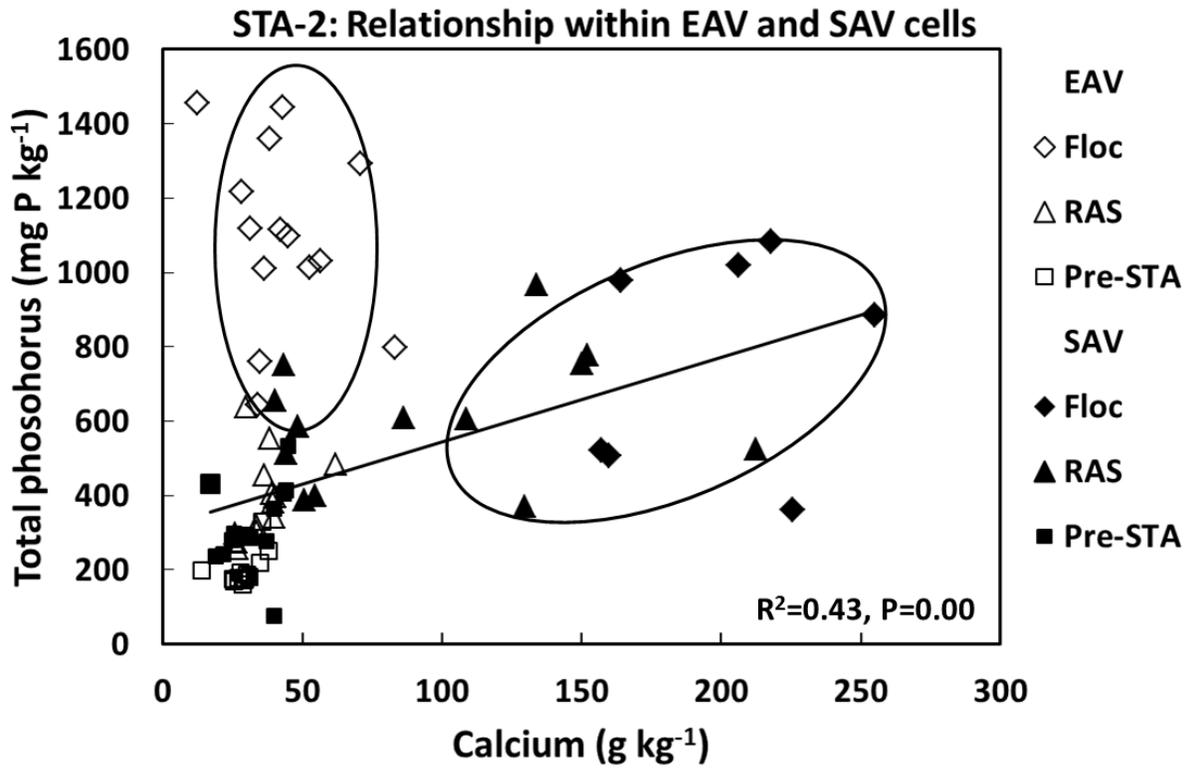


Figure 5-10. Relationship between phosphorus (mg P kg⁻¹) and calcium (g Ca kg⁻¹) in EAV and SAV cells of STA-2. Open symbols represent EAV cells and closed symbols represent SAV cells. (n=75) For regression line n= 33, P-value < 0.01.

CHAPTER 6 CONCLUSIONS

Constructed treatment wetlands are dynamic ecosystems primarily established in urban or agricultural watersheds to treat nutrient/ contaminant-rich water. These systems are attractive because of their low cost and ability to provide additional ecosystem services. Often these systems are evaluated simply by monitoring inflow and outflow contaminant concentrations, with limited information about the internal processes regulating contaminant removal, transformation or retention in the system. The lack of detailed information on nutrient cycling among different wetland compartments (including water column, plant biomass, surface litter and soil) result in the 'black box' approach that is generally used to evaluate treatment wetland's performance (Zurayk and others, 1997). An in-depth understanding of interactions between the biogeochemical processes responsible for water treatment could aid in performance optimization, reduction in operational costs, and prediction of future treatment responses to varied operating conditions.

This dissertation research is one attempt towards advancing our understanding about the main processes regulating treatment efficiency of constructed wetlands. This was done by quantifying changes in various nutrient storage pools in soils and using this information to understand the biogeochemical processes and transformations that take place in wetland soils. Specifically, by measuring the quantity and chemical stability of soil phosphorus (P) fractions, the long-term sustainable performance prospect of treatment wetlands were examined.

Free water surface treatment wetlands located in southern Florida were selected as the main sites for this study. These wetlands, referred to as the Everglades

Stormwater Treatment Areas (STAs), were strategically located in several agricultural watersheds to remove excess P in surface runoff originating from agricultural farms. In context of the STAs, understanding the internal processes that regulate treatment efficiency is of great importance (and urgency) because these systems not only represent a huge financial investment, but the legally mandated water treatment goals and the ecological risks to the Everglades of ineffective treatment are very high. By investigating the storage and movement of P fractions within STA soil layers, an attempt was made to recognize factors that control and regulate important biogeochemical processes that affect long-term removal efficiency and P storage in treatment wetlands. The value of this research is enhanced by the fact that the results can be directly applied to enhance treatment efficiency of the STAs.

Wetland soils are the main repository of removed nutrients (particularly P), therefore this dissertation started with quantification of soil nutrient storage pools and examined how those pools changed over time, and ultimately established relationships between soil nutrient storage and STA age (Chapter 2). This was followed by developing a simple change-point technique (CPT) to aid in measuring of soil and P accretion rates in treatment wetlands (Chapter 3). The boundary between recently accreted soils (RAS) and pre-STA soil was identified by CPT. Soil accretion rates in STAs were determined by utilizing depth of RAS layer from the surface and the STA age where as P mass in RAS was used to calculate P accretion rates. Subsequently, P mass storages in floc, RAS and pre-STA soil were calculated and P mass balances were developed for STA-1W, STA-2 and STA-3/4 (Chapter 4). Long-term sustainable P removal depends on the stability of accreted P, hence chemical characterization of

accreted P in STA soils was performed (Chapter 5). In the following sections of this chapter, each dissertation research objective presented in the Introduction (Chapter 1) is re-evaluated in the context of the knowledge gained from this research and the goal of having better understanding of P removal mechanisms in treatment wetlands. This research was guided by following objectives and supporting hypotheses -

- Objective 1: Review available datasets on STA soil physico-chemical variables and determine spatio-temporal changes in surface and sub-surface soil nutrient storage. Explore relationship between hydraulic and water quality parameters, soil nutrient storages and STA age. Perform preliminary P mass balance using these data (Chapter 2).

Hypothesis: STAs' treatment efficiency or P removal efficiency declines after a protracted period of operation.

- Objective 2: Determine the soil accretion rate in the STAs, by utilizing stratigraphic characteristics of the soil profiles to identify the boundary between recently accreted soil (RAS) and antecedent pre-STA soil (Chapter 3).

Hypothesis: The STAs are accreting systems and accumulating organic matter conserves attributes of prevailing conditions (e.g. nutrient loading, vegetation community). Changes in these stratigraphic characteristics can be exploited to identify the depth of RAS deposited on top of pre-STA soil.

- Objective 3: Explore the relationship between soil accretion rates and operational age of the STAs. Perform P mass balance using P storages in RAS and pre-STA soil and the amount of P removed from the water column. Determine P cycling within different P storage compartments of the STAs (Chapter 4).

Hypothesis: Most of the P retained from the water column is stored in RAS, which has a higher P concentration than pre-STA soil. With increasing age, the rate of soil and P accretion declines, resulting in higher outflow P concentrations. Internal re-distribution of P within RAS and pre-STA soil is mediated by vegetation. This controls whether the STAs function as a nutrient source or sink.

- Objective 4: Determine the relative proportion of reactive and non-reactive P pools in the STAs. Assess the influence of wetlands vegetation communities (EAV vs. SAV) on reactivity of P pools (Chapter 5).

Hypothesis: Different vegetation types (EAV vs. SAV) will influence the proportion of P forms incorporated into RAS and sequestered in the STAs. The presence of more reactive (i.e., potentially mobile) P forms will reduce the long-term sustainability of the STAs.

Objective 1: Spatio-Temporal Changes in Soil Nutrient Storages

An inventory of nutrients (P, N and C) stored in STA soils was developed by reviewing all existing data on floc and soil nutrient storages and subsequently exploring changes in those pools over time. Phosphorus concentration and storage within various compartments of the STAs – the water column, floc (unconsolidated detritus), surface soil (0-10 cm), and sub-surface soil (below 10 cm) were determined. Analysis of the physico-chemical attributes of STA soils allowed investigation of temporal changes in nutrient storage and examination of relationships between changes in nutrient storage with respect to STA performance and operational age (Chapter 2).

Annual P storage rates declined with increasing STA operational age, although the proportion of P stored in surface soil increasingly came from P retained from the water column over time. The decline in P storage rates could indicate that accumulation of refractory organic P fractions in the STAs was not uniform throughout each STA's operational history. Continued P loading of the STAs resulted in an increased proportion of soil P pools being derived from P retained from the water column.

Temporal changes in P storage within the active compartments of the STAs were used to generate estimates of P flux between these compartments and develop an overall P mass balance. Over the period of STA operation, it was observed that surface soils of STAs changed from being a source into net sink for P. However, this analysis was restricted to P storage within the top 10 cm of surface soil, which may not have included the entire depth of RAS, hence conclusions drawn from these data are more akin to 'best estimates' of accretion rates and P storages. Subsequently, a more complete mass balance was developed after identification of the boundary between RAS and pre-STA soil (Chapter 4).

Objective 2: Soil Accretion in Treatment Wetlands

Soil accretion is related to the performance of treatment wetlands as soils provide a long-term sink for various pollutants. Knowledge of soil accretion rates in the STAs is important to quantify P mass storages accurately and develop robust mass balances; however, it was difficult to measure accretion rates in the absence of a marker horizon. Therefore, a novel analytical technique, CPT, was developed by exploiting the stratigraphic characteristics of RAS. This allowed for identification of the boundary between RAS and pre-STA soil, and hence RAS depth in three STAs of varying age – STA-1W, STA-2 and STA-3/4 (Chapter 3).

Objective 3: Soil Accretion and Operational Age of Treatment Wetlands

Soil accretion is the long-term sustainable mechanism for removal of nutrients (specifically P in this case) in wetlands; however, it remains the least investigated component of treatment wetland performance (Kadlec and Wallace, 2009). Changes in soil accretion rates with increasing operational age of the STAs were evaluated. Wetland soils aggregate biotic and abiotic processes, hence, results from this study were useful in understanding some of the biogeochemical processes that control and regulate P removal in the STAs. Soil and P accretion rates were determined using RAS depths identified with CPT (Chapter 2). A declining trend in soil and P accretion rates with increasing age was observed for STA-1W, STA-2 and STA-3/4, which had operational ages of 16, 11 and 7 years, respectively (Chapter 4). This confirmed the hypotheses that with increasing age, the rate of soil and P accretion declines.

Developing reliable P mass balances for these wetlands required accurate estimates of soil accretion rates and associated soil P storages. The ability to differentiate between P storages in RAS and pre-STA with reasonable confidence

allowed calculation of total P flux from pre-STA soil into RAS. The results of P mass balances developed using this approach are presented in Chapter 4. High P flux from pre-STA soil to RAS was indicative of the role of vegetation in mining subsurface P and deposition on the surface through detrital accumulation, which eventually becomes a part of RAS (Reddy and DeLaune, 2008; Reddy and others, 2002). The movement of P from pre-STA to RAS layer involved a series of complex biological processes including growth, senescence and decomposition of wetland vegetation and microbial assemblages.

Objective 4: Stability of Phosphorus in Recently Accreted Soil

Phosphorus sequestered in wetlands that can be mobilized in response to changes in nutrient concentration gradients or changes in physical and chemical conditions (such as redox, electron acceptors and hydrologic regimes) is considered reactive. Reactive P that becomes bio-available can have adverse ecological impacts. It therefore was important to investigate the composition and stability of P in RAS to determine the long-term efficacy of P retention in the STAs.

Chemical characterization of P present in STA soils was carried out using an operationally defined fractionation scheme modified from Ivanoff and others, (1998). Phosphorus-enriched STA surface layers (floc and RAS) contained a higher proportion of reactive P than did pre-STA soil. This reactive pool was comprised of P_i and P_o fractions that together accounted for 65-70% of all TP in floc and RAS. Investigations of the influence of vegetation type on partitioning of P found significant effect on P_r fraction. The relative proportion of P_r was lower in EAV cells compared to SAV cells in STA-1W, whereas no vegetation effect was observed for P_r in STA-2 (Chapter 5).

A separate evaluation of floc, RAS and pre-STA soil found that the influence of vegetation type on P fractions in STA-1W were not significant except for differences in P_o in floc and pre-STA soil. For STA-2, significant differences in P fractions were observed between EAV and SAV cells for floc (P_o), RAS (P_i) and pre-STA soil (P_o , P_i and P_r) (Chapter 5).

Phosphorus mass balances suggested that a large portion of P in RAS was mined from pre-STA soil. Fractionation analysis indicated that about 70% of P in RAS was reactive and potentially could be mobilized. This highlights the risk of P loss from the STAs following changes in the environment (e.g., redox and pH changes, availability of electron acceptors, etc.). A decline in soil accretion rate was observed with increasing STA operation age of, which raised an important question regarding continued performance of the STAs. Without continued high rates of soil accretion, the treatment performance of the STAs could diminish.

Synthesis

Phosphorus retention pathways in treatment wetlands are comprised of complex biotic and abiotic processes. This complexity is mainly due to multiple physical, biological and chemical mechanisms that interact simultaneously to provide treatment. These reactions result in removal of P from the water column, conversion of constituents from dissolved to particulate and inorganic to organic forms and vice versa (Reddy and DeLaune, 2008). Along with these conversions, mobilization of sequestered P and redistribution of P pools within the soil profile also take place. While P is cycled through various storage compartments within wetlands, different functional forms of P undergo transformations (Koch and Reddy, 1992; Newman and Pietro, 2001; Qualls and Richardson, 2003; Reddy and others, 1999a). Such changes influence the stability

of accreted P and overall treatment performance in wetlands. The main goal of this study was to understand the impacts of operational age, hydraulic and P loading rates, dominant vegetation type on regulation of the stability of accreted P in treatment wetlands. These efforts were aimed to understand how these factors may have affected treatment performance and long-term fate of P in the STAs.

A summary based on the outcomes of this dissertation research at one site (STA -2) is presented in Figure 6-1 (A= EAV cells and B= SAV cells). This synthesis highlights the passage that influent P takes as it is removed from the water column and eventually is stored as accreted soil in EAV and SAV cells. The schematic indicates the partitioning of accreted P into reactive and non-reactive forms within the main storage compartments of STA soils. Phosphorus loading rates experienced by EAV cells were slightly lower than in SAV cells for the POR and the annual rate of P retention (water column to floc) was similar for both vegetation types. However, the annual P accretion rate to RAS in SAV cells was twice that of EAV cells. Comparison of the proportion of reactive and non-reactive P in floc, RAS and pre-STA soil found a higher percentage of reactive P throughout the soil profile. A greater proportion of reactive P (Pi and Po fractions combined) was observed in the floc and RAS of SAV cells compared to EAV cells, i.e., floc and RAS of SAV cells contained a larger proportion of P that was prone to mobilization in response to changes in environmental conditions than in EAV cells. Positive correlations between TP and Ca in floc and RAS suggested Ca-P co-precipitation as an important mechanism of P removal in SAV cells. Among reactive P pools, the proportion of Pi was higher in SAV cells while Po was greater in EAV cells.

Residual P comprised 30-35% of TP in floc and RAS of both vegetation types. Only Pr can be considered as truly removed from the standpoint of future bio-availability. There is insufficient knowledge regarding the underlying reasons for the chemical stability of Pr pool in wetlands and further studies are necessary to identify reasons that impart chemical stability. With advanced scientific techniques such as nuclear magnetic resonance (NMR) and X-ray Absorption Near Edge Structure (XANES) absorption spectroscopy, the elemental composition and the structure of the stable P fraction could possibly be determined (Cheesman and others, 2012). With regard to continued P removal by STAs, factors that promote the transformation of retained P into non-reactive forms need to be further investigated.

Future Outlook and Sustainability of STAs

The ecosystems of south Florida are hydrologically linked, beginning from the headwaters of the Kissimmee River and ending with Florida Bay and the Florida Keys. Human perturbation has caused many social, economic and environmental impacts on this system. The impacts of agricultural drainage waters from the Everglades Agricultural Area (EAA) on the Water Conservation Areas and the southern Everglades have received much attention, and the six STAs constructed to remedy some of those problems. STAs represent a huge financial commitment in terms of initial capital costs and annual operating and management costs. Although, cumulatively the STAs removed 1500 mt of P (Ivanoff and others, 2012), which otherwise would have adversely impacted the Everglades ecosystem, there are multiple issues that bring the long-term sustainability of the STAs and the stability of their sequestered P into question.

First, declining trend in soil and P accretion rates with increasing age as observed for STA-1W, STA-2 and STA-3/4 is an indicator of slow-down of P removal rates. With STA age decrease in the quantity of TP retained from the water column could result in failure to meet legally stipulated outflow P concentration.

Second, an independent economic analysis conducted by the National Research Council found that the cost of P removal by the STAs is \$240 kg⁻¹ (Council, 2011), which escalates to \$600 - \$1200 when the proportion of Pr in RAS (30 ± 10 %) is considered. Such high cost for storage of P in non-reactive fractions may require greater financial investments, which may not be readily available in the current economic environment. The environmental risks associated with the potential mobilization and release of reactive P from the STAs to the downstream Everglades remains a grave concern.

Third, a vast amount of P exists both in the native soils and has been imported into the Everglades basin as fertilizer, and the STAs potential to remove P in runoff is not limitless. The total quantity of P fertilizer applied in the EAA greatly exceeds the design parameters used to estimate P removal by STAs (Reddy and others, 2011). The STAs have been loaded with P for many years now and floc and RAS which exist as an interface with overlying water column have higher TP concentration than pre-STA soil.

Fourth, promotion of best management practices upstream of the STAs may result in decreasing P concentration in inflow waters, however the introduction of low-P-concentration water to the STAs could cause P flux from the soil back to the overlying water column (Reddy and others, 2012).

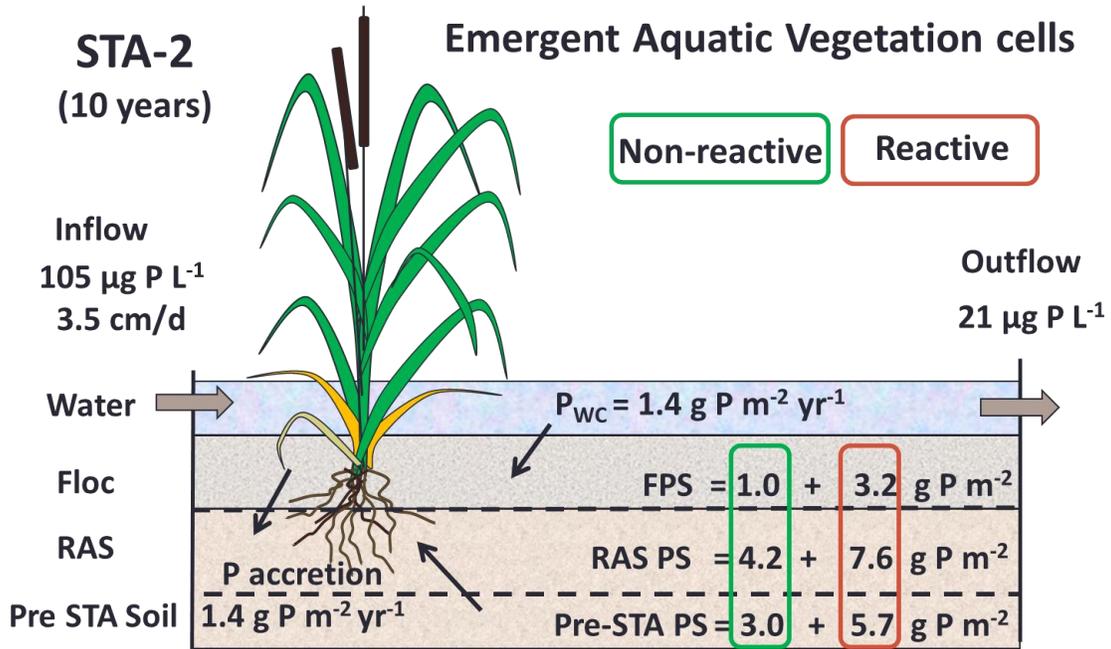
Fifth, south Florida is prone to extreme weather events such as tropical storms and droughts, and based on recent weather trends, it is not difficult to conclude that the probability of such events reoccurring in future is high. The existing safe guards against these extreme events are less than adequate for existing network of six STAs. Hurricanes have caused considerable damage to vegetation in some STA cells, necessitating costly rehabilitation efforts to bring those cells back online. STA managers face increasingly tough challenges to keep STA cells hydrated during summer months when water demand throughout the District soars. During large rain events when huge volumes of water pass through STAs scouring channels and negatively impacting system hydraulics. The flooding situation, however might improve after the construction of Compartments B and C (Figure 1-3) are completed, which will provide more storage capacity and control in the timing and volume of flow through the STAs.

Sixth, an action plan once STA's reach the end of their projected operational life is missing. One option is to transport STA soil with its sequestered P out of the Everglades basin, but the economic implications for such action could be very high. If P is translocated within the basin then it will only delay the ecological consequences unless adequate measures are taken to prevent remobilization. During years 2005-2007, rehabilitation of STA-1W resulted in the removal of approximately 180,000 yd³ of floc and subsurface soils, equivalent to 19 mt of P, in which soil was disposed in a manner that precluded its P from reaching the Everglades. Some experts have even suggested reopening the STAs for farming. Recently accreted organic soils with high quantities of P could serve as productive agricultural soils. Another option is *in situ* immobilization by application of specialized chemicals that have high affinity for P.

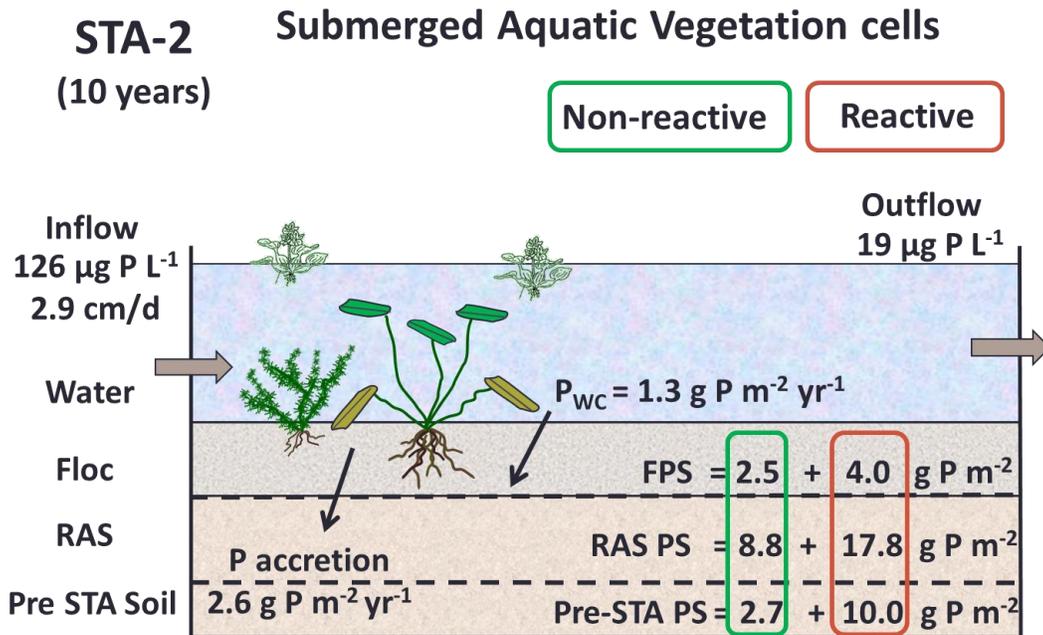
However, these steps can be seen as very practical, particularly when the economics of implementing these options over the STA's entire treatment footprint of 18,000 ha.

Although the above mentioned points may seem to suggest a bleak outlook where long-term sustainability of the STAs is concerned, there are benefits that the STAs provide. Other than being the best substitute for natural wetlands that were once part of the historical landscapes, the STAs offer other benefits that go beyond their main function of P removal. For instance, the STAs provide high quality habitat for fish, birds and other wildlife and fulfill ecological functions in the landscape. The accreted soil of STAs sequesters C and N along with P. Calculations for surface soil (10 cm) suggested that the STAs store thousands of metric tons of C (Chapter 2, Table 2-8). When nutrient removal costs for both C and N are included in total costs, then the per unit cost of P removal does not appear so high.

STAs already provide popular recreation activities such as bird watching, photography, fishing and hunting. The vast amount of data that has been collected from regular monitoring of the STAs could be mined to enhance the design of interventions that improve P removal in the STAs and other treatment wetlands. The role of STAs in reduction of P inputs to the Everglades and the success of Everglades restoration efforts cannot be overstated. In light of the knowledge gained from this dissertation on the quantity and quality of sequestered P, further steps can be taken to improve the efficiency and future of these large treatment wetlands.



A



B

Figure 6-1. Summary of total phosphorus (TP) loading rates, TP accretion rates and distribution of reactive and non-reactive TP pools in floc, recently accreted soils (RAS) and pre-STA soil. A) Emergent aquatic vegetation. B) Submerged aquatic vegetation cells of STA-2.

APPENDIX A
 ADDITIONAL DATA AND INFORMATION PERTAINING TO CHAPTER 1

Table A-1. Treatment Wetland Technology conferences. Source: (Kadlec and Wallace, 2009)

Year	Location	Title (Proceedings)
1976	Ann Arbor, Michigan	Freshwater Wetland and Sewage Effluent Disposal
1978	Tallahassee, Florida	Environmental Quality Through Wetlands Utilization
1978	Lake Buena Vista, Florida	Wetland Functions and Values
1979	Higgins Lake, Michigan	Freshwater Wetland and Sanitary Wastewater Disposal
1979	Davis, California	Aquaculture Systems for Wastewater Treatment
1981	St. Paul, Minnesota	Wetland Values and Management
1982	Amherst, Massachusetts	Ecological Considerations in Wetlands Treatment of Municipal Wastewaters
1986	Orlando, Florida	Aquatic Plants for Water Treatment and Resource Recovery
1988	Chattanooga, Tennessee	1st International Conference on Constructed Wetlands for Wastewater Treatment
1989	Tampa, Florida	Wetlands: Concerns and Successes
1990	Cambridge, United Kingdom	2nd International Conference on Constructed Wetlands for Water Pollution Control
1991	Pensacola, Florida	Constructed Wetlands for Water Quality Improvement
1992	Columbus, Ohio	INTECOL Wetlands Conference
1992	Sydney, Australia	3rd International Conference on Wetland Systems for Water Pollution Control
1994	Guangzhou, China	4th International Conference on Wetland Systems for Water Pollution Control
1994	Atlanta, Georgia	On-Site Wastewater Treatment; 7th Symposium on Individual and Small Community Sewage Systems
1995	Třeboň, Czech Republic	Nutrient Cycling and Retention in Wetlands and Their Use for Wastewater Treatment
1996	Vienna, Austria	5th International Conference on Wetland Systems for Water Pollution Control
1996	Niagara-on-the-Lake, Ontario	Constructed Wetlands in Cold Climates
1997	Romulus, Michigan	Constructed Wetlands for the Treatment of Landfill Leachates

Table A-1. Continued.

Year	Location	Title (Proceedings)
1997	Třeboň, Czech Republic	Nutrient Cycling and Retention in Natural and Constructed Wetlands
1998	Aguas de São Pedro, Brazil	6th International Conference on Wetland Systems for Water Pollution Control
1998	Orlando, Florida	On-Site Wastewater Treatment; 8th Symposium on Individual and Small Community Sewage Systems
1999	Salt Lake City, Utah	Wetlands and Remediation
1999	Třeboň, Czech Republic	Transformations of Nutrients in Natural and Constructed Wetlands
1999	Baltimore, Maryland	Wetlands for Wastewater Recycling
1999	Tartu, Estonia	Constructed Wetlands for Wastewater Treatment in Cold Climates
2000	Quebec, Canada	INTECOL Wetlands Conference
2000	Orlando, Florida	7th International Conference on Wetland Systems for Water Pollution Control
2001	Burlington, Vermont	Wetlands and Remediation II
2001	Třeboň, Czech Republic	Wetlands: Nutrients, Metals, and Mass Cycling
2001	Fort Worth, Texas	On-Site Wastewater Treatment: 9th Symposium on Individual and Small Community Sewage Systems
2002	Dar es Salaam, Tanzania	8th International Conference on Wetland Systems for Water Pollution Control
2003	Borová Lada, Czech Republic	Natural and Constructed Wetlands: Nutrients, Metals, and Management
2003	Tartu, Estonia	Constructed and Riverine Wetlands for Optimal Control of Wastewater at Catchment Scale
2003	Lisbon, Portugal	The Use of Aquatic Macrophytes for Wastewater Treatment in Constructed Wetlands
2004	Wexford, Ireland	Nutrient Management in Agricultural Watersheds: A Wetlands Solution
2004	Avignon, France	9th International Conference on Wetland Systems for Water Pollution Control
2005	Ghent, Belgium	1st Wetland Pollutant Dynamics and Control (WETPOL)
2006	Třeboň, Czech Republic	Wastewater Treatment, Plant Dynamics, and Management in Constructed and Natural Wetlands
2006	Lisbon, Portugal	10th International Conference on Wetland Systems for Water Pollution Control
2007	Padua, Italy	Multi-Functions of Wetland Systems
2007	Tartu, Estonia	2nd Wetland Pollutant Dynamics and Control

APPENDIX B
ADDITIONAL DATA AND INFORMATION PERTAINING TO CHAPTER 2

STA Description

Stormwater Treatment Area 1 East (STA-1E) is located northeast of the Arthur R. Marshall Loxahatchee National Wildlife Refuge (LNWR) in Palm Beach County, FL and began operation in WY2005. This STA has three flow-ways (East, Central, and West) covering approximately 2,104 ha. STA-1E has been adversely affected by high hydraulic loading during storm events (in WY2006), water control structure failures, topographic issues (Cells 5 and 7), dryout of cells during regional drought (WY2009) and vegetation die-off. Through WY2012, STA-1E has treated over 600,000 ac-ft of water and retained approximately 94 mt of TP (Ivanoff and others, 2012). The period-of-record (POR) inflow flow-weighted mean (FWM) TP concentration was $176 \mu\text{g L}^{-1}$, while the POR outflow FWM TP concentration was $57 \mu\text{g L}^{-1}$ (Ivanoff and others, 2012).

Stormwater Treatment Area 1 West (STA-1W) began operation in WY1995 and is located northwest of the Arthur R. Marshall LNWR. It has three flow-ways totaling 2,700 ha of effective treatment area: East (Cells 1A, 1B and 3), West (Cells 2A, 2B and 4), and North (Cells 5A and 5B). The East and West Flow-ways were formerly known as the Everglades Nutrient Removal Project; the North Flow-way was added in WY2000. Cells 1 and 2 were reconfigured in WY2007, creating Cells 1A, 1B, 2A and 2B. Supplemental water has been delivered from Lake Okeechobee to maintain hydration during dry months. To date, STA-1W has treated over 3.3 million ac-ft of water and retained approximately 480 mt of TP (Ivanoff and others, 2012). The POR mean inflow FWM TP concentration was $171 \mu\text{g L}^{-1}$, while the POR mean outflow FMW TP concentration was $51 \mu\text{g L}^{-1}$ (Ivanoff and others, 2012). Over its period of operation,

STA-1W has been impacted by extreme weather events (regional droughts and tropical storms), construction activities, and high hydraulic and nutrient loadings. STA-1W underwent a substantial rehabilitation and enhancement effort during 2005-2007. Approximately 180,000 yd³ of P-enriched floc and surface soil were removed from Cells 1B and 4. This resulted in a total removal of 19 mt P from STA-1W. The WY2007 soil phosphorus storage (SPS) values in Table 2-9 reflect P storage before soil removal, while soil samples collected in WY2008 represent post-rehabilitation SPS. The observed decrease in SPS in the later samples could be attributed to the rehabilitation activities.

Stormwater Treatment Area 2 (STA-2) is located in western Palm Beach County immediately west of WCA-2A. STA-2 originally consisted of three one-cell flow-ways (Cells 1, 2 and 3) with a combined 2,565 ha of effective treatment area and began operation in the WY2000. The treatment area was expanded by 770 ha with the construction of Cell 4, which became operational in December 2006. Compartment B construction will add approximately 2,760 ha of additional treatment area to STA-2. From WY2000–WY2012, STA-2 has treated over 2.8 million ac-ft of water and retained approximately 269 mt of TP (Ivanoff and others, 2012). The POR inflow FWM TP concentration was 102 µg L⁻¹ while the POR outflow FWM TP concentration was 22 µg L⁻¹ (Ivanoff and others, 2012).

Stormwater Treatment Area 3/4 (STA-3/4) is located northeast of the Holey Land Wildlife Management Area and north of WCA-3A. It has a total treatment area of 6,691 ha and receives runoff originating within the S-2/7, S-3/8, S-236 and C-139 basins and water releases from Lake Okeechobee. STA-3/4 has three flow-ways: East

(Cells 1A and 1B), Central (Cells 2A and 2B) and West (Cells 3A and 3B). Since it began operation in October 2003, STA-3/4 has treated approximately 3.7 million ac-ft of runoff, retaining over 440 mt of TP, and reducing the FWM TP concentration from 114 $\mu\text{g L}^{-1}$ at the inflow to 18 $\mu\text{g L}^{-1}$ at the outflow (Ivanoff and others, 2012). Similar to the other STAs, STA-3/4 has been impacted by extreme weather events (regional droughts and tropical storms) and high hydraulic loadings during the wet season. The WY2011 dry season resulted in a complete dry out of all cells in STA-3/4 in June 2011.

Stormwater Treatment Area 5 (STA-5) totals 2,465 ha and is located west of Rotenberger wildlife management area. It is divided into three west-to-east oriented flow-ways each with two cells. STA-5 began operation in WY1999. Since WY2000, STA-5 has treated over 1.2 million ac-ft of runoff water and retained approximately 212 mt of TP. The POR inflow FWM TP was 225 $\mu\text{g L}^{-1}$ and the POR outflow FWM TP concentration was 93 $\mu\text{g L}^{-1}$ (Ivanoff and others, 2012). Over its period of operation, STA-5 has been impacted by high inflow nutrient concentrations and extreme weather events (regional droughts and tropical storms).

Stormwater Treatment Area 6 (STA-6) is the smallest of the six STAs with a footprint of 915 ha. It is divided into three east-to-west oriented flow-ways each with only one cell. The two southernmost cells - Cells 3 and 5 comprise Section 1 while the northern Section 2 has only Cell 2 which was added in WY2007. The completion of Compartment C construction will connect STA-5 and STA-6 and they may be identified as STA-5/6 in the future. The POR inflow TP FWM concentration in STA-6 was 100 $\mu\text{g L}^{-1}$ and POR outflow FMW TP concentration was 34 $\mu\text{g L}^{-1}$ (Ivanoff and others, 2012).

Table B-1. Mean total nitrogen concentration in floc and soils in STAs (g N kg⁻¹; mean ± 1 SD). Values represent entire floc depth and the top 10 cm of surface soil.

WY	STA-1E	STA-1W	STA-2	STA-3/4	STA-5	STA-6
Floc*						
2003	--	--	--	--	30 ± 5	--
2007	15.1 ± 0*	23 ± 2	14 ± 3	18 ± 2	28 ± 2	--
Soil						
1995	--	28 ± 2	--	--	--	--
1996	--	32 ± 4	--	--	--	--
2000	--	30 ± 3	--	--	--	--
2001	--	--	3 ± 0	--	26 ± 6	13 ± 3
2003	--	--	--	--	22 ± 7	--
2004	--	28 ± 3	28 ± 3	--	23 ± 7	21 ± 6
2005	5.9 ± 5.1	--	--	26 ± 5	--	--
2006	--	27 ± 3	--	--	--	--
2007	5.6 ± 4.8	26 ± 7	28 ± 2	25 ± 5	21 ± 6	--
2008	--	28 ± 4	--	--	--	--

*Total nitrogen concentration for floc was not available for STAs 1W, 2, 5 and 6 during WY2004.

Table B-2. Mean total carbon concentration in floc and soils in STAs (g C kg⁻¹; mean ± SD). Values represent entire floc depth and the top 10 cm of surface soil.

Year	STA-1E	STA-1W	STA-2	STA-3/4	STA-5	STA-6
Floc*						
2003	--	--	--	--	389 ± 56	--
2007	--	274 ± 13	242 ± 32	275 ± 22	375 ± 28	--
Soil						
1995	--	360 ± 12	--	--	--	--
1996	--	510 ± 46	--	--	--	--
2000	--	483 ± 40	--	--	--	--
2001	--	--	466 ± 9	--	381 ± 80	169 ± 46
2003	--	--	--	--	312 ± 91	--
2004	--	467 ± 47	419 ± 55	--	322 ± 102	266 ± 79
2005	87 ± 76	--	--	391 ± 85	--	--
2006	--	450 ± 38	--	--	--	--
2007	82 ± 71	398 ± 69	452 ± 38	381 ± 79	297 ± 94	--
2008	--	450 ± 60	--	--	--	--

*Total carbon concentration for floc was not available for STA- 1W, 2, 5 and 6 during WY2004.

Table B-3. STA performance for WY2011 (May 1, 2010–April 30, 2011) and the period of record (POR) 1994–2011.
Source: (Ivanoff and others, 2012)

	STA-1E	STA-1W	STA-2	STA-3/4	STA-5	STA-6	All STAs
Effective Treatment Area in Permit (acres)	5,132	6,670	8,240	16,543	6,095	2,257	44,937
Adjusted Effective Treatment Area (acres) ^a	4,881	6,670	7,406	16,543	5,660	1,584	42,744
Rainfall							
Total Annual Rainfall (inches)	34.0 ^b	35.0 ^b	38.1	40.2	39	42.2 ^b	38.1
South Florida Water Management Model (SFWMM) Simulation Rainfall Range (inches)	39.8–77.5	36.6–77.4	35.4–71.6	32.3–70.7	38.6–61.4	46.8–57.6	---
Inflow							
Total Inflow Volume [acre-feet (ac-ft)]	35,616	125,933	170,838	303,447	26,609	72,722	735,165
Total Inflow total phosphorus (TP) Load [metric ton (mt)]	4.955	23.461	15.248	26.208	5.258	10.141	85.271
Flow-weighted Mean (FWM) Concentration Inflow TP [parts per billion (ppb)]	113	151	72	70	160	113	94
Hydraulic Loading Rate (HLR) [centimeters per day (cm/d)] ^d	0.61	1.58	1.93	1.53	0.39	3.83	1.44
TP Loading Rate (PLR) [grams per square meter per year (g/m ² /yr)] ^d	0.25	0.87	0.51	0.39	0.23	1.58	0.49
Outflow							
Total Outflow Volume (ac-ft)	25,758	126,881	159,914	312,067	24,319	74,591	723,530
Total Outflow TP Load (mt)	0.691	3.99	3.049	6.305	1.42	2.317	17.772
FWM Concentration Outflow TP (ppb)	22	25	15	16	47	25	20
Outflow Plus Diversion Structures FWM TP (ppb)	22	25	15	17	47	25	20
Hydraulic Residence Time (days)	49	27	23	28	13	5	---
TP Retained (mt)	4.264	19.471	12.199	19.903	3.838	7.824	67.499
TP Removal Rate (g/m ² /yr)	0.22	0.72	0.41	0.3	0.17	1.22	0.39
Load Reduction (percent)	86%	83%	80%	76%	73%	77%	79%
Period of Record Performance							
Start Date	Sep-04	Oct-93	Jun-99	Oct-03	Oct-99	Oct-97	1994–2011
Total Inflow Volume (ac-ft)	563,131	3,160,086	2,568,599	3,369,553	1,182,264	671,380	11,515,014
Total TP Load Retained to Date (mt)	84.469	465.434	250.619	400.612	205.029	64.132	1,470.30
FWM Concentration TP Outflow to Date (ppb)	62	52	23	17	95	33	38

Table B-3. Continued.

a Adjusted effective treatment areas (AETA) reflect treatment cells temporarily off-line for plant rehabilitation, infrastructure repairs, or Long-Term Plan (LTP) enhancements (see Table 5-4 in Volume I, Chapter 5 for more information about the operational status of the STAs). AETA = # days online/365 (for each flow-way or cell) * (effective treatment area for each flow-way or cell) then add the AETAs for all cells in each STA.

b The total annual rainfall received by the STA was below the range of values used to develop the interim effluent limits (IELs).

c SFWMM – South Florida Water Management Model.

d Inflow volume or TP load/adjusted effective treatment area.

APPENDIX C
ADDITIONAL DATA AND INFORMATION PERTAINING TO CHAPTER 3

Table C-1. Number of 2-cm sections produced by sectioning soil cores collected from sampling locations in STA-1W. (Total 733 core sections)

Cell 1A	129	Cell 2A	78	Cell 3	97	Cell 5A	86
1B#	15	2F	19	3B	24	5A112	16
1B(i)	23	2Q	18	3I	21	5A112(a)	18
1I	24	2Q(a)	20	3I(a)	16	5A112(b)	16
1I (a)*	22	2Q(b)	21	3I(b)	17	5A150	17
1I (b)*	23	-	-	3P	19	5A74	19
1P	22	-	-	-	-	-	-
Cell 1B	85	Cell 2B	70	Cell 4	74	Cell 5B	114
1AB	12	2AB	17	4C	13	5B 108	21
1AB(a)	19	2U	16	4F	16	5B 125	12
1AB(b)	16	2U(a)	18	4F(a)	14	5B 125(a)	14
1AE	17	2U(b)	19	4F(b)	16	5B 125(b)	14
1T	21	-	-	4J	15	5B 162	19
-	-	-	-	-	-	5B 202	18
-	-	-	-	-	-	5B 83	16

This site was located in a canal so another soil core [1B(i)] was collected 3 m away from the canal. *(a) and (b) indicate replicate soil cores collected from this site.

Table C-2. Number of 2-cm sections produced by sectioning soil cores collected from sampling locations in STA-2..(Total 505 core sections)

Cell 1	106	Cell 2	201	Cell 3	105	Cell 4	93
A103	20	B117	22	C129	18	D111	8
A103 (a)*	15	B151	20	C165	15	D124	19
A103 (b)*	20	B187	20	C201	16	D124 (a)	15
A138	21	B26	17	C21	13	D124 (b)	21
A172	16	B31	23	C75	18	D129	18
A51	14	B31(a)	22	C75 (a)	16	D139	12
-	-	B81	22	C75 (b)	9	-	-
-	-	B98	14	-	-	-	-
-	-	B98(a)	21	-	-	-	-
-	-	B98(b)	20	-	-	-	-

Table C-3. Number of 2-cm sections produced by sectioning soil cores collected from sampling locations in STA-3/4. (Total 573 core sections)

Cell 1A	138	Cell 1B	177	Cell 2A	133	Cell 2B	125
1A-19~	2	1B-24	9	2A-1	19	2B-13	8
1A-21	11	1B-28	13	2A-12	7	2B-17	6
1A-3	8	1B-4	10	2A-16	13	2B-17(a)	7
1A-32	11	1B-52	6	2A-24	5	2B-17(b)	7
1A-32 (a)*	12	1B-52(a)	12	2A-24(a)	7	2B-21	11
1A-32 (b)*	14	1B-52(b)	7	2A-24(b)	6	2B-24	16
1A-36	6	1B-56	17	2A-28	4	2B-28	8
1A-48	14	1B-60	19	2A-28(a)	5	2B-3	7
1A-52	9	1B-60(a)	20	2A-28(b)	5	2B-40	8
1A-52(a)	8	1B-60(b)	17	2A-38	9	2B-44	8
1A-52(b)	8	1B-8	7	2A-42	7	2B-44(a)	11
1A-56	10	1B-80	17	2A-5	13	2B-44(b)	12
1A-7	9	1B-84	12	2A-53	14	2B-55	8
1A-71	9	1B-87	11	2A-53(a)	3	2B-59	8
1A-74	7	-	-	2A-57	16	-	-

~ Soil cores too short to be considered for analysis * (a) and (b) depicts two replicates collected from same site.

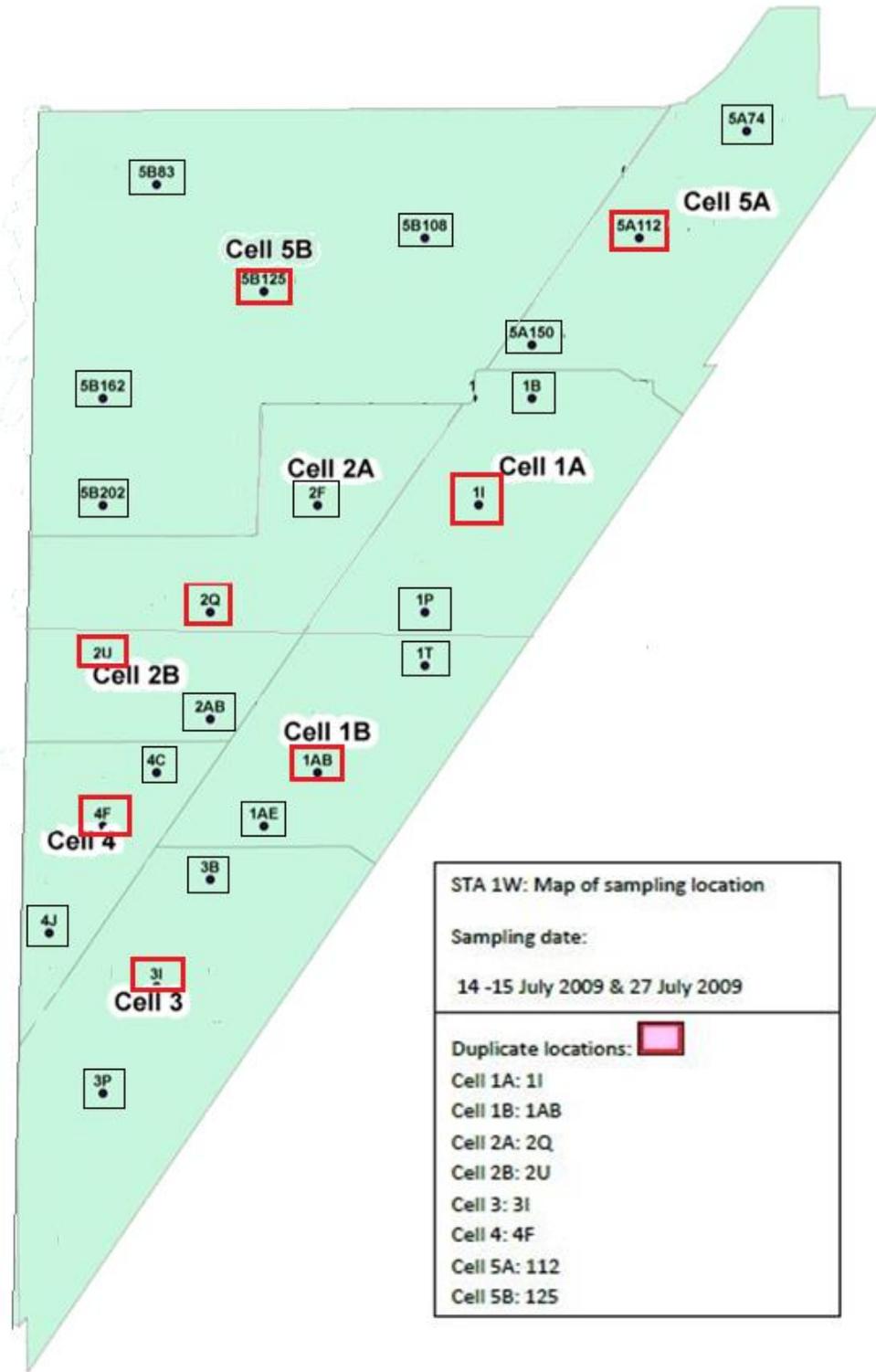


Figure C-1. Soil core sampling locations in each cell of STA-1W. (Base map source: SFWMD).

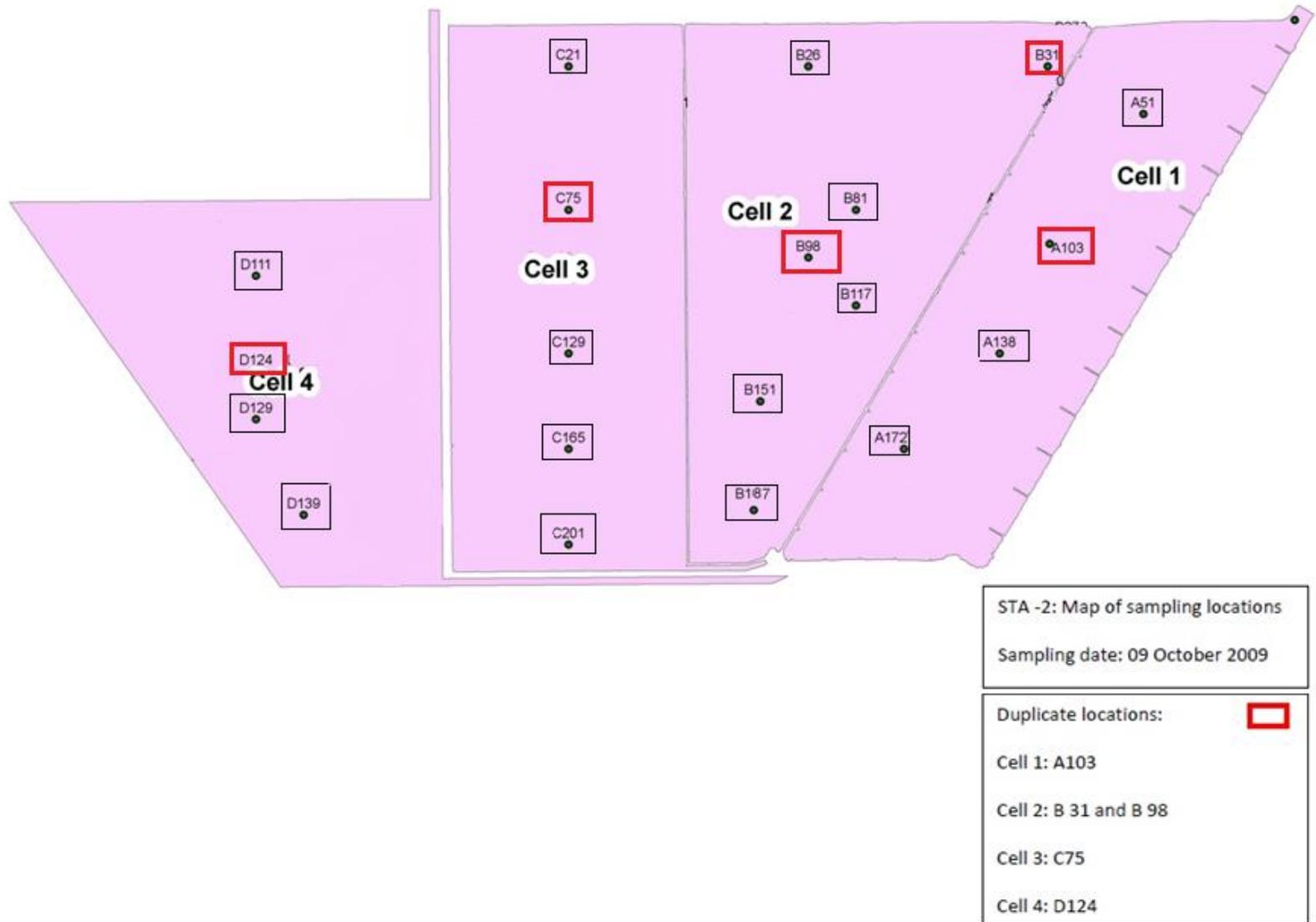


Figure C-2. Soil core sampling locations in each cell of STA-2. (Base map source: SFWMD).

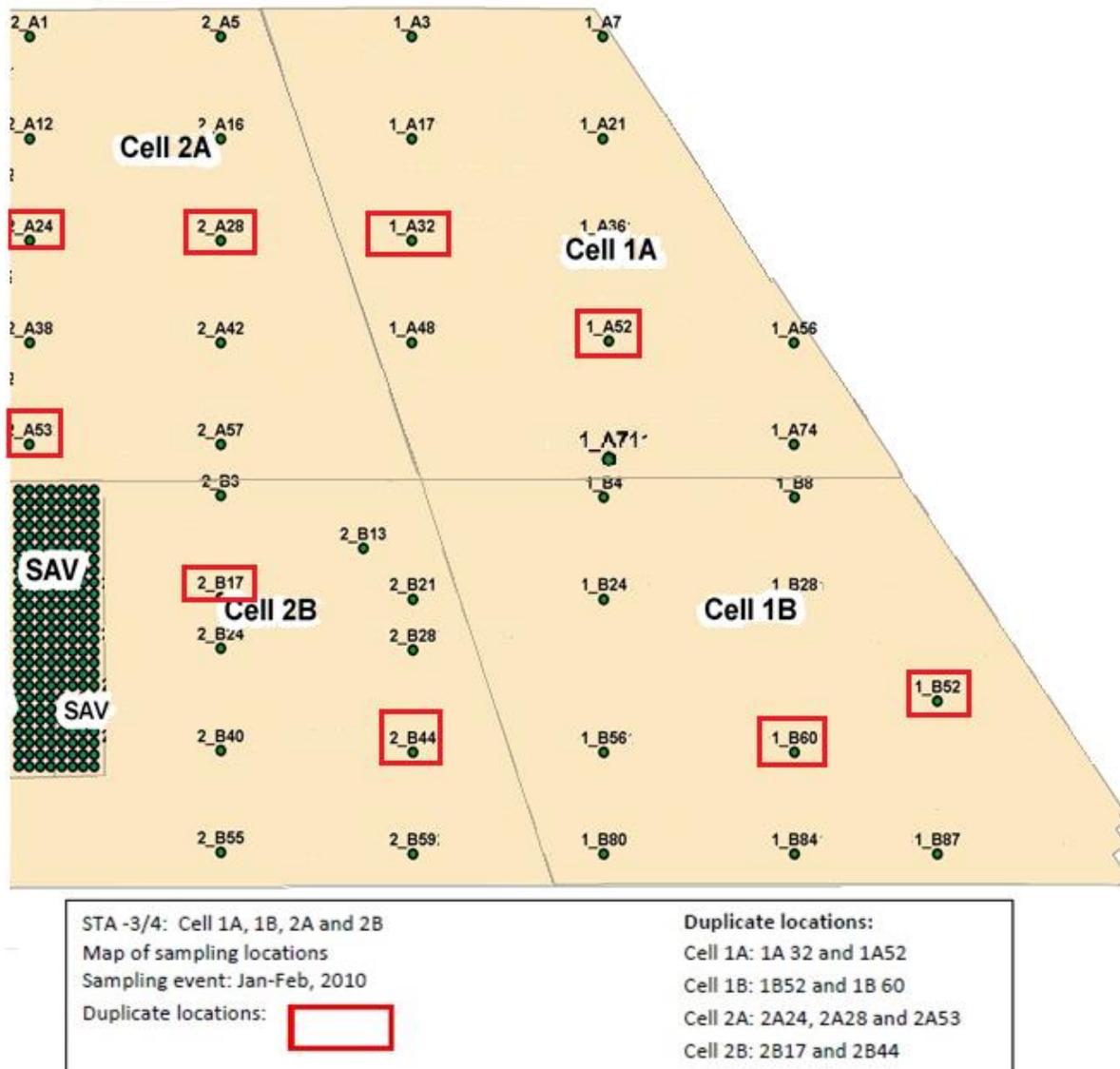


Figure C-3. Soil core sampling locations in each cell of STA-3/4.(Base map source: SFWMD).

APPENDIX D
ADDITIONAL DATA AND INFORMATION PERTAINING TO CHAPTER 4

Soil Profiles - Difference between Operational Cells

STA-1W

Soil physico-chemical parameters along the soil profile were averaged over each 2-cm strata in all soil cores from each cell of STA-1W (Figure D-1). Since not all cells in STA-1W became operational at the same time, differences in cell age and could be responsible for the variability observed in different parameters. Cells 2B and 4 underwent significant rehabilitation work during WY 2006-2007, including tilling and removal of surface soil, therefore soil $\delta^{15}\text{N}$ (‰) and $\delta^{13}\text{C}$ (‰) values for soil cores from these two cells were not determined.

Higher bulk density in the top layers of Cells 4 and 2B (Figure D-1 (a)) could be a result of compaction from earth-moving equipment used during rehabilitation activities, or consolidation and compaction caused by other processes. The concentration of TP was highest on the surface and showed decrease with increasing depth in all STA-1W cells (Figure D-1 (b)). This could be attributable to the fact that surface soil layer interacts with the overlying water column, periphyton and floc, and often serve as a major repository of P inputs to the system, while deeper soil layers experience P depletion as a result of P mining by plants.

Except for Cell 1B, all cells in STA-1W showed greater values for $\delta^{15}\text{N}$ (‰) in the upper soil layers (approximately 10-12 cm) relative to deeper sections (Figure D-1 (c)). Cells 3 and 1A showed $\delta^{13}\text{C}$ (‰) greater values in the top soil layers whereas Cells 1B and 5A showed lesser enrichment near the soil surface (Figure D-1(d)). In comparison to other cells, Cell 5B (SAV) showed decrease in the $\delta^{13}\text{C}$ (‰) values. The average soil

C:N ratio in all cells of STA-1W was relatively constant with depth (Figure D-1 (e)).

However, average N:P ratio of soil cores in STA-1W showed an increasing trend with depth (Figure D-1 (f)).

STA-2

Various physico-chemical parameters along soil profile were averaged over each 2-cm strata in all soil cores collected from each cell of STA-2 (Figure D-2). Cells 1, 2 and 3 had been in operation since WY2000 while Cell 4 was still in its stabilization phase as late as WY2007 (3 years before soil sampling). Differences in cell age could account for some of the variability in various parameters among the cells.

Bulk density was low in the top soil layers, which increased in deeper layers (Figure D-2 (a)). Cell 1 and 2 had considerably lower bulk density at depth compared to Cells 3 and 4. Total P decreased with depth. This could be attributable to the fact that surface soil layer interacts with the overlying water column, periphyton and floc, and often serve as a major repository of P inputs to the system, while deeper soil layers experience P depletion as a result of P mining by plants (Figure D-2 (b)). Total P in surface layers was relatively higher in Cells 1 and 2 (EAV) compared to Cells 3 and 4 (SAV). All cells of STA-2 had higher $\delta^{15}\text{N}$ (‰) values in the top 10-12 cm of soil (Figure D-2 (c)). However, only the top soil layers of Cells 3 and 4 (SAV cells) exhibited greater $\delta^{13}\text{C}$ (‰) whereas Cells 1 and 2 (EAV cells) did not show this trend (Figure D-2 (d)). The reason for divergent trend in $\delta^{13}\text{C}$ (‰) values for EAV and SAV cells can be attributed to differences in C processing by different vegetation types in these cells. The C:N mass ratio was relatively constant with increasing depth across all cells (Figure D-2 (e)). However, N:P ratios in Cells 1 and 2 showed a consistent increasing trend with the

depth while Cells 3 and 4 exhibited a decreasing N:P ratio after 20-25-cm (Figure D-2 (f)). The varying trends seen in the deeper soil depths could reflect past land use prior to the establishment of the STAs.

STA-3/4

Variation with depth among different soil physico-chemical parameters in all soil cores collected from STA-3/4 is shown in Figure D-3. Cell 1B functioned as an EAV cell for most of its operational history before it was converted to SAV cell in WY2008. Soil sampling was carried out WY2010. Therefore, the variability observed in surface soil in this cell may be a result of changed vegetation as a consequence of new hydroperiod.

Bulk density showed a consistent increasing trend with soil depth in all cells except for a small increase around 19-21 cm (Figure D-3 (a)). Cell 1B had lower bulk density compared to Cells 1A, 2A and 2B. Total P decreased with depth with relatively higher TP values in the surface layers Cells 1A and 2A (EAV) than in Cells 1B and 2B (SAV) (Figure D-3 (b)). Cells 1A and 2A were enriched for heavier $\delta^{15}\text{N}$ (‰) in the top soil layers down to 8 cm, below which the soils from all four cells had similar $\delta^{15}\text{N}$ (‰) content (Figure D-3 (c)). Cells 1A, 2A and 2B had greater $\delta^{13}\text{C}$ (‰) values in the surface layers, whereas Cell 1B showed no increase in $\delta^{13}\text{C}$ (‰) values in the top soil sections (Figure D-3 (d)). Carbon:nitrogen mass ratios were relatively uniform with depth across all cells (Figure D-3 (e)). However, N:P ratio, in all cells generally increased with depth (Figure D-3 (f)) although the N:P ratio in cells 2A and 2B decreased after 27 cm and 21 cm depth, respectively.

Table D-1. STA-1W soil core collection sites by vegetation type and cell. A total of 41 soil cores were collected from these locations.

EAV	EAV	EAV	SAV	SAV	SAV	EAV Conversion	
Cell 1A	Cell 2A	Cell 5A	Cell 2B	Cell 4	Cell 5B	Cell 3	Cell 1B
1B [#]	2F	5A112	2AB	4C	5B108	3B	1AB
1B(i)	2Q	5A112(a)	2U	4F	5B125	3I	1AB(a)
1I	2Q(a)	5A112(b)	2U(a)	4F(a)	5B125(a)	3I(a)	1AB(b)
1I (a)*	2Q(b)	5A150	2U(b)	4F(b)	5B125(b)	3I(b)	1AE
1I (b)*	-	5A74	-	4J	5B202	3P	1T
1P	-	-	-	-	5B83	-	-
-	-	-	-	-	5B162	-	-

#This site was located in a canal so another soil core (1B(i)) was collected 3 m away from the canal. *(a) and (b) indicate replicate soil cores collected from this site.

Table D-2. STA-2 soil core collection sites by vegetation type and cell. A total of 29 soil cores were collected from these locations.

EAV	EAV	SAV	SAV
Cell 1	Cell 2	Cell 3	Cell 4
A103	B117	C129	D111
A103(a)*	B151	C165	D124
A103(b)*	B187	C201	D124(a)
A138	B26	C21	D124(b)
A172	B31	C75	D129
A51	B31(a)	C75(a)	D139
-	B81	C75(b)	-
-	B98	-	-
-	B98(a)	-	-
-	B98(b)	-	-

* (a) and (b) signify replicate soil cores collected from this site.

Table D-3. STA-3/4 soil core collection sites by vegetation type and cell. A total 58 soil cores were collected from these locations.

EAV	EAV	SAV	SAV
Cell 1A	Cell 2A	Cell 1B	Cell 2B
1A-19	2A-1	1B-24	2B-13
1A-21	2A-12	1B-28	2B-17
1A-3	2A-16	1B-4	2B-17(a)
1A-32	2A-24	1B-52	2B-17(b)
1A-32(a)*	2A-24(a)	1B-52(a)	2B-21
1A-32(b)*	2A-24(b)	1B-52(b)	2B-24
1A-36	2A-28	1B-56	2B-28
1A-48	2A-28(a)	1B-60	2B-3
1A-52	2A-28(b)	1B-60(a)	2B-40
1A-52(a)	2A-38	1B-60(b)	2B-44
1A-52(b)	2A-42	1B-8	2B-44(a)
1A-56	2A-5	1B-80	2B-44(b)
1A-7	2A-53	1B-84	2B-55
1A-71	2A-53(a)	1B-87	2B-59
1A-74	2A-57	-	-

* (a) and (b) signify replicate soil cores collected from this site.

Table D-4. Summary statistics for change point depths calculated with SegReg in soil cores collected from STA-1W, STA-2 and STA-3/4.

	EAV	EAV	EAV	SAV	SAV	SAV	EAV conversion	
STA 1W	Cell 1A	Cell 2A	Cell 5A [#]	Cell 2B	Cell 1B	Cell 4	Cell 3	Cell 5B [#]
Sites (n)	5	4	5	4	5	5	5	7
Mean (cm)	19.3	16.7	10.4	15.8	13.5	10.8	12.9	12.4
Standard deviation (cm)	7.3	1.5	4.2	5.4	2.7	3.5	4.8	6.5
CV* (%)	38	9	40	34	20	32	37	52
STA-2	Cell 1	Cell 2	Cell 3	Cell 4	--	--	--	--
Sites (n)	6	10	7	6	--	--	--	--
Mean (cm)	8.9	10.4	12.5	12.9	--	--	--	--
Standard deviation (cm)	1.8	2.6	4	3.8	--	--	--	--
CV* (%)	20	25	32	29	--	--	--	--
STA-3/4	Cell 1A	Cell 2A	Cell 1B	Cell 2B	--	--	--	--
Sites (n)	10	6	13	10	--	--	--	--
Mean (cm)	8.2	11.9	12.1	8.4	--	--	--	--
Standard deviation (cm)	2.9	6.7	5	2.8	--	--	--	--
CV* (%)	35	56	41	33	--	--	--	--

* Coefficient of variation

[#] Cell 5A and 5B went online in WY2000, while the other cells in STA-1W started operation in WY1994.

Table D-5. Bulk density profiles in soil cores collected from each cell of STA-1W

Depth (cm)	Mean bulk density (g cm ⁻³) ± 1 SD							
	Cell 1A	Cell 1B	Cell 2A	Cell 2B	Cell 3	Cell 4	Cell 5A	Cell 5B
-1	0.19 ± 0.09	0.31 ± 0.02	0.11 ± 0.05	0.29 ± 0.06	0.2 ± 0.04	0.34 ± 0.07	0.21 ± 0.14	0.23 ± 0.04
-3	0.22 ± 0.07	0.35 ± 0.07	0.16 ± 0.06	0.31 ± 0.04	0.21 ± 0.05	0.37 ± 0.09	0.32 ± 0.25	0.3 ± 0.03
-5	0.24 ± 0.06	0.33 ± 0.02	0.18 ± 0.06	0.34 ± 0.06	0.23 ± 0.06	0.45 ± 0.06	0.42 ± 0.26	0.32 ± 0.04
-7	0.27 ± 0.03	0.3 ± 0.04	0.24 ± 0.04	0.36 ± 0.04	0.27 ± 0.07	0.44 ± 0.06	0.4 ± 0.08	0.31 ± 0.07
-9	0.25 ± 0.06	0.27 ± 0.06	0.26 ± 0.04	0.36 ± 0.03	0.33 ± 0.05	0.44 ± 0.08	0.37 ± 0.07	0.33 ± 0.11
-11	0.25 ± 0.01	0.28 ± 0.09	0.28 ± 0.02	0.38 ± 0.02	0.34 ± 0.06	0.43 ± 0.07	0.34 ± 0.08	0.28 ± 0.07
-13	0.25 ± 0.03	0.28 ± 0.07	0.31 ± 0.03	0.38 ± 0.04	0.35 ± 0.03	0.4 ± 0.03	0.33 ± 0.11	0.29 ± 0.1
-15	0.28 ± 0.01	0.31 ± 0.08	0.33 ± 0.03	0.37 ± 0.06	0.33 ± 0.05	0.37 ± 0.03	0.33 ± 0.09	0.28 ± 0.11
-17	0.26 ± 0.03	0.31 ± 0.06	0.33 ± 0.02	0.35 ± 0.03	0.35 ± 0.05	0.36 ± 0.03	0.32 ± 0.1	0.29 ± 0.09
-19	0.25 ± 0.04	0.28 ± 0.07	0.35 ± 0.03	0.35 ± 0.01	0.36 ± 0.05	0.36 ± 0.04	0.32 ± 0.07	0.27 ± 0.11
-21	0.24 ± 0.05	0.26 ± 0.04	0.37 ± 0.04	0.36 ± 0.08	0.35 ± 0.04	0.32 ± 0.05	0.3 ± 0.1	0.27 ± 0.08
-23	0.24 ± 0.07	0.26 ± 0.08	0.36 ± 0.03	0.31 ± 0.05	0.35 ± 0.02	0.31 ± 0.07	0.3 ± 0.11	0.26 ± 0.06
-25	0.23 ± 0.09	0.26 ± 0.07	0.34 ± 0.08	0.28 ± 0.08	0.33 ± 0.07	0.23 ± 0.05	0.29 ± 0.12	0.25 ± 0.08
-27	0.21 ± 0.07	0.24 ± 0.01	0.33 ± 0.08	0.25 ± 0.07	0.32 ± 0.07	0.23 ± 0.09	0.26 ± 0.1	0.23 ± 0.06
-29	0.19 ± 0.07	0.22 ± 0.06	0.34 ± 0.11	0.22 ± 0.05	0.29 ± 0.08	0.23 ± 0.09	0.26 ± 0.09	0.19 ± 0.03
-31	0.18 ± 0.06	0.19 ± 0.01	0.32 ± 0.1	0.22 ± 0.06	0.27 ± 0.08	--	0.24 ± 0.09	0.17 ± 0.04
-33	0.18 ± 0.06	0.18 ± 0.06	0.26 ± 0.06	0.19 ± 0.05	0.32 ± 0.1	--	0.17 ± 0.03	0.17 ± 0.02
-35	0.15 ± 0.03	0.24 ± 0.1	0.22 ± 0.06	--	0.27 ± 0.05	--	--	0.16 ± 0.04
-37	0.14 ± 0.02	0.16 ± 0.02	0.2 ± 0.02	--	0.19 ± 0.04	--	--	--
-39	0.13 ± 0.01	--	0.19 ± 0	--	0.22 ± 0.05	--	--	--
-41	0.12 ± 0.02	--	--	--	0.19 ± 0.01	--	--	--
-43	0.13 ± 0.03	--	--	--	--	--	--	--

Table D-6. Total phosphorus profiles in soil cores collected from each cell of STA-1W

Depth (cm)	Mean total phosphorus (mg/kg) \pm 1 SD							
	Cell 1A	Cell 1B	Cell 2A	Cell 2B	Cell 3	Cell 4	Cell 5A	Cell 5B
-1	1033 \pm 455	435 \pm 129	1475 \pm 245	729 \pm 242	802 \pm 219	542 \pm 95	1085 \pm 437	941 \pm 256
-3	811 \pm 343	365 \pm 119	1209 \pm 304	525 \pm 68	744 \pm 281	557 \pm 113	769 \pm 398	714 \pm 164
-5	672 \pm 381	296 \pm 164	1074 \pm 216	533 \pm 113	744 \pm 336	405 \pm 55	482 \pm 200	570 \pm 156
-7	562 \pm 423	277 \pm 164	868 \pm 325	554 \pm 68	449 \pm 199	398 \pm 81	442 \pm 167	412 \pm 117
-9	469 \pm 443	297 \pm 224	704 \pm 249	455 \pm 124	346 \pm 260	338 \pm 114	378 \pm 147	401 \pm 116
-11	466 \pm 406	341 \pm 340	590 \pm 130	382 \pm 120	265 \pm 117	280 \pm 117	373 \pm 163	374 \pm 108
-13	452 \pm 364	211 \pm 44	420 \pm 45	387 \pm 115	231 \pm 65	217 \pm 32	332 \pm 108	388 \pm 200
-15	345 \pm 86	205 \pm 40	364 \pm 54	361 \pm 111	213 \pm 46	211 \pm 23	273 \pm 67	353 \pm 173
-17	250 \pm 14	187 \pm 23	466 \pm 296	354 \pm 110	203 \pm 37	199 \pm 11	260 \pm 78	336 \pm 174
-19	220 \pm 10	180 \pm 15	299 \pm 37	390 \pm 136	204 \pm 41	192 \pm 11	262 \pm 82	325 \pm 194
-21	203 \pm 17	168 \pm 23	309 \pm 36	354 \pm 110	200 \pm 43	189 \pm 14	237 \pm 81	299 \pm 159
-23	190 \pm 18	168 \pm 29	298 \pm 36	313 \pm 114	199 \pm 31	180 \pm 21	222 \pm 117	295 \pm 138
-25	177 \pm 23	168 \pm 31	272 \pm 67	235 \pm 109	190 \pm 48	174 \pm 19	229 \pm 117	263 \pm 70
-27	174 \pm 22	155 \pm 18	259 \pm 95	195 \pm 101	185 \pm 40	160 \pm 26	212 \pm 114	263 \pm 141
-29	169 \pm 16	130 \pm 26	255 \pm 95	165 \pm 85	180 \pm 45	163 \pm 21	216 \pm 126	198 \pm 46
-31	165 \pm 10	110 \pm 19	240 \pm 90	166 \pm 86	171 \pm 53	--	165 \pm 106	156 \pm 28
-33	165 \pm 19	113 \pm 42	207 \pm 67	147 \pm 25	193 \pm 44	--	77 \pm 14	144 \pm 22
-35	161 \pm 8	140 \pm 58	192 \pm 64	--	174 \pm 41	--	--	136 \pm 20
-37	153 \pm 18	106 \pm 11	133 \pm 29	--	149 \pm 36	--	--	--
-39	149 \pm 23	--	130 \pm 0	--	140 \pm 14	--	--	--
-41	160 \pm 10	--	--	--	167 \pm 34	--	--	--
-43	155 \pm 14	--	--	--	--	--	--	--

Table D-7. Bulk density and total phosphorus profiles in soil cores collected from each cell of STA-2.

STA-2								
Depth (cm)	Mean bulk density (g cm ⁻³) ± 1 SD				Mean total phosphorus(mg kg ⁻¹) ± 1 SD			
	Cell 1	Cell 2	Cell 3	Cell 4	Cell 1	Cell 2	Cell 3	Cell 4
-1	0.11 ± 0.01	0.14 ± 0.08	0.28 ± 0.1	0.25 ± 0.08	1460 ± 397	1413 ± 305	779 ± 257	901 ± 248
-3	0.14 ± 0.04	0.16 ± 0.07	0.28 ± 0.07	0.33 ± 0.11	758 ± 259	1129 ± 436	776 ± 353	637 ± 144
-5	0.17 ± 0.02	0.21 ± 0.07	0.32 ± 0.07	0.35 ± 0.1	433 ± 96	746 ± 333	614 ± 290	549 ± 99
-7	0.21 ± 0.02	0.28 ± 0.06	0.33 ± 0.05	0.38 ± 0.06	315 ± 58	533 ± 151	660 ± 314	503 ± 107
-9	0.22 ± 0.04	0.26 ± 0.08	0.34 ± 0.06	0.41 ± 0.03	290 ± 61	361 ± 69	589 ± 295	483 ± 115
-11	0.22 ± 0.04	0.26 ± 0.07	0.33 ± 0.06	0.44 ± 0.08	259 ± 27	311 ± 76	562 ± 259	459 ± 134
-13	0.2 ± 0.06	0.25 ± 0.09	0.31 ± 0.08	0.47 ± 0.2	226 ± 33	265 ± 61	411 ± 127	410 ± 108
-15	0.2 ± 0.04	0.24 ± 0.08	0.3 ± 0.07	0.42 ± 0.22	211 ± 25	239 ± 39	372 ± 61	377 ± 134
-17	0.2 ± 0.03	0.22 ± 0.07	0.29 ± 0.06	0.27 ± 0.04	196 ± 29	223 ± 39	472 ± 199	332 ± 90
-19	0.2 ± 0.03	0.22 ± 0.07	0.27 ± 0.06	0.25 ± 0.03	181 ± 36	214 ± 45	363 ± 87	275 ± 29
-21	0.19 ± 0.01	0.2 ± 0.06	0.27 ± 0.05	0.24 ± 0.02	162 ± 17	197 ± 42	344 ± 45	254 ± 26
-23	0.17 ± 0.01	0.2 ± 0.06	0.32 ± 0.09	0.25 ± 0.02	161 ± 29	194 ± 38	320 ± 74	250 ± 20
-25	0.17 ± 0.02	0.18 ± 0.05	0.44 ± 0.25	0.27 ± 0.04	149 ± 35	197 ± 51	271 ± 91	224 ± 20
-27	0.17 ± 0.01	0.2 ± 0.07	0.57 ± 0.47	0.29 ± 0.07	138 ± 21	209 ± 115	206 ± 54	231 ± 43
-29	0.16 ± 0.01	0.21 ± 0.1	0.56 ± 0.63	0.3 ± 0.06	135 ± 27	210 ± 127	203 ± 78	228 ± 41
-31	0.16 ± 0.02	0.22 ± 0.14	0.57 ± 0.66	0.33 ± 0.02	132 ± 22	206 ± 107	209 ± 79	206 ± 16
-33	0.15 ± 0.01	0.26 ± 0.28	0.33 ± 0.05	0.31 ± 0.03	117 ± 15	177 ± 47	197 ± 94	223 ± 12
-35	0.16 ± 0.03	0.17 ± 0.03	0.34 ± 0	0.34 ± 0.03	120 ± 0	166 ± 27	152 ± 0	214 ± 39
-37	0.14 ± 0.02	0.18 ± 0.02	--	0.29 ± 0.04	110 ± 0	155 ± 21	--	224 ± 62
-39	0.13 ± 0.03	0.18 ± 0.01	--	0.41 ± 0	110 ± 0	161 ± 24	--	290 ± 0
-41	0.14 ± 0	0.18 ± 0.02	--	0.47 ± 0	100 ± 0	154 ± 11	--	303 ± 0
-43	--	0.17 ± 0.01	--	--	--	145 ± 6	--	--
-45	--	0.13 ± 0	--	--	--	150 ± 0	--	--

Table D-8. Bulk density and total phosphorus profiles in soil cores collected from each cell of STA-3/4.

STA-3/4								
Depth (cm)	Mean bulk density (g cm ⁻³) ± 1 SD				Mean total phosphorus (mg kg ⁻¹) ± 1 SD			
	Cell 1A	Cell 1B	Cell 2A	Cell 2B	Cell 1A	Cell 1B	Cell 2A	Cell 2B
-1	0.17 ± 0.13	0.13 ± 0.06	0.22 ± 0.18	0.27 ± 0.13	1298 ± 948	979 ± 275	1026 ± 375	770 ± 182
-3	0.24 ± 0.16	0.18 ± 0.09	0.28 ± 0.15	0.37 ± 0.15	1100 ± 1017	780 ± 257	881 ± 265	738 ± 241
-5	0.27 ± 0.13	0.23 ± 0.09	0.36 ± 0.13	0.46 ± 0.16	699 ± 138	670 ± 222	764 ± 211	679 ± 208
-7	0.38 ± 0.2	0.28 ± 0.09	0.39 ± 0.14	0.48 ± 0.13	540 ± 99	547 ± 242	705 ± 193	631 ± 151
-9	0.45 ± 0.29	0.31 ± 0.12	0.44 ± 0.16	0.52 ± 0.1	476 ± 103	446 ± 146	659 ± 152	574 ± 86
-11	0.45 ± 0.22	0.34 ± 0.13	0.46 ± 0.2	0.5 ± 0.11	420 ± 99	413 ± 164	595 ± 169	523 ± 109
-13	0.45 ± 0.15	0.33 ± 0.24	0.43 ± 0.19	0.46 ± 0.1	418 ± 152	354 ± 148	564 ± 254	487 ± 126
-15	0.49 ± 0.18	0.35 ± 0.31	0.43 ± 0.29	0.47 ± 0.07	368 ± 103	322 ± 112	509 ± 266	480 ± 80
-17	0.42 ± 0.15	0.4 ± 0.4	0.48 ± 0.27	0.41 ± 0.09	340 ± 137	295 ± 98	544 ± 285	445 ± 110
-19	0.41 ± 0.15	0.32 ± 0.18	0.45 ± 0.19	0.37 ± 0.09	349 ± 80	288 ± 71	558 ± 246	307 ± 68
-21	0.47 ± 0.1	0.38 ± 0.23	0.43 ± 0.13	0.31 ± 0.02	288 ± 19	265 ± 60	461 ± 254	295 ± 129
-23	0.54 ± 0.05	0.33 ± 0.16	0.48 ± 0.18	0.33 ± 0	248 ± 40	254 ± 80	436 ± 261	345 ± 0
-25	0.67 ± 0.04	0.29 ± 0.08	0.51 ± 0.29	0.34 ± 0	198 ± 62	265 ± 90	390 ± 361	342 ± 0
-27	--	0.35 ± 0.11	0.38 ± 0.17	0.34 ± 0	--	255 ± 100	480 ± 511	373 ± 0
-29	--	0.42 ± 0.17	0.51 ± 0.28	0.53 ± 0	--	208 ± 107	475 ± 385	170 ± 0
-31	--	0.46 ± 0.11	0.61 ± 0	--	--	160 ± 40	543 ± 0	--
-33	--	0.44 ± 0.1	0.62 ± 0	--	--	168 ± 37	656 ± 0	--
-35	--	0.57 ± 0.27	0.56 ± 0	--	--	158 ± 56	671 ± 0	--
-37	--	0.63 ± 0.11	0.5 ± 0	--	--	142 ± 74	706 ± 0	--
-39	--	0.62 ± 0	--	--	--	187 ± 0	--	--

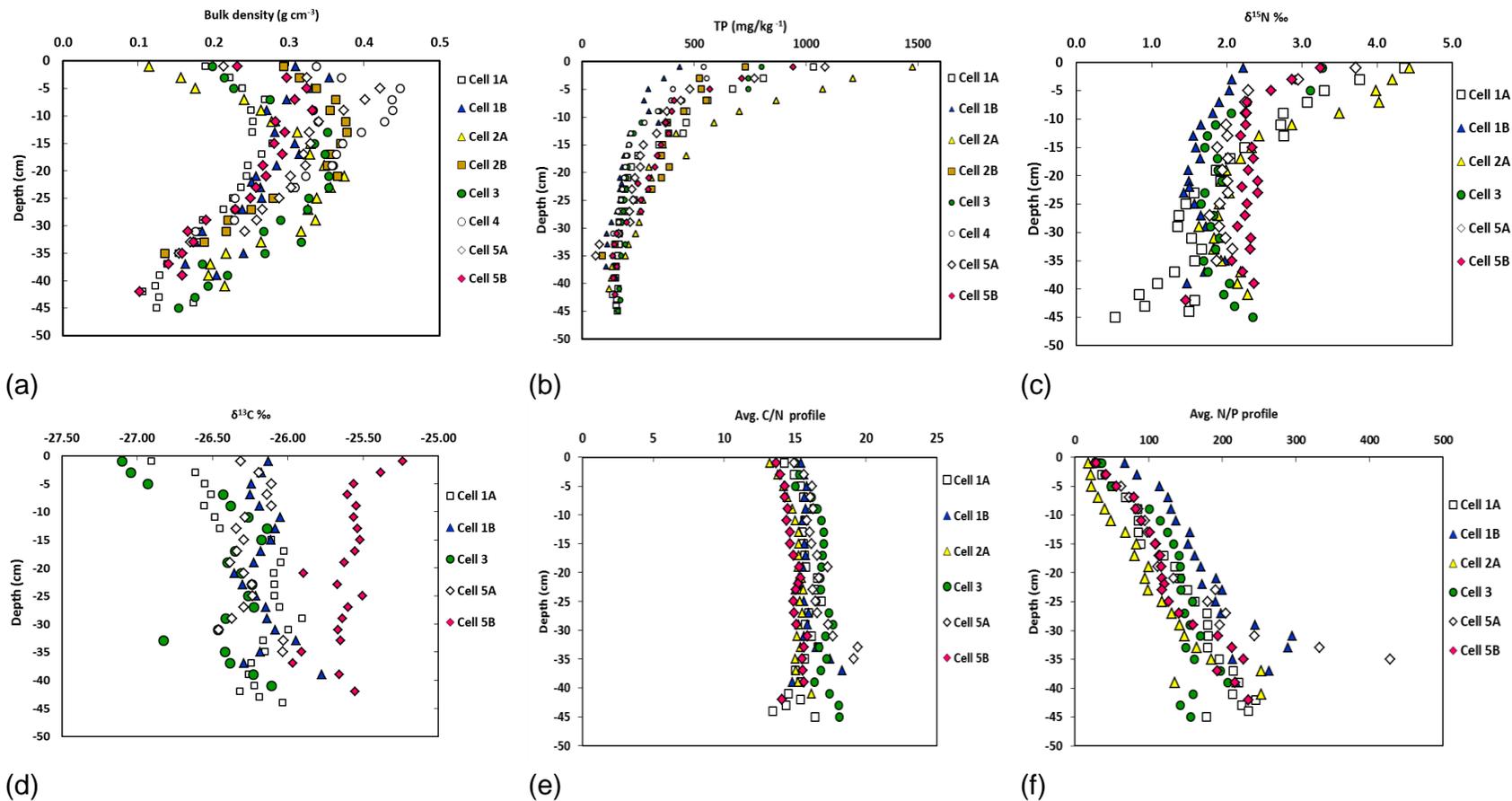


Figure D-1. Profiles of mean (a) bulk density, (b) total phosphorus content, (c) soil $\delta^{15}\text{N}$ (‰), (d) soil $\delta^{13}\text{C}$ (‰), (e) C:N ratio and (f) N:P ratio in 2-cm soil core sections collected from each cell in STA-1W.

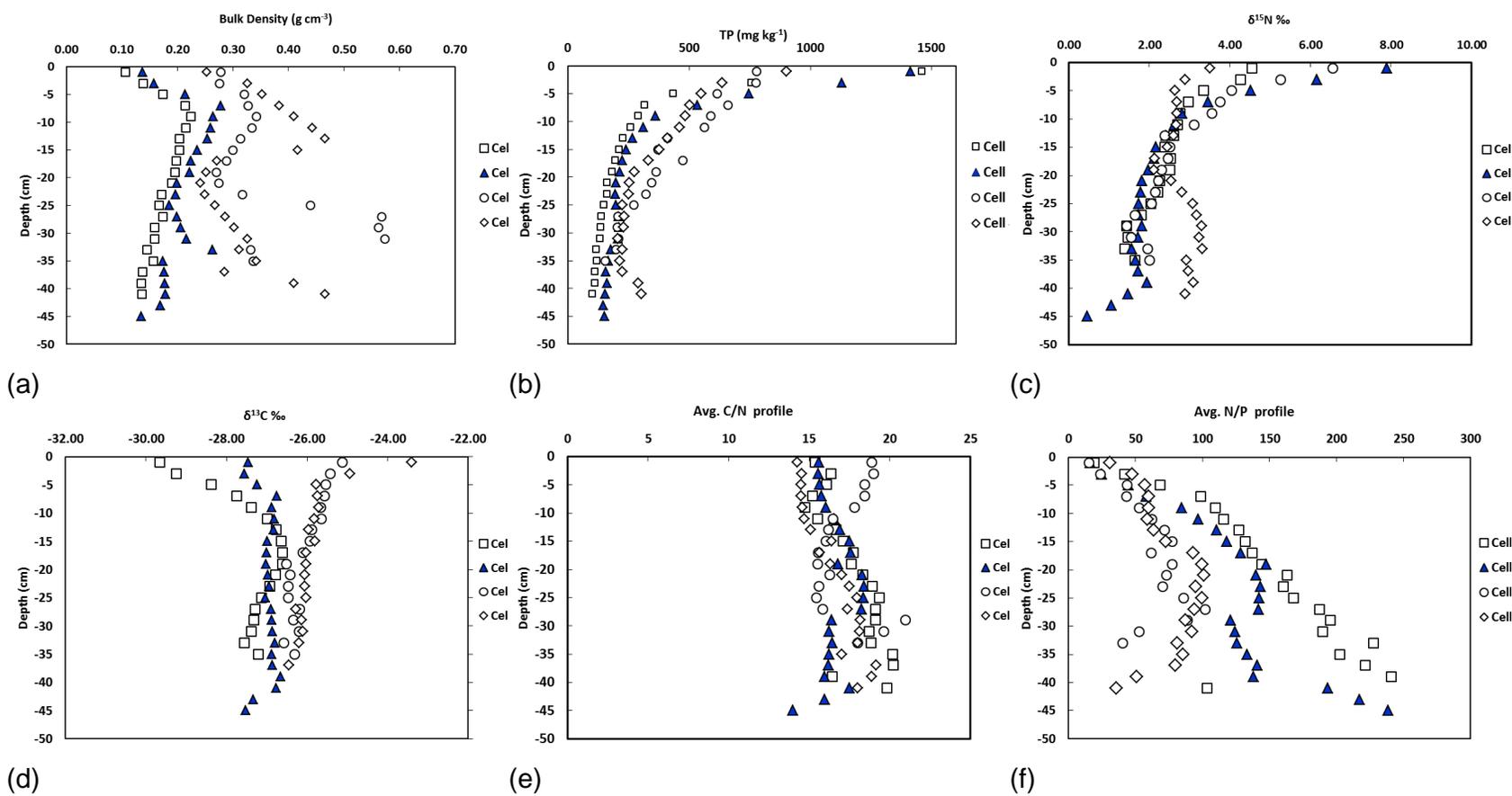


Figure D-2. Profiles of mean (a) bulk density, (b) total phosphorus content, (c) soil $\delta^{15}\text{N}$ (‰), (d) soil $\delta^{13}\text{C}$ (‰), (e) C:N ratio and (f) N:P ratio in 2-cm soil cores sections collected from each cell in STA-2.

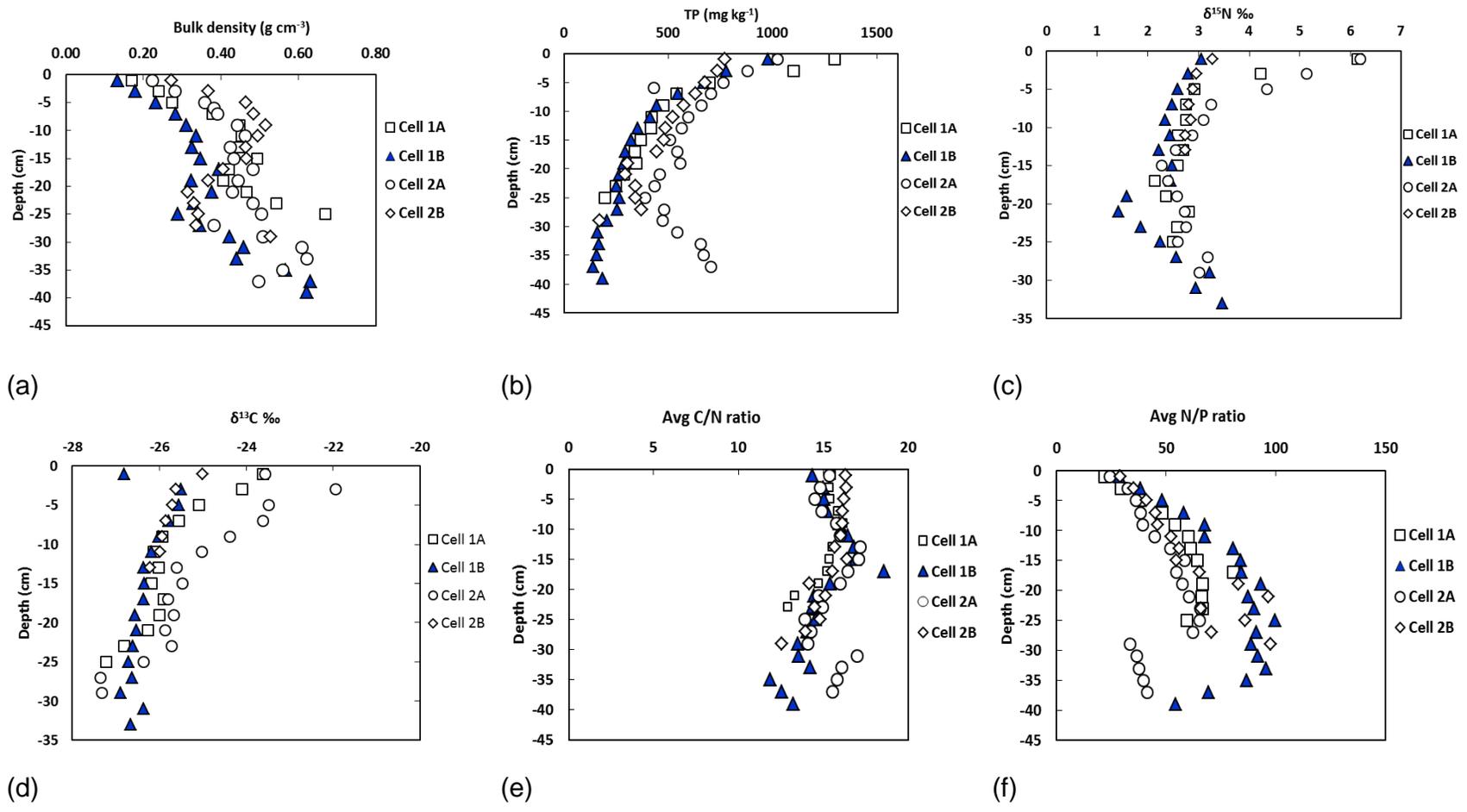


Figure D-3. Profiles of mean (a) bulk density, (b) total phosphorus, (c) soil $\delta^{15}\text{N}$ (‰), (d) soil $\delta^{13}\text{C}$ (‰), (e) C:N ratio and (f) N:P ratio in 2-cm soil cores sections collected from each cell in STA-3/4.

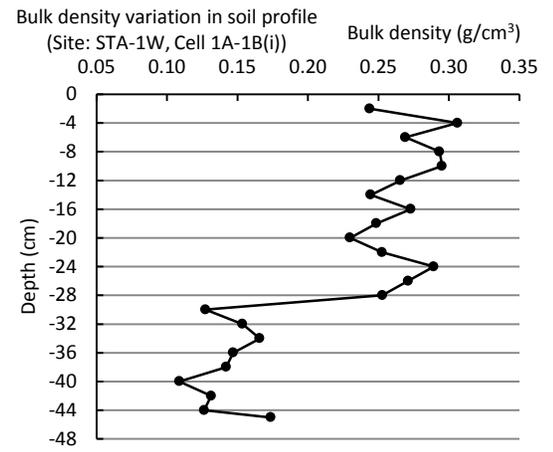
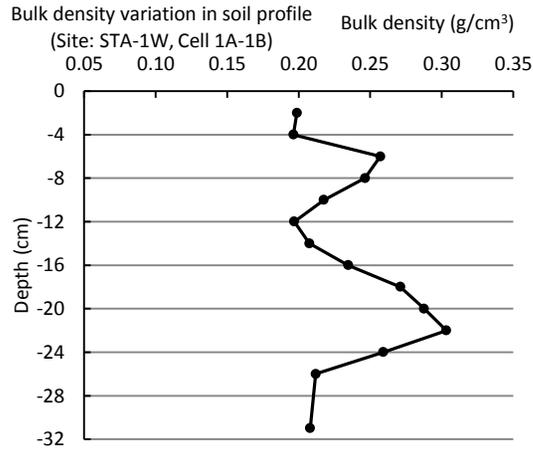
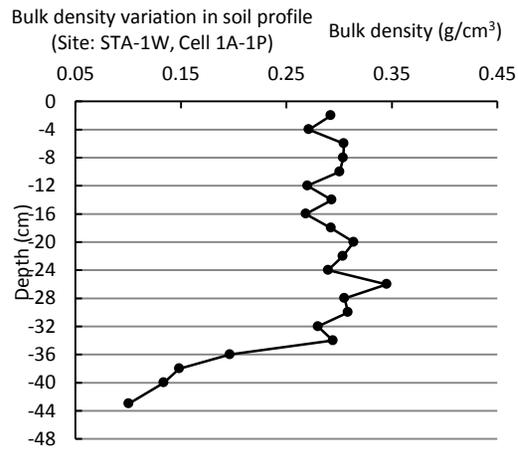
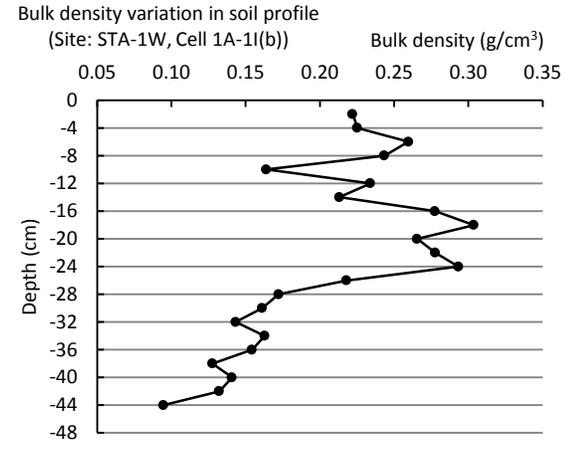
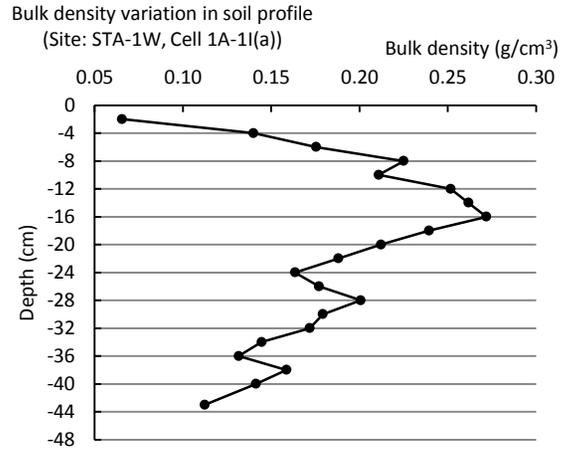
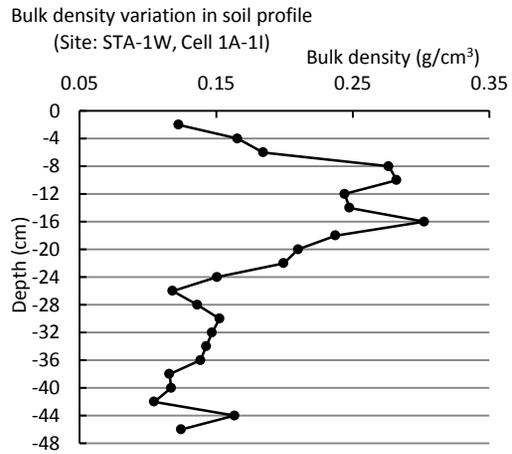


Figure D-4. Bulk density profile in each soil core collected from STA-1W.

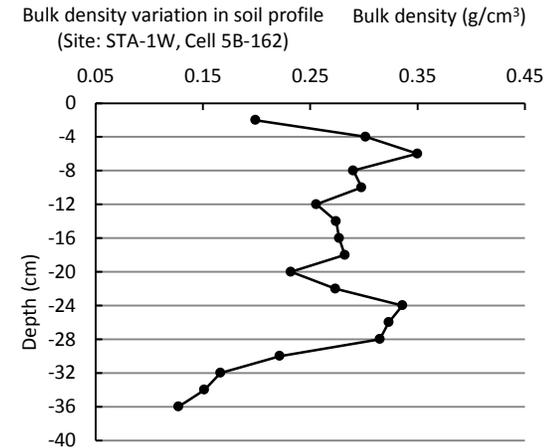
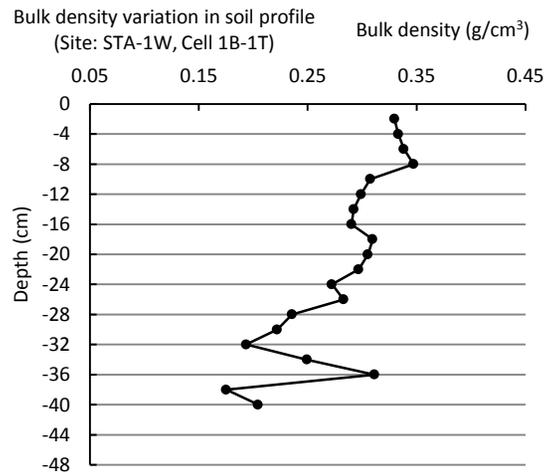
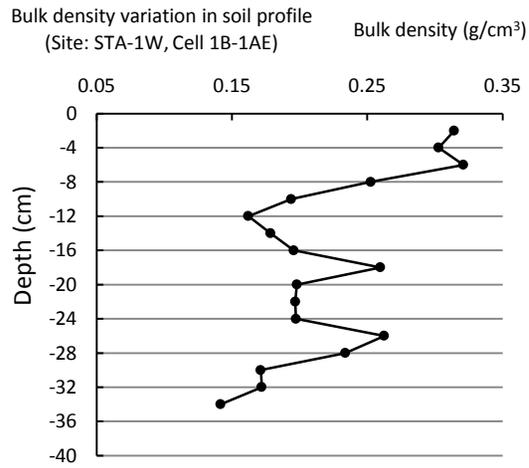
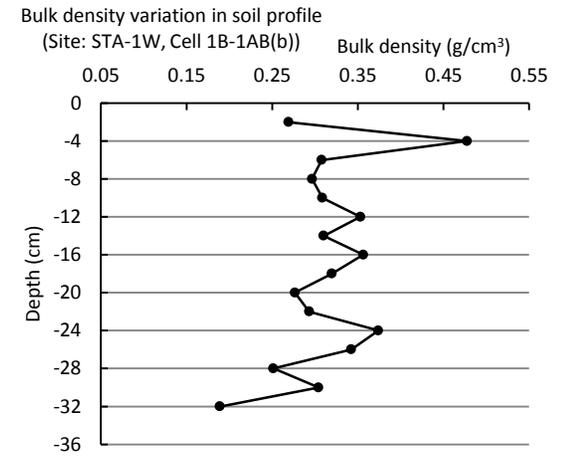
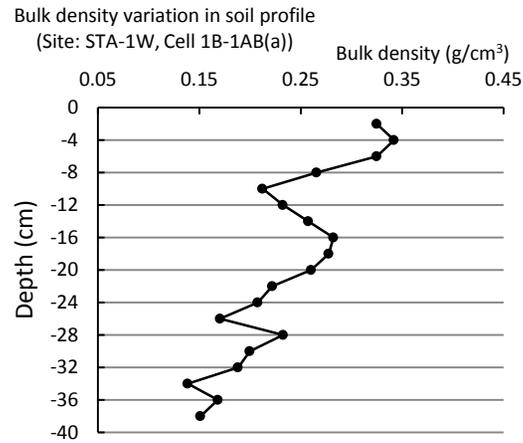
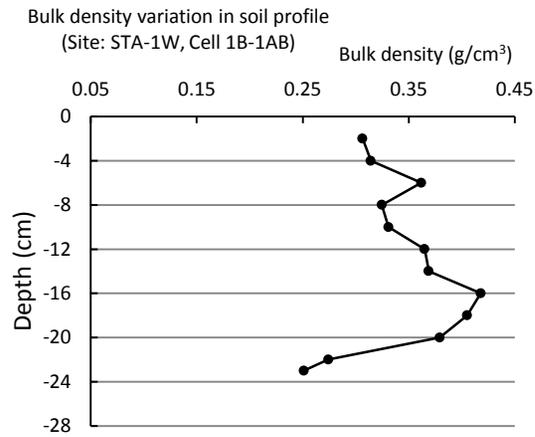


Figure D-4. Continued.

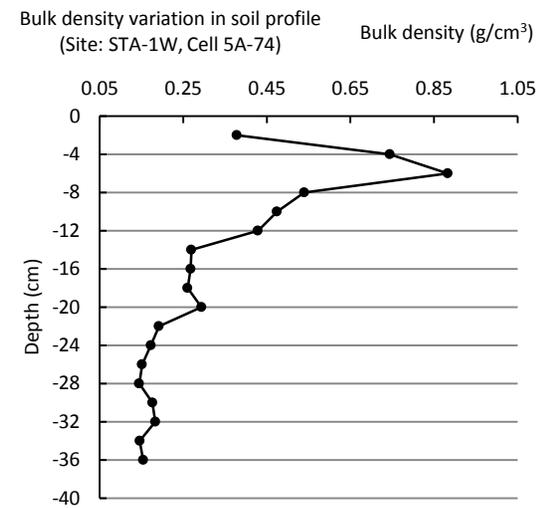
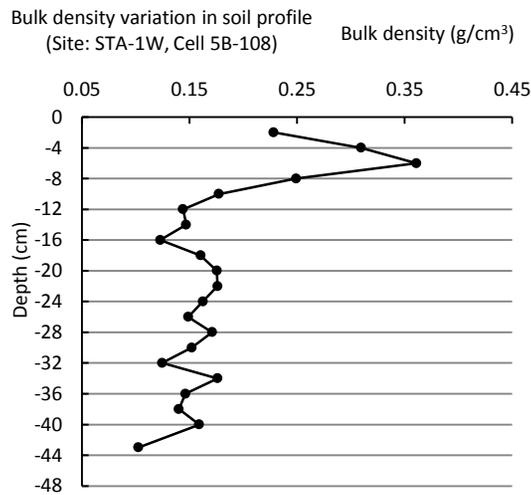
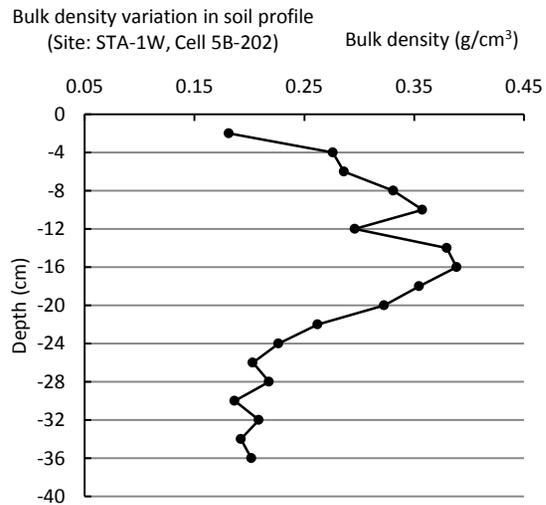
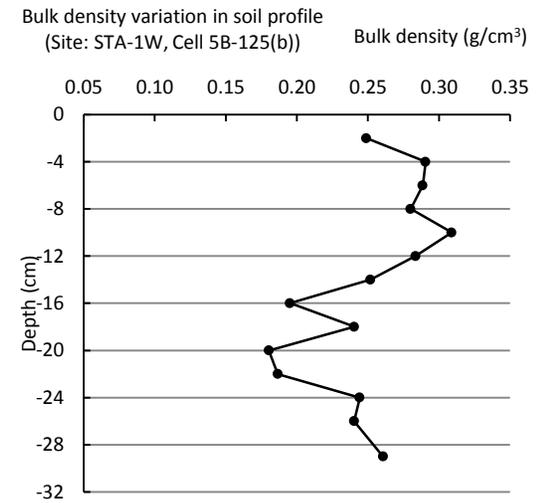
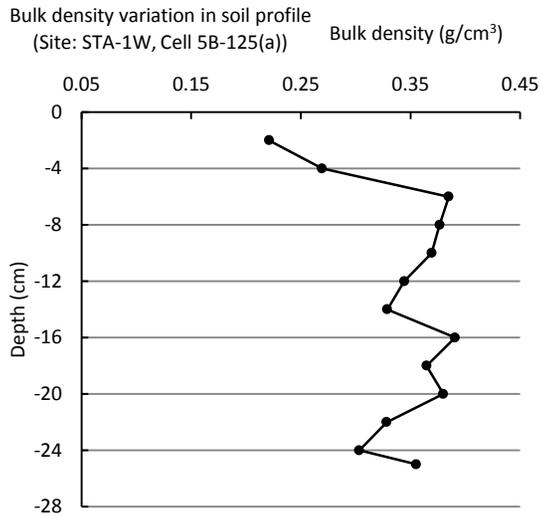
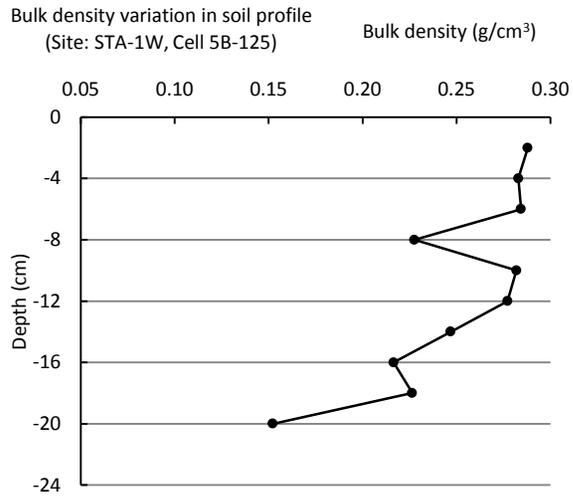


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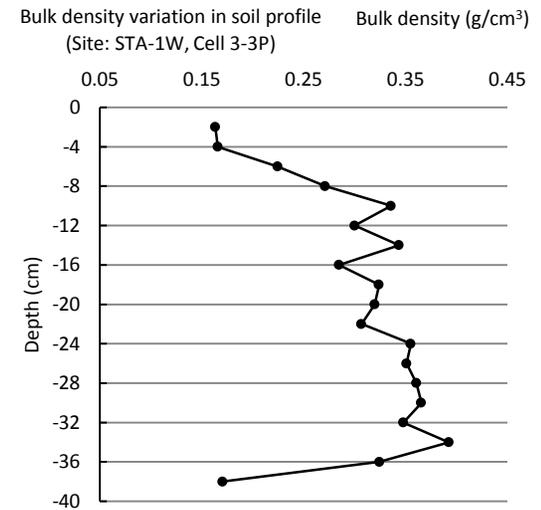
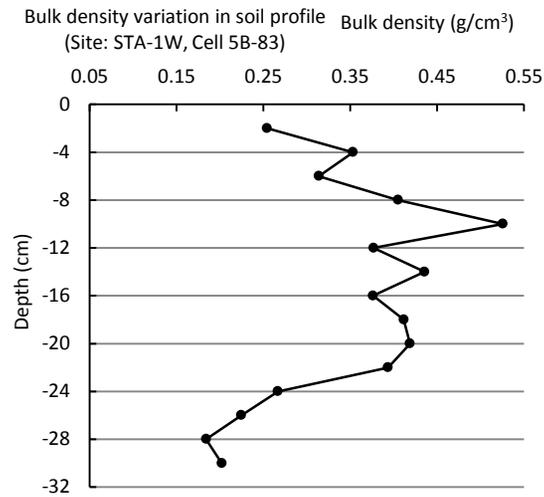
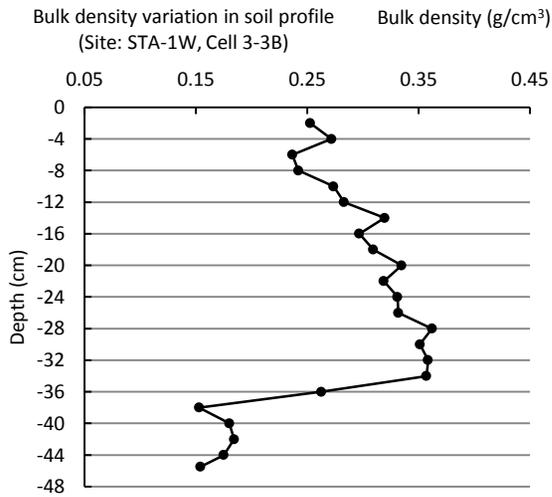
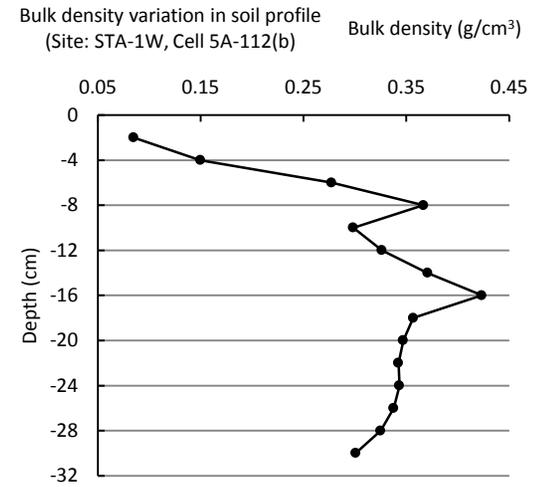
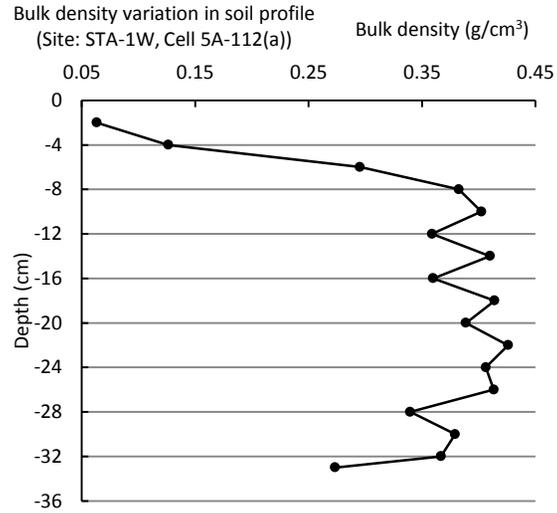
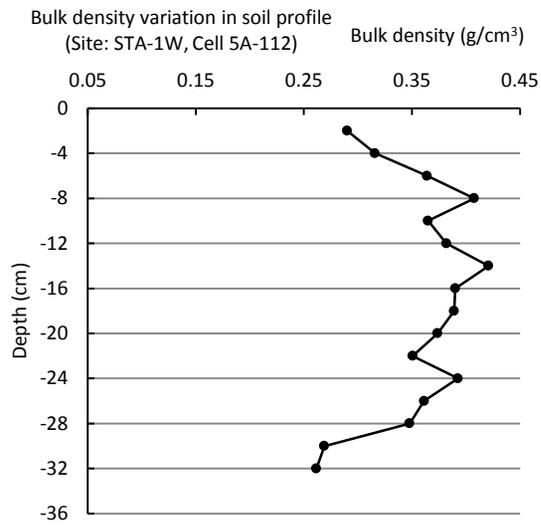


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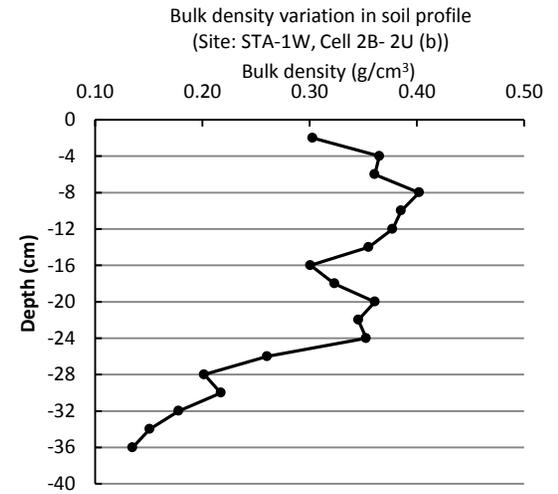
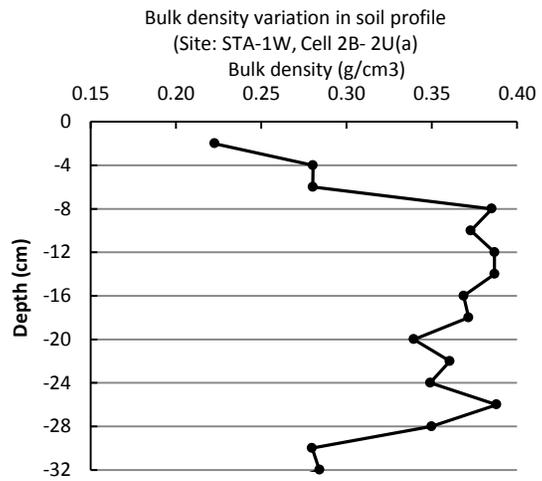
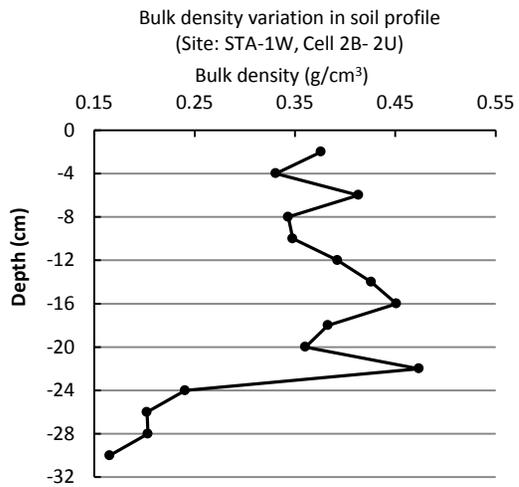
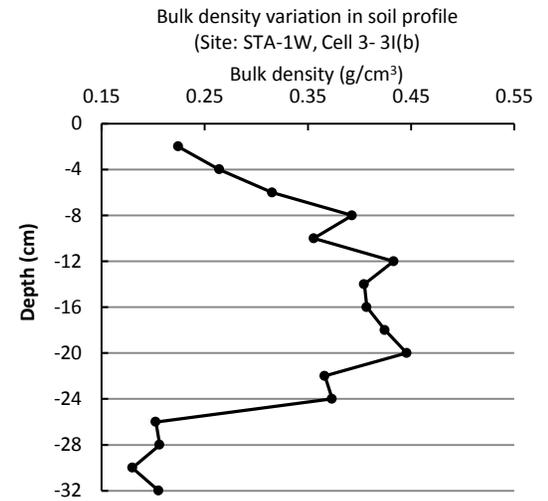
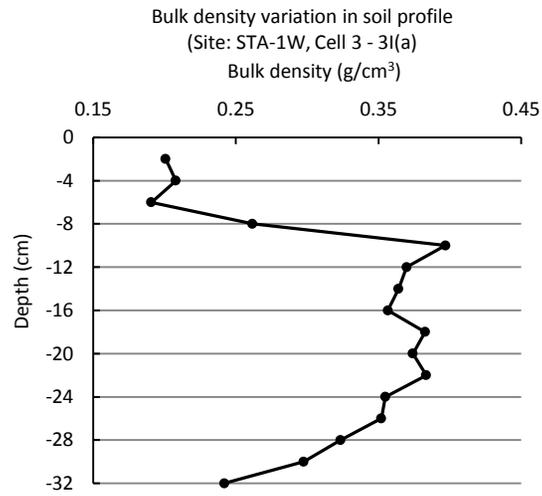
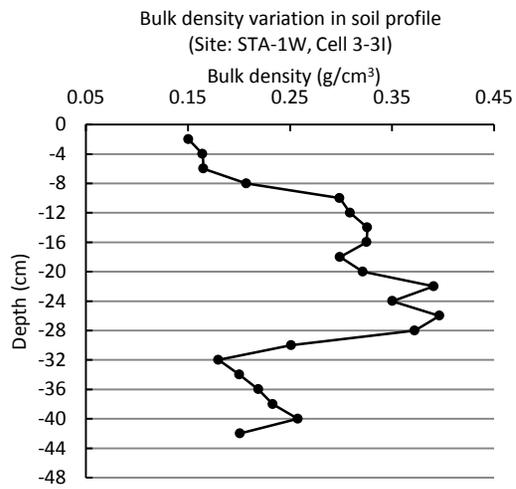


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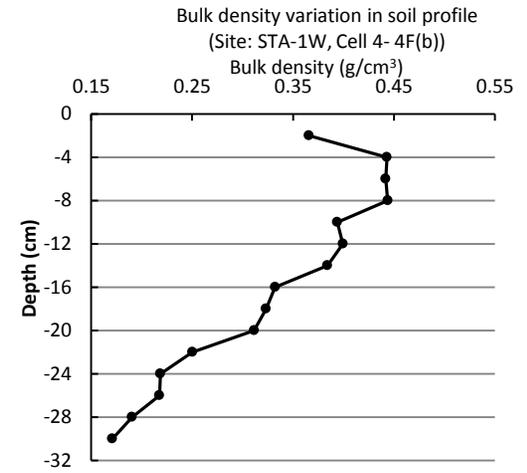
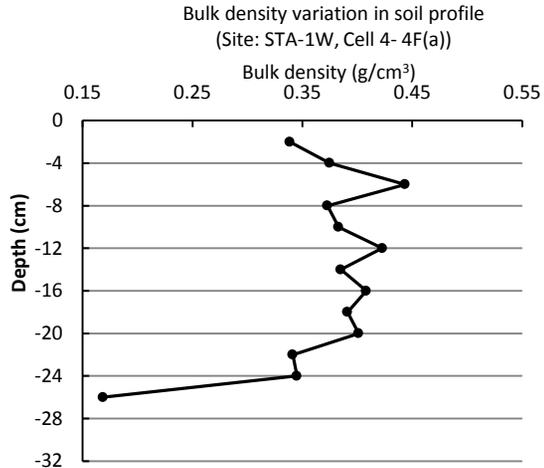
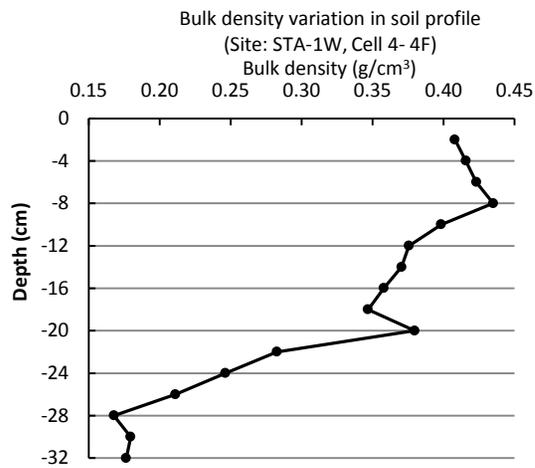
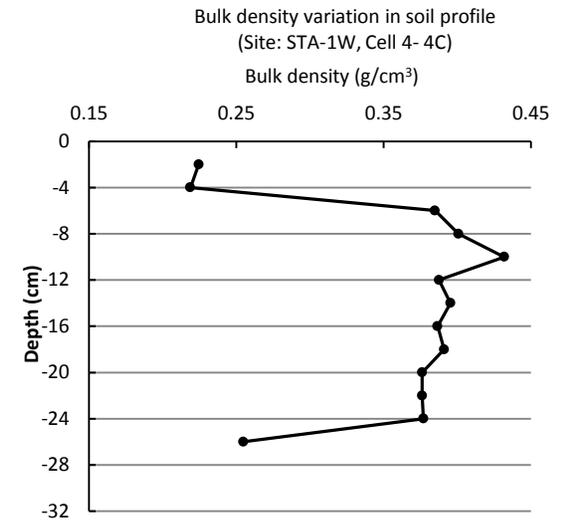
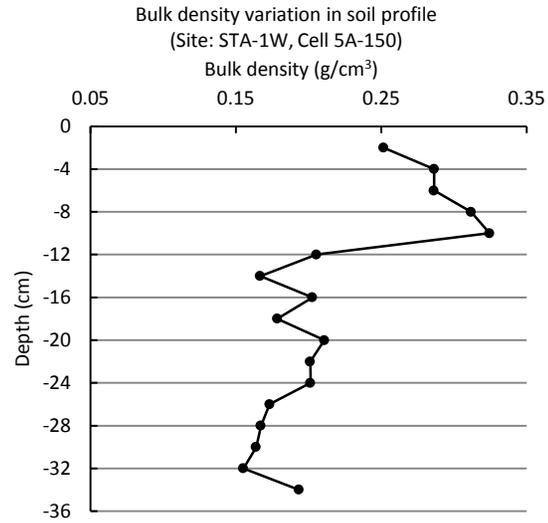
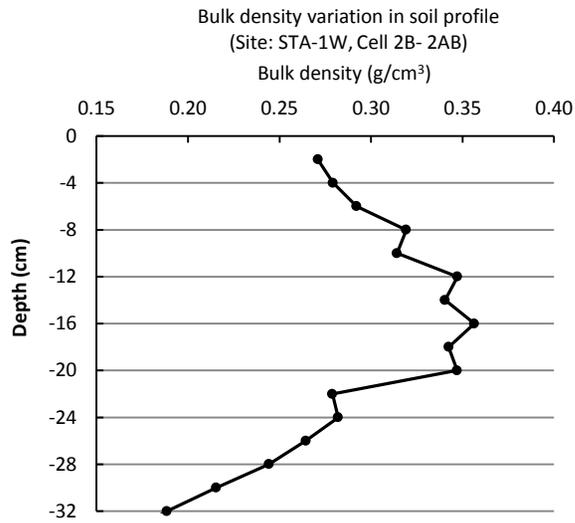


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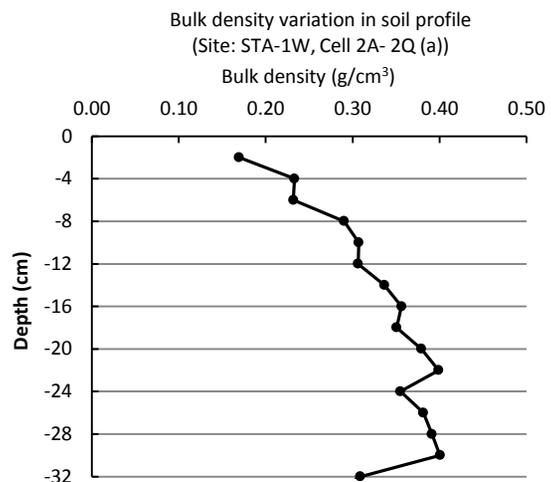
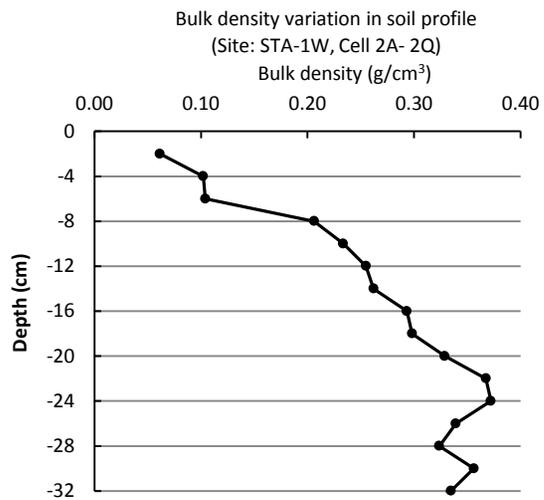
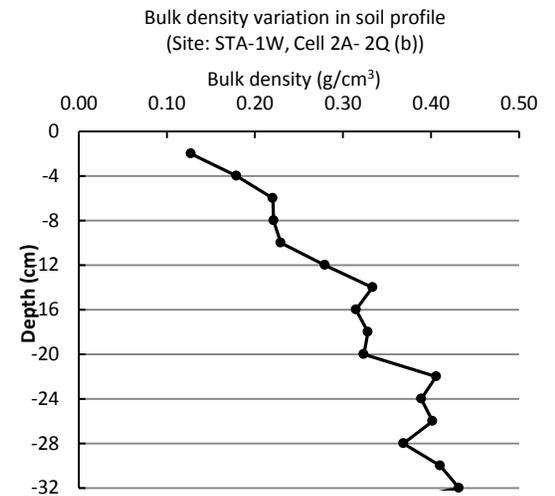
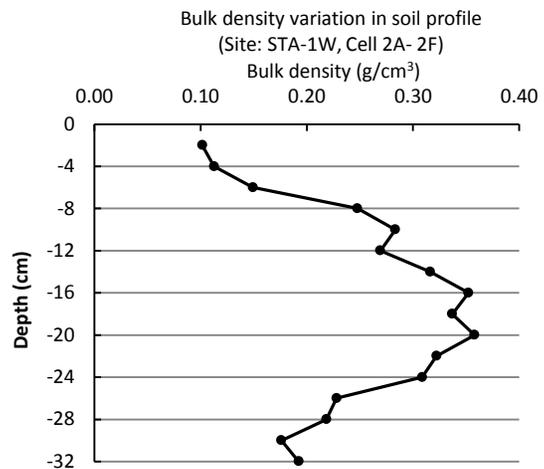
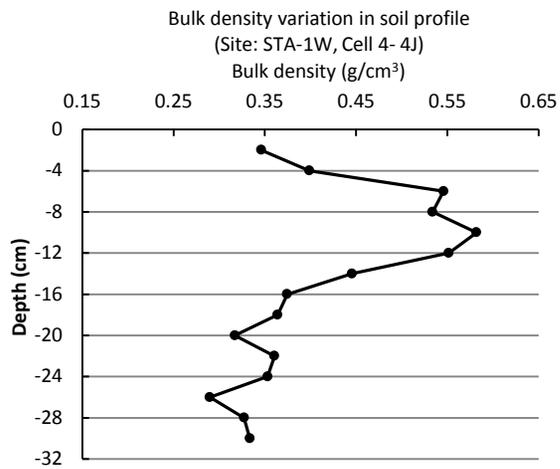


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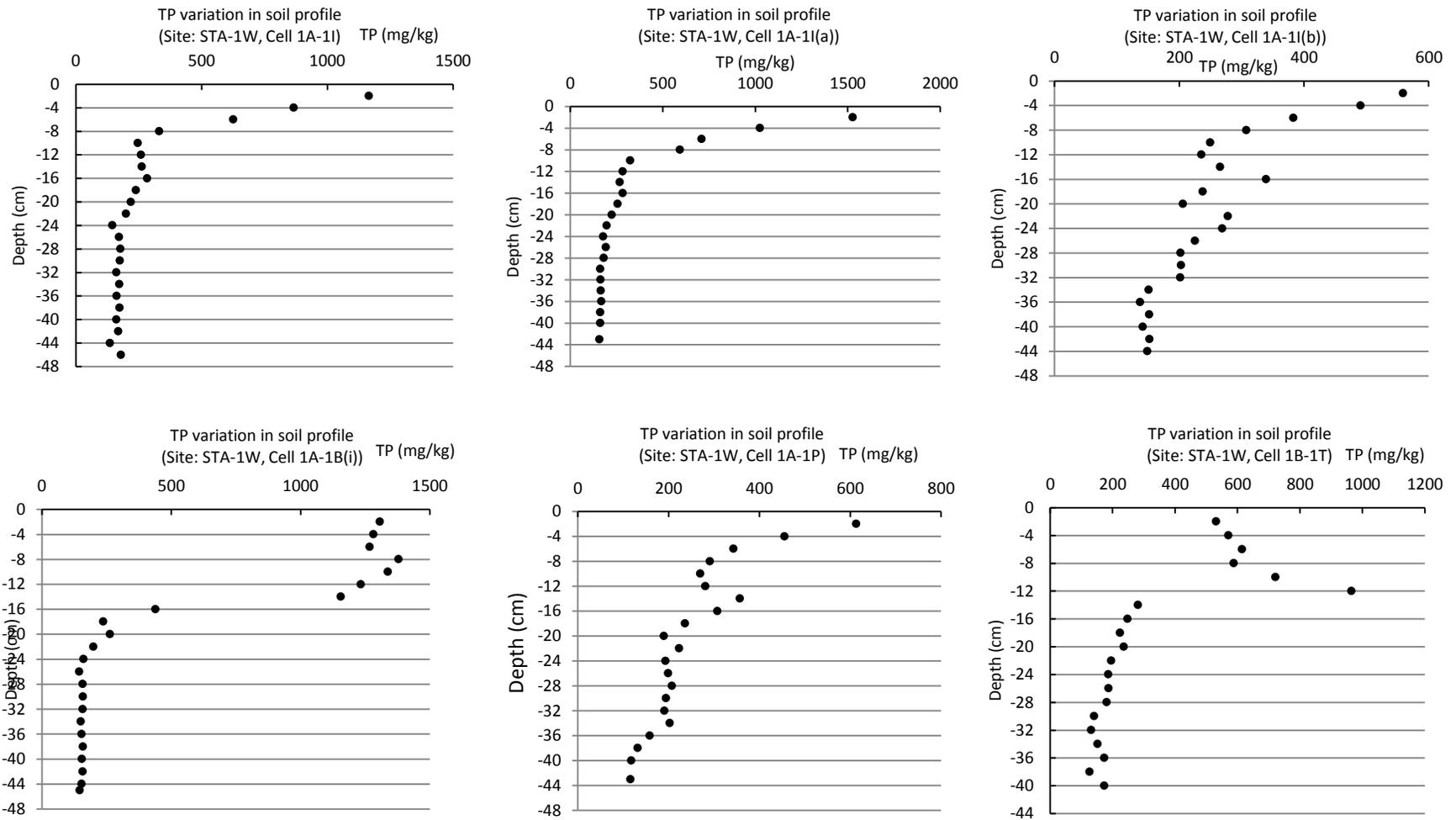


Figure D-5. Total phosphorus profile in each soil core collected from STA-1W.

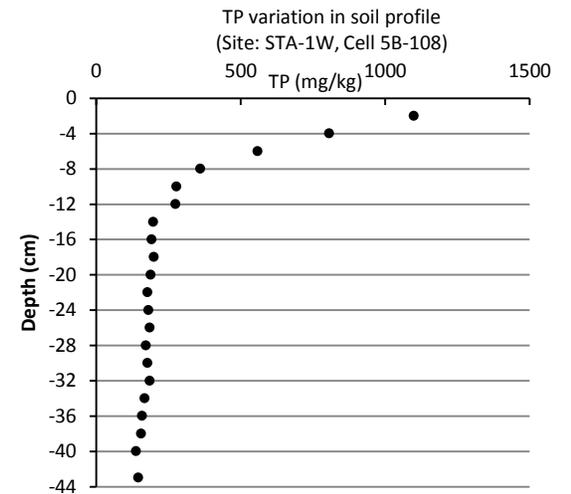
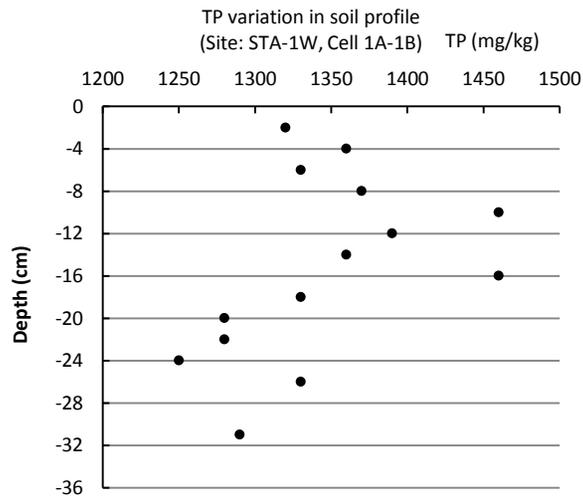
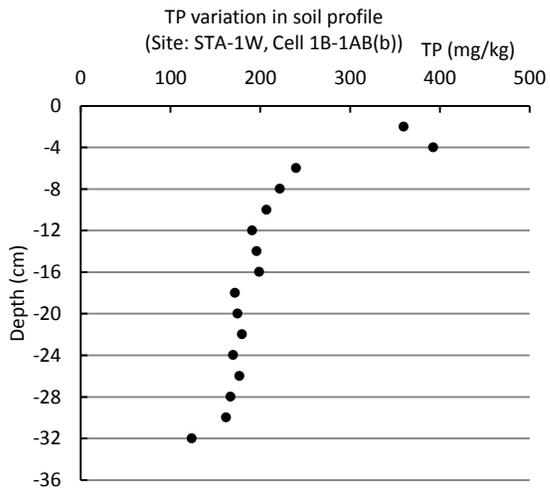
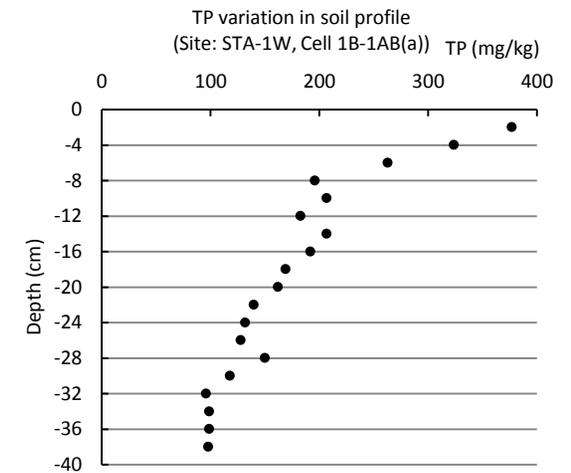
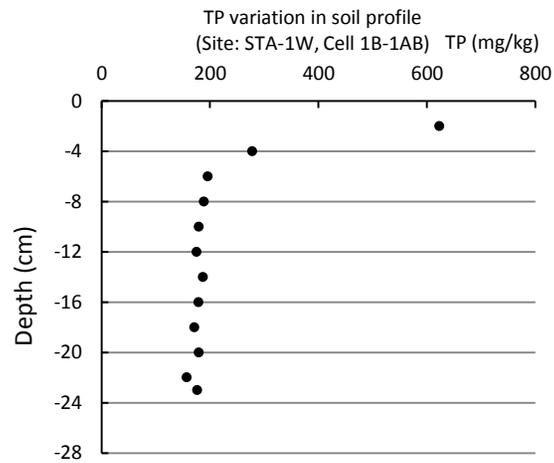
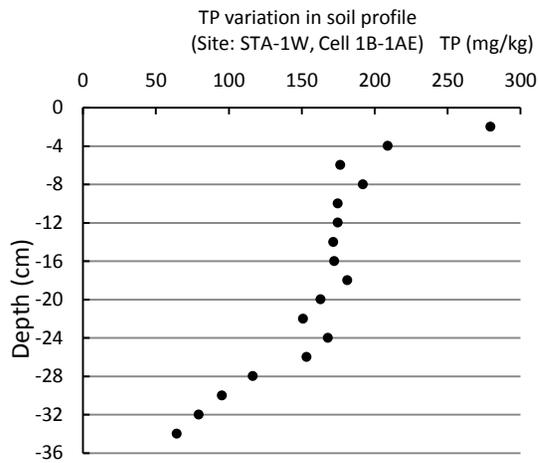


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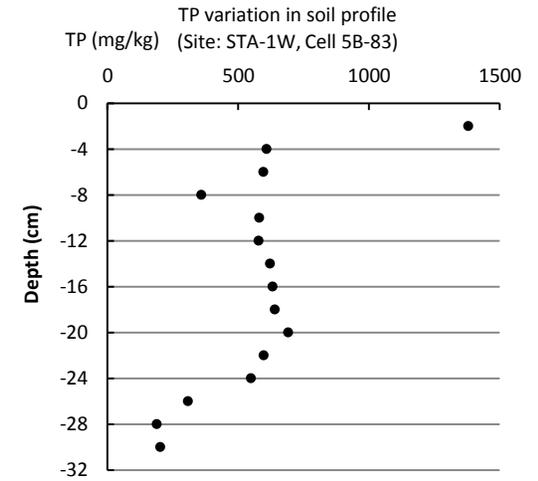
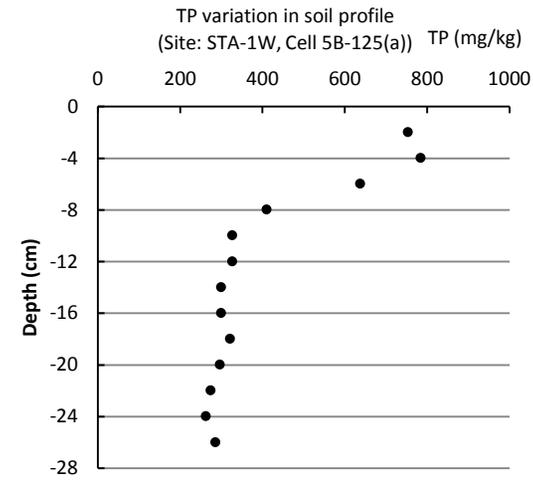
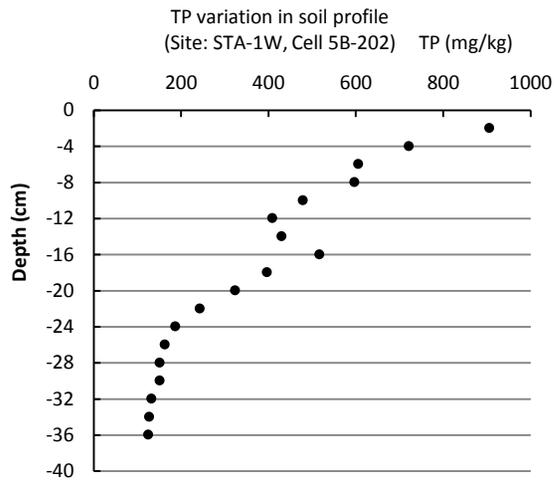
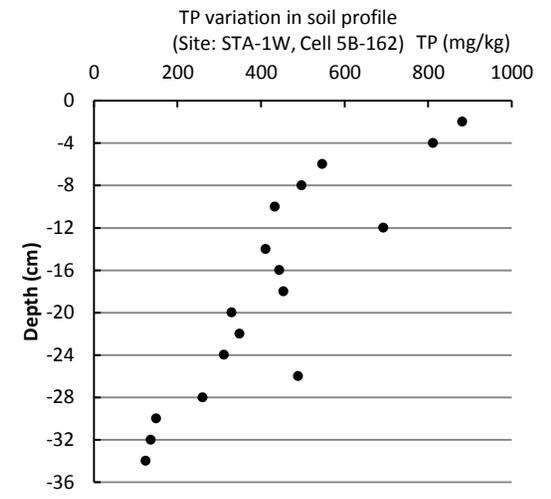
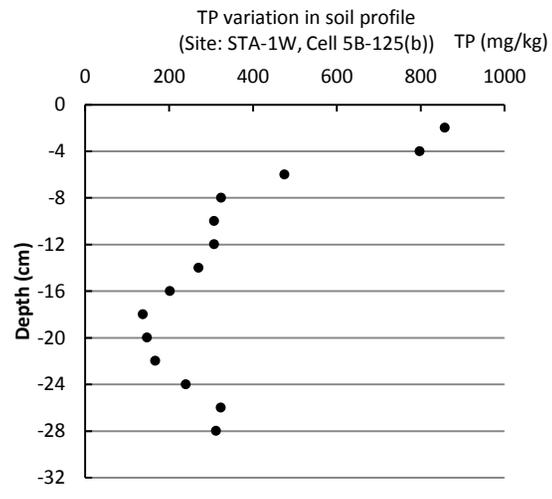
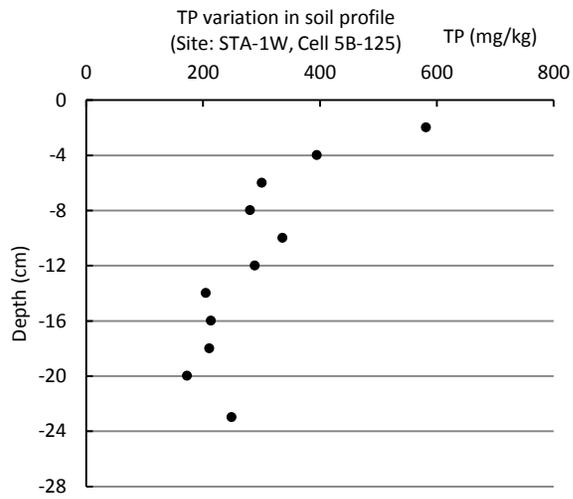


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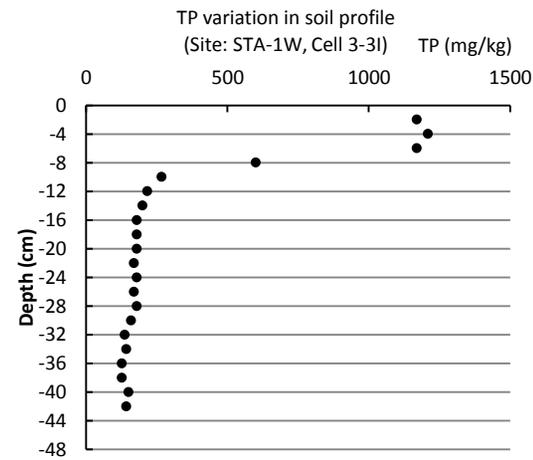
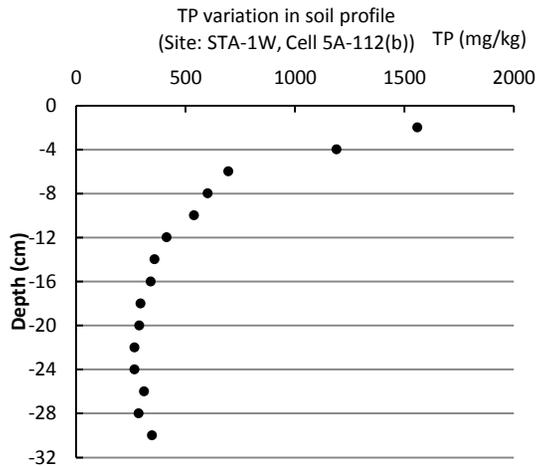
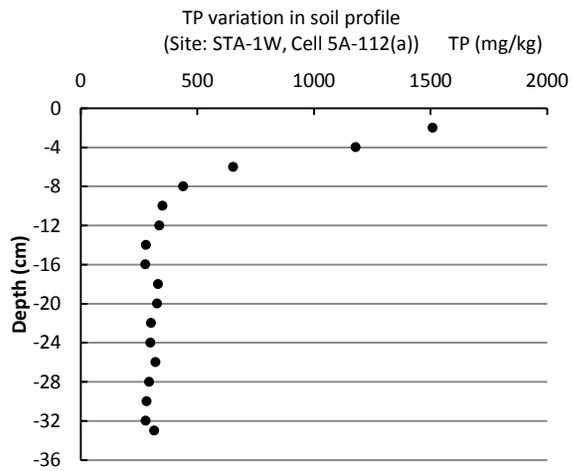
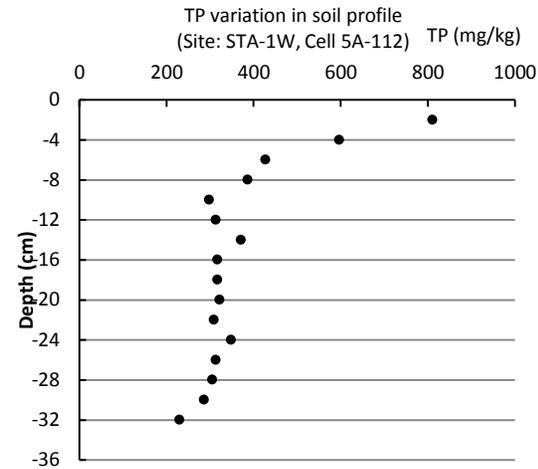
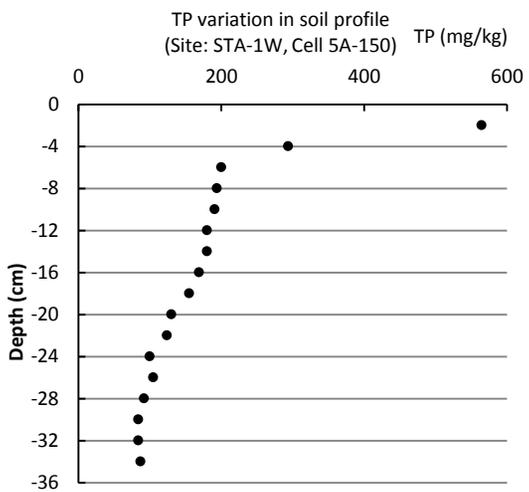
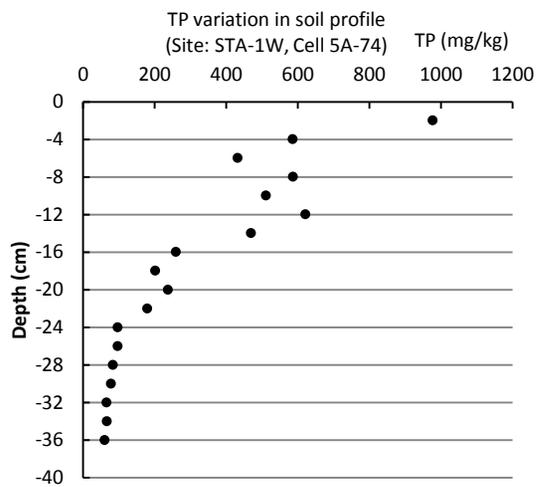


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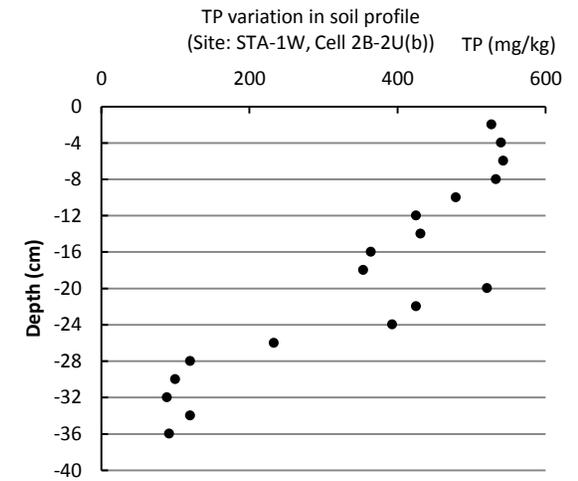
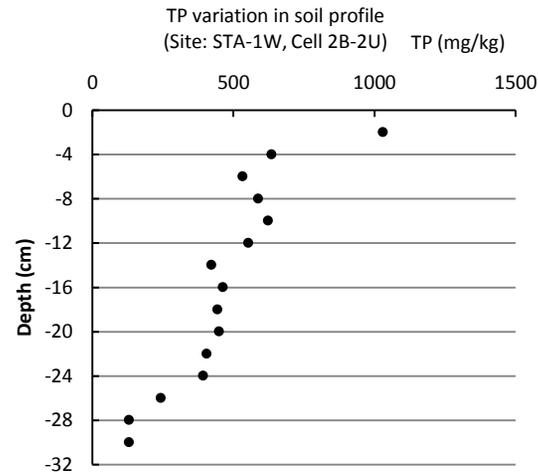
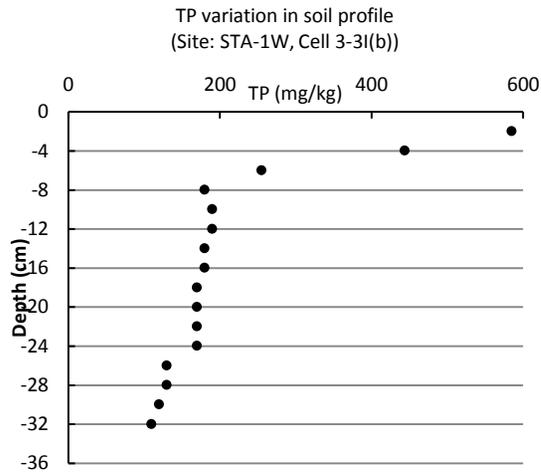
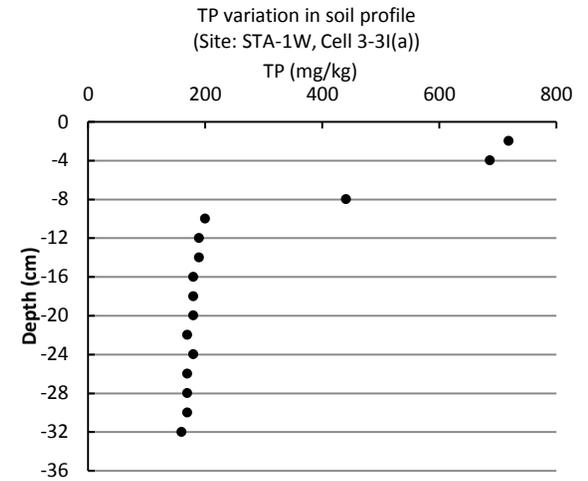
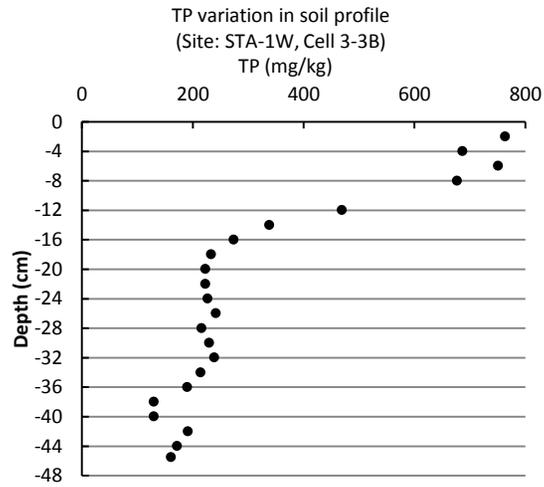
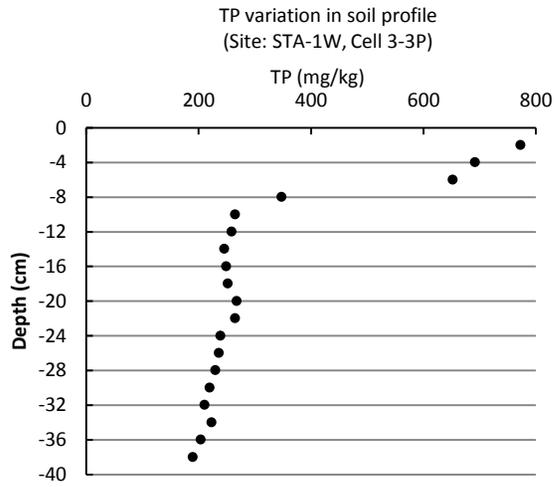


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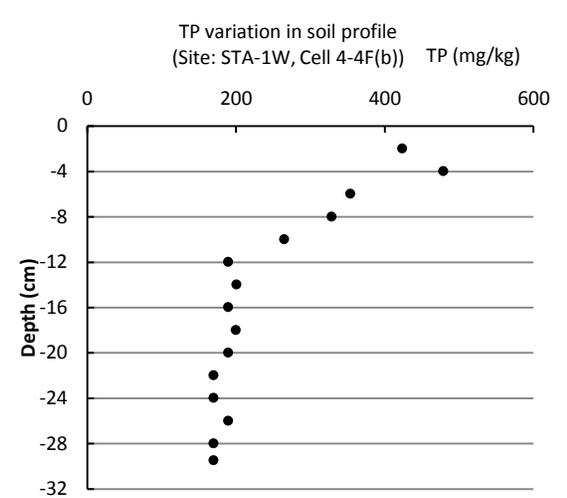
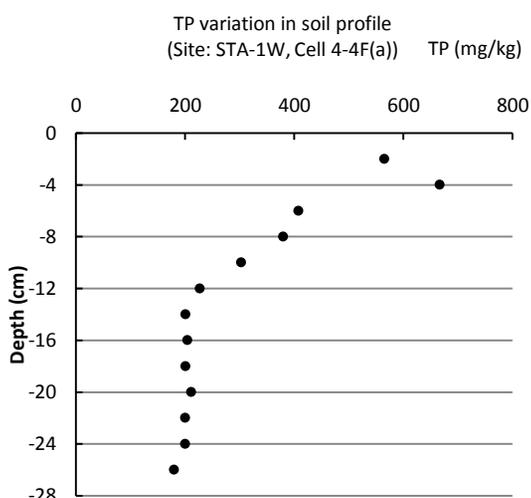
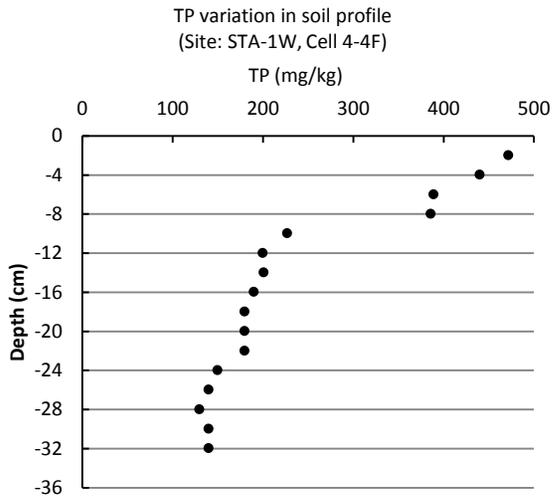
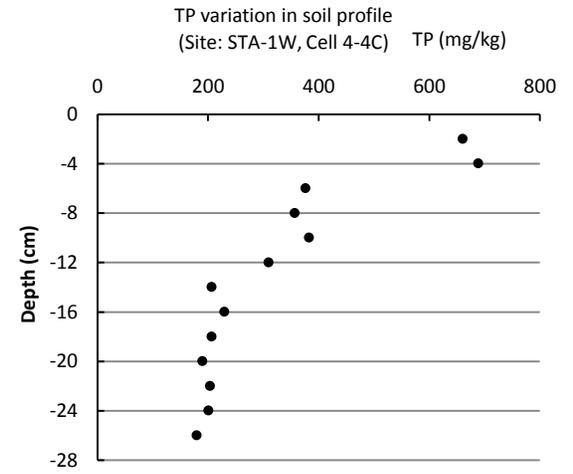
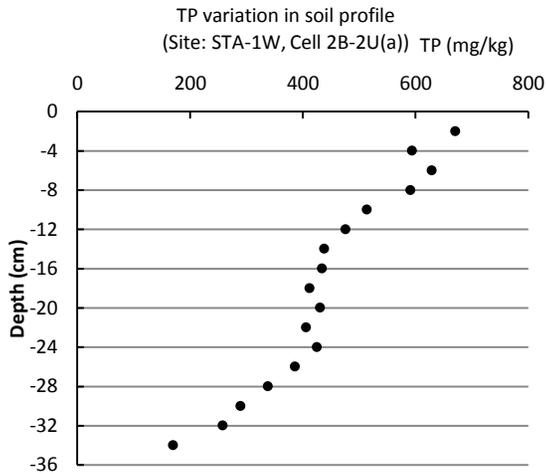
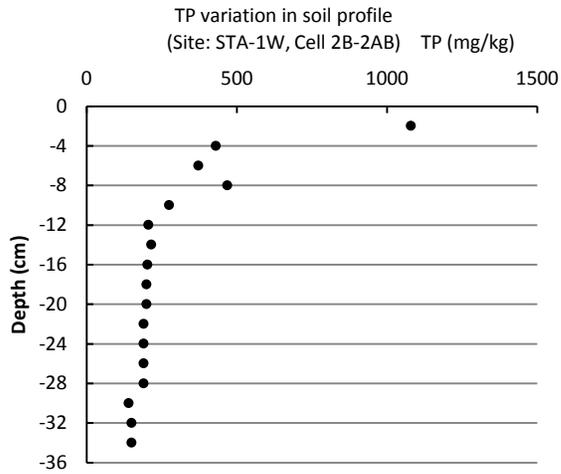


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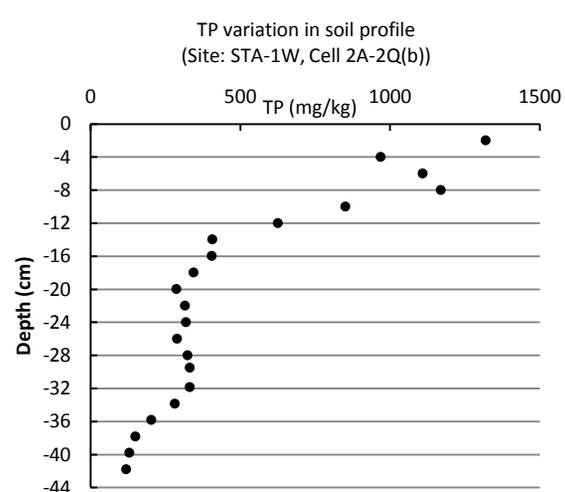
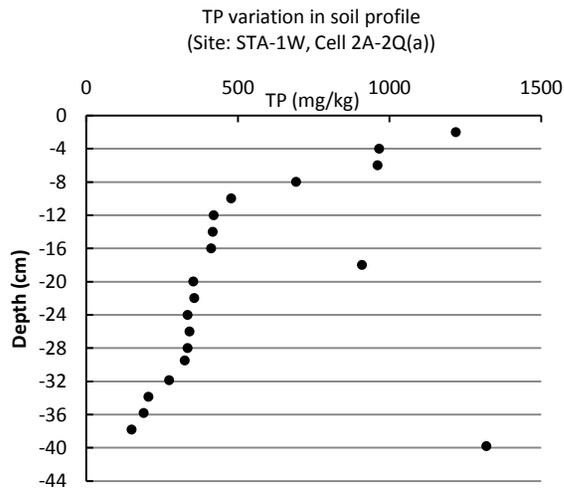
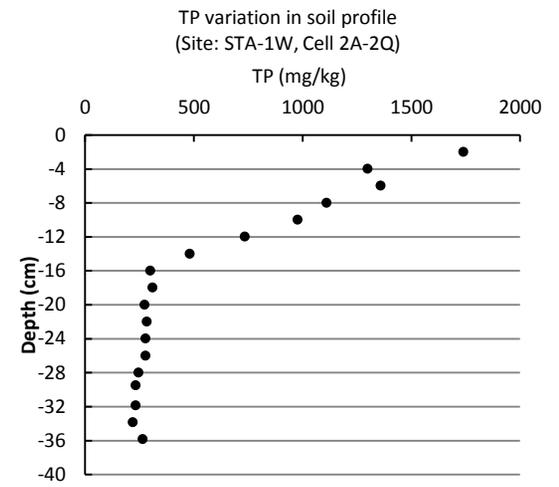
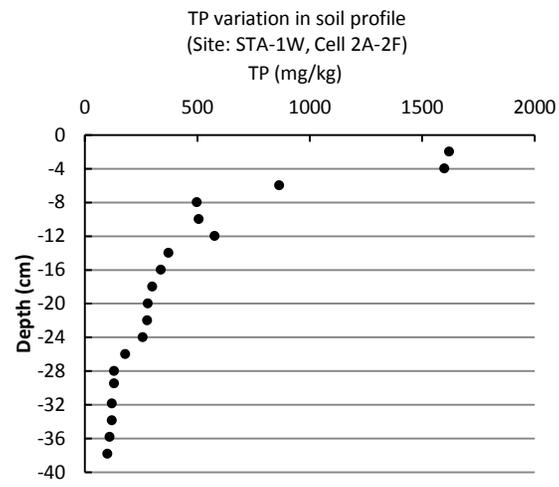
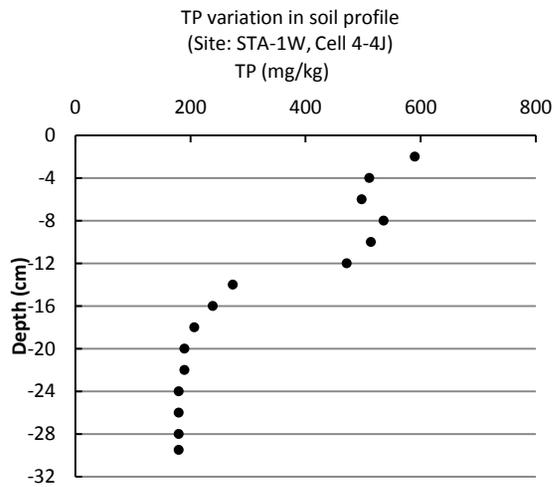


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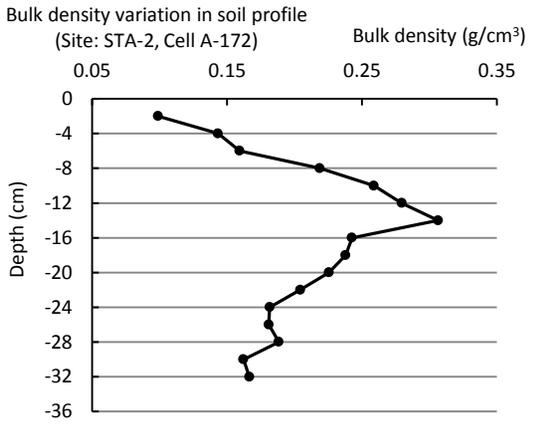
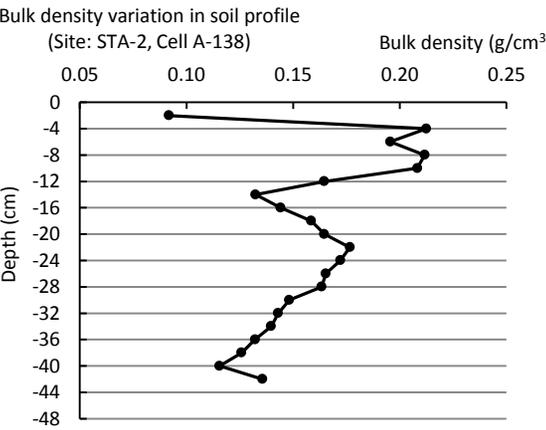
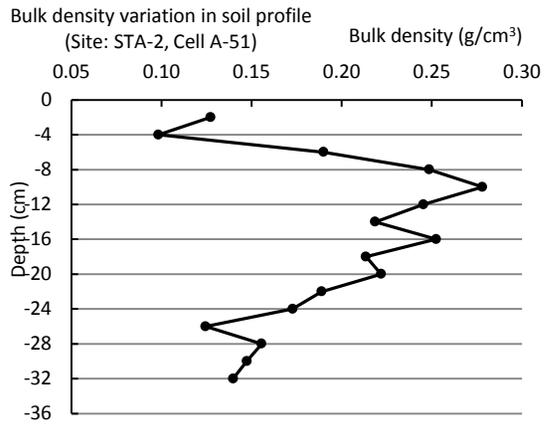
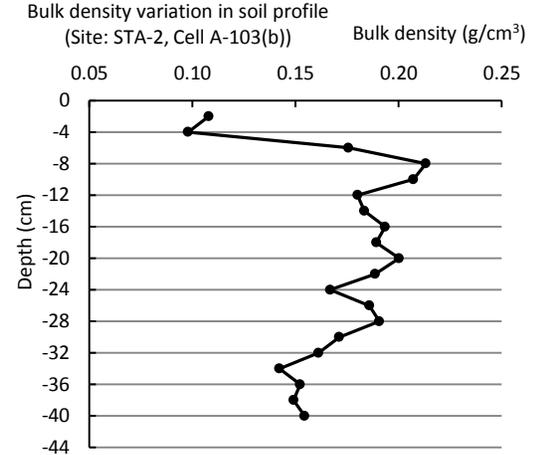
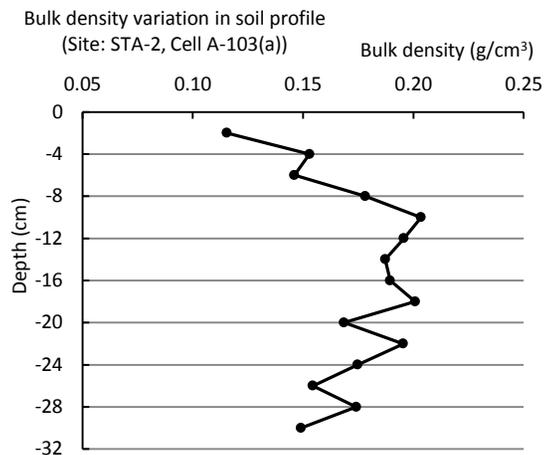
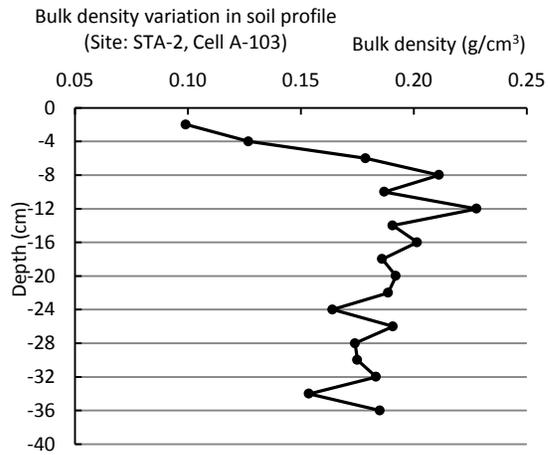


Figure D-6. Bulk density profile in each soil core collected from STA-2.

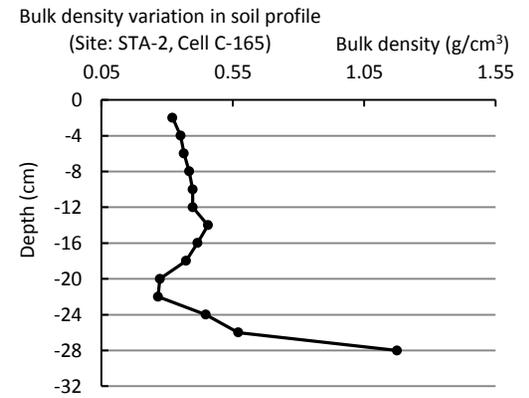
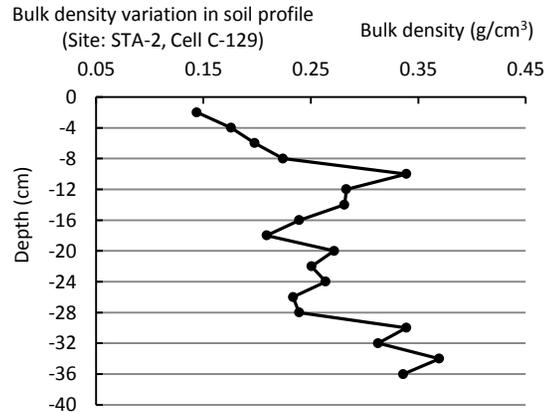
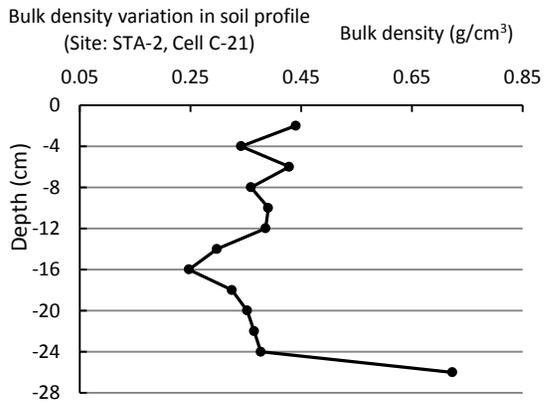
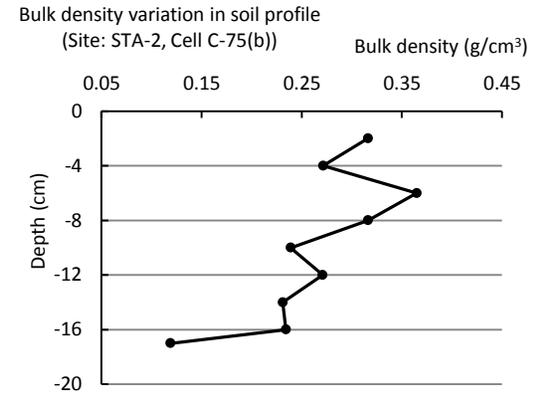
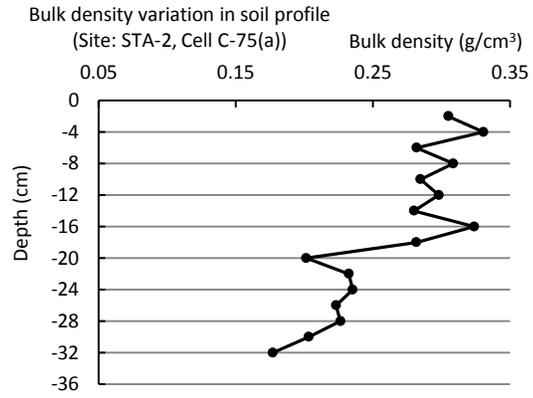
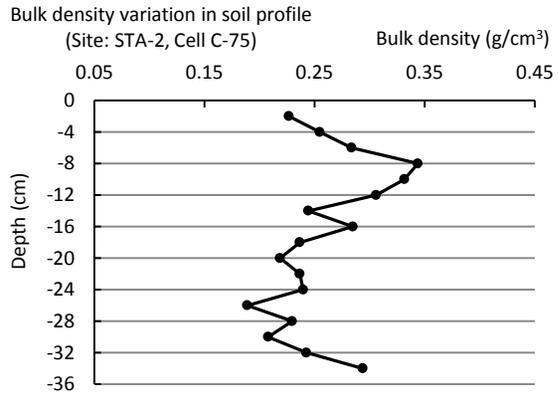


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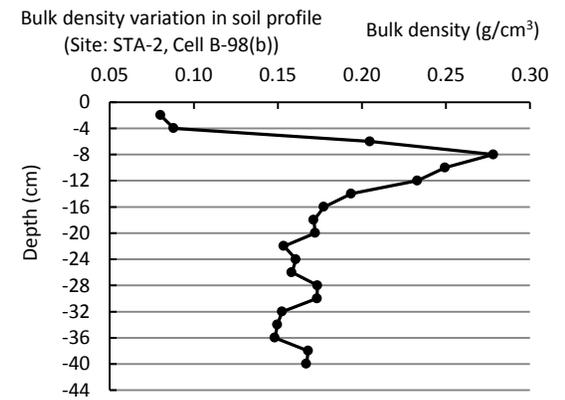
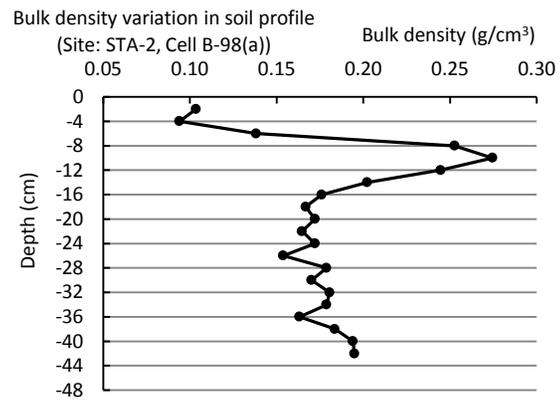
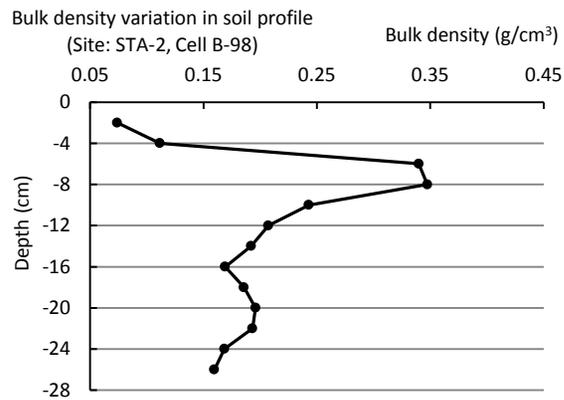
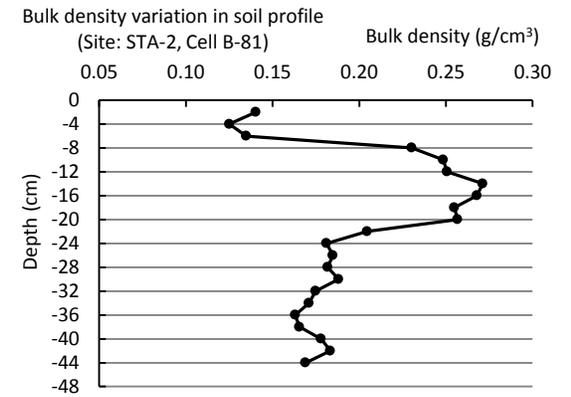
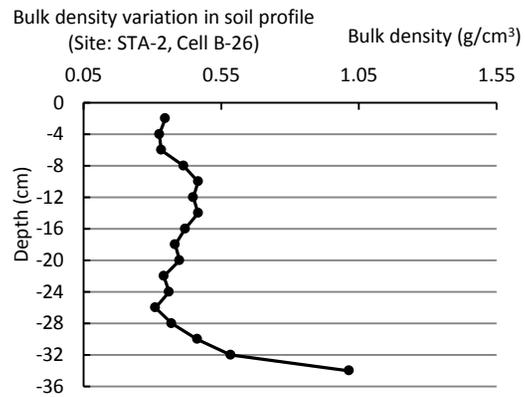
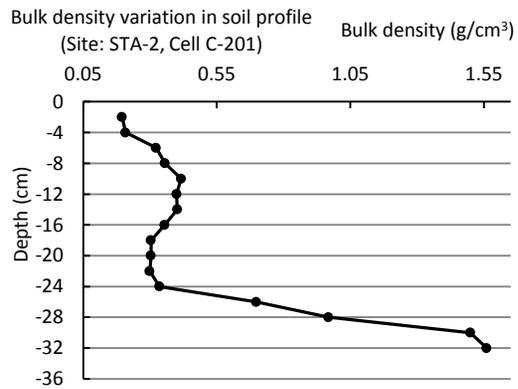


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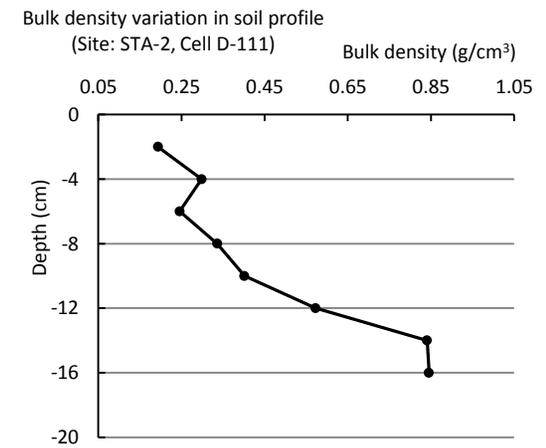
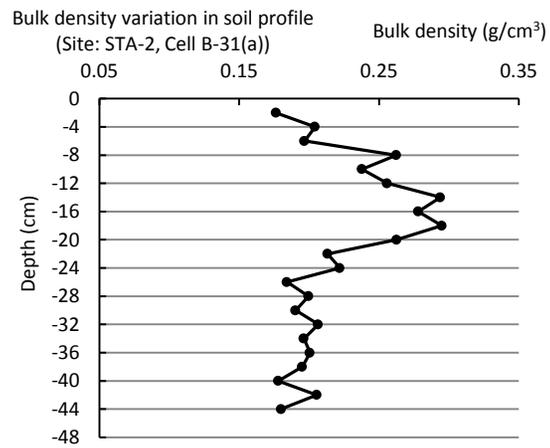
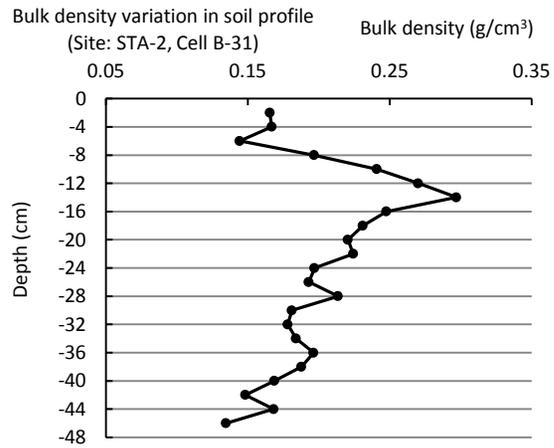
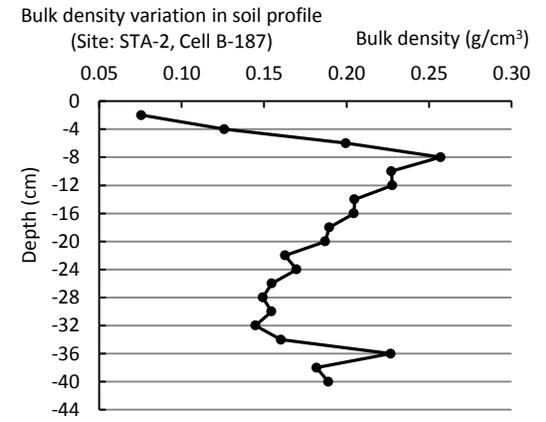
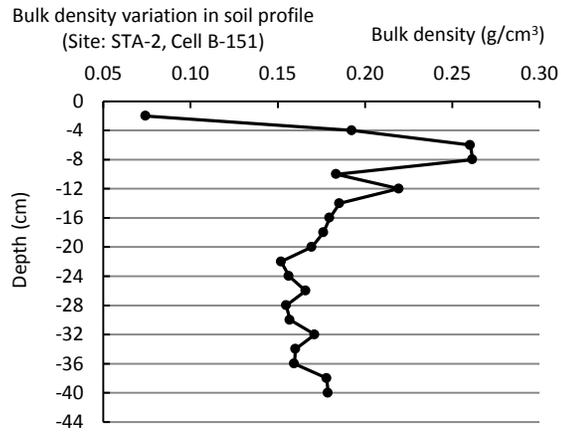
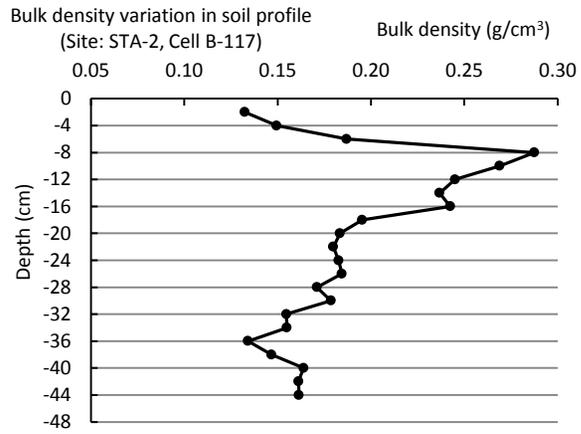


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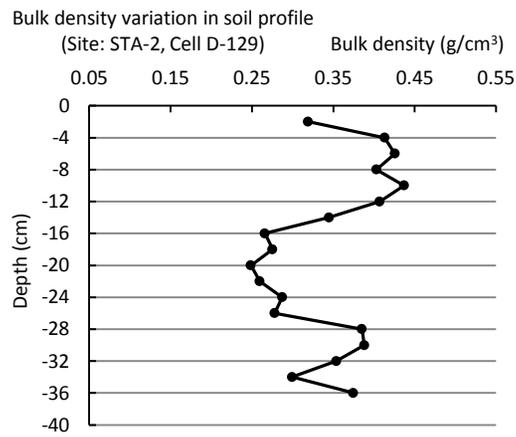
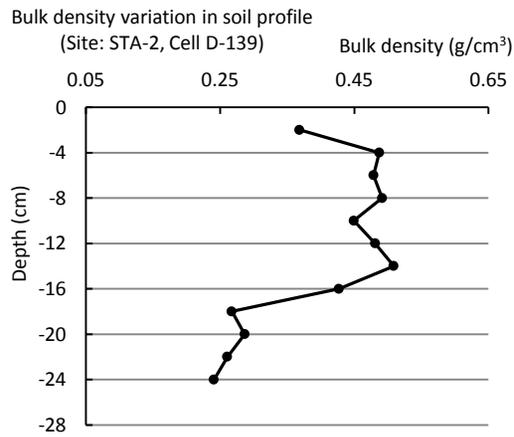
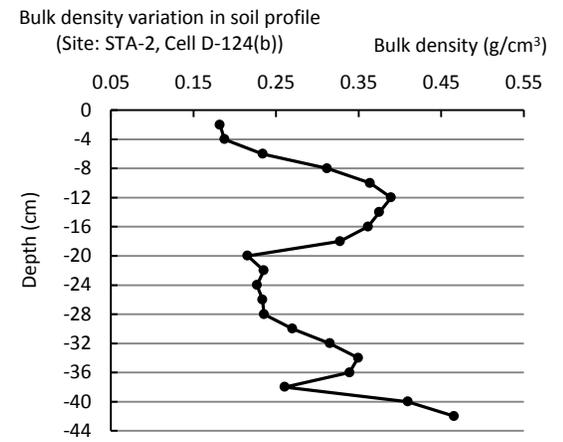
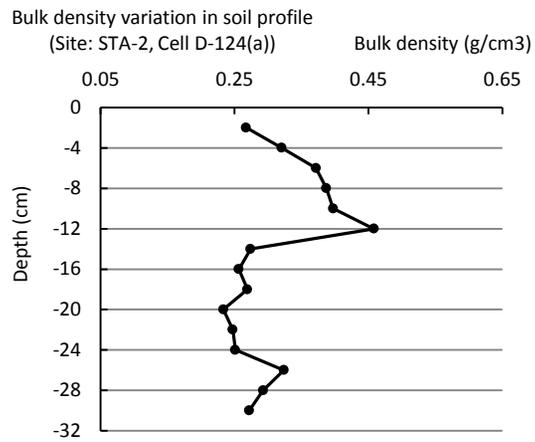
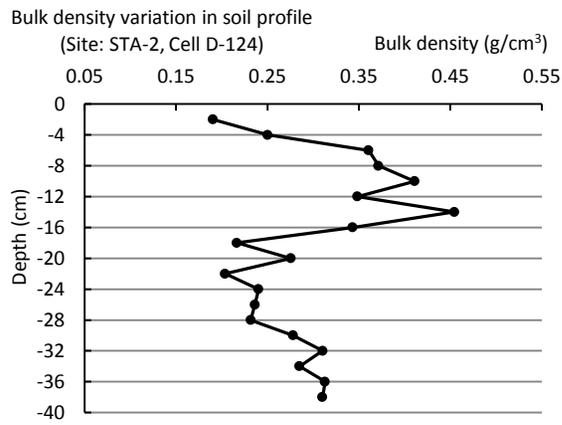


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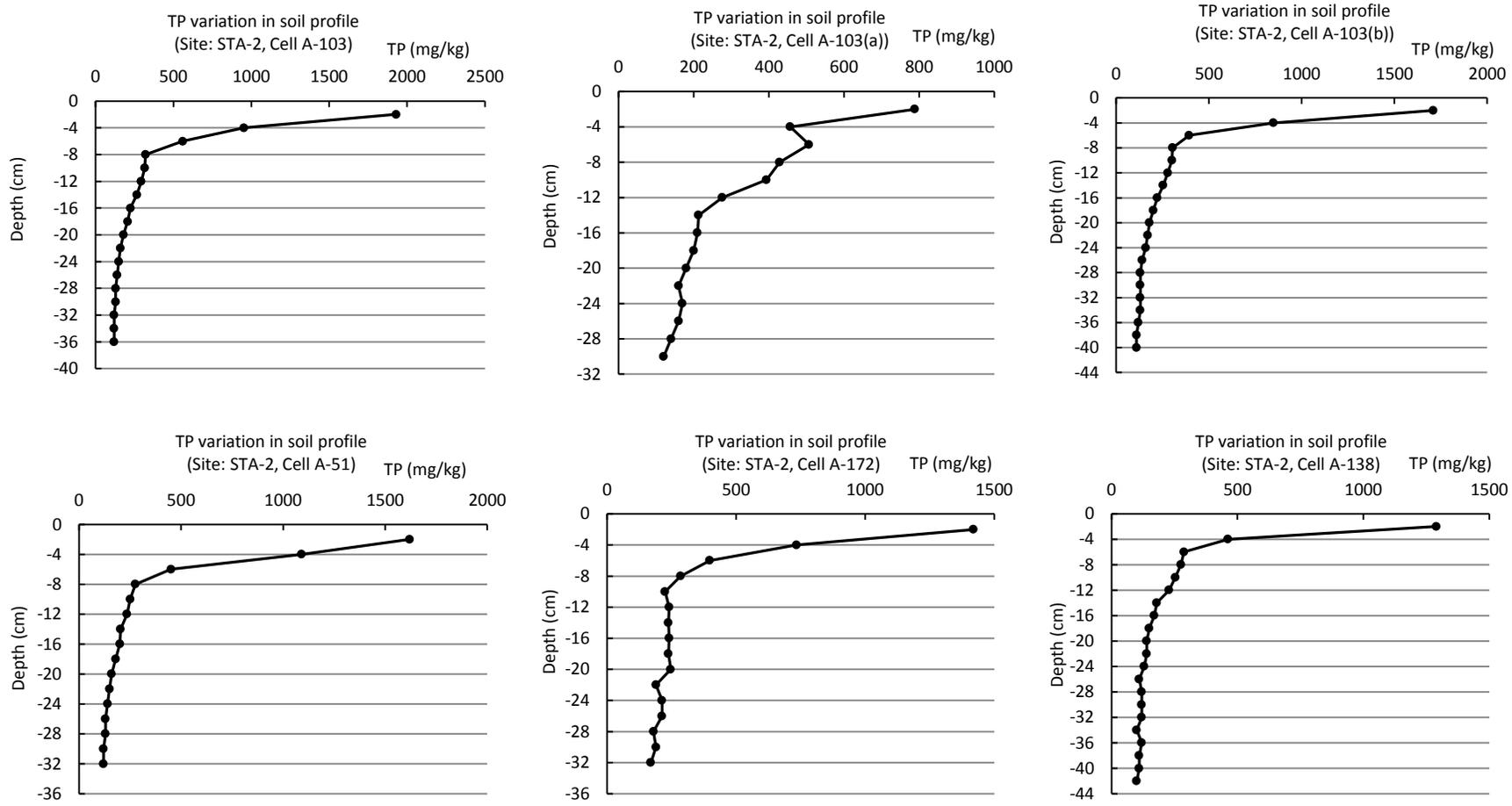


Figure D-7. Total phosphorus profile in each soil core collected from STA-2.

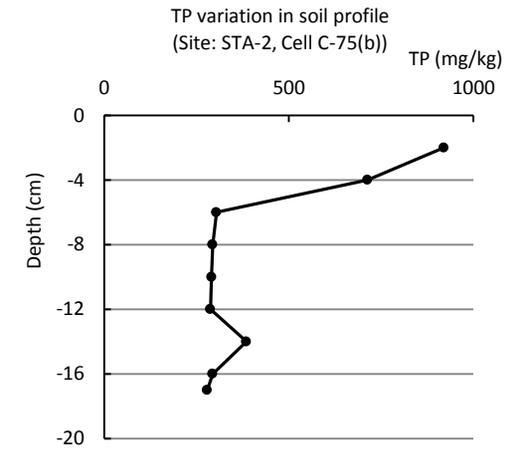
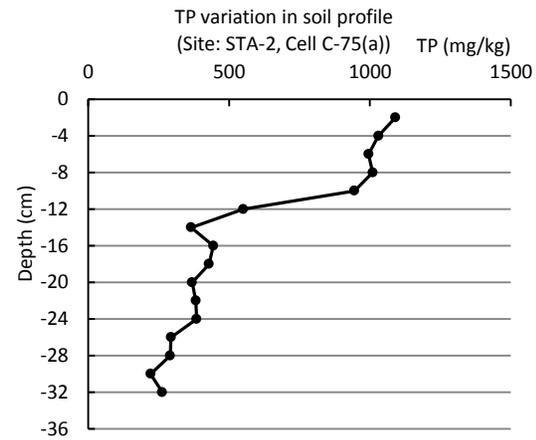
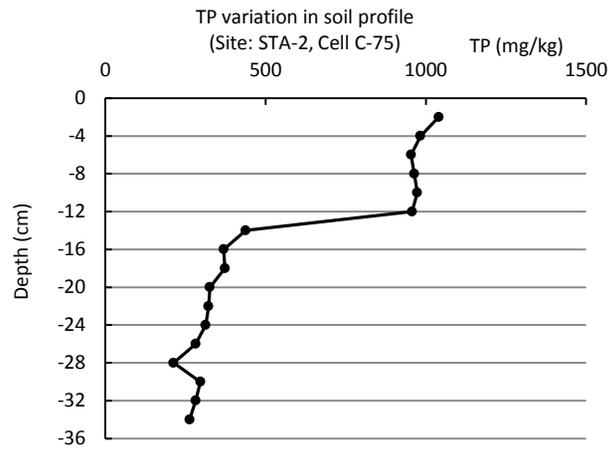
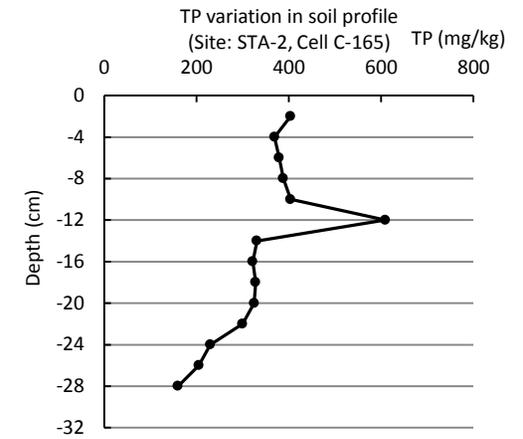
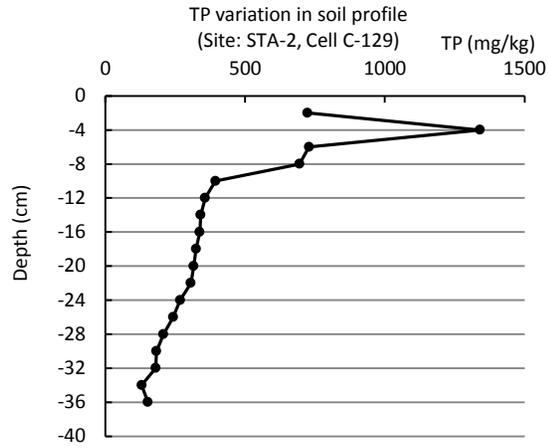
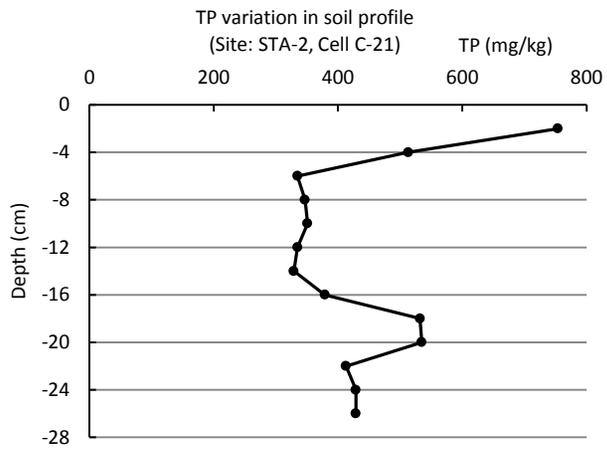


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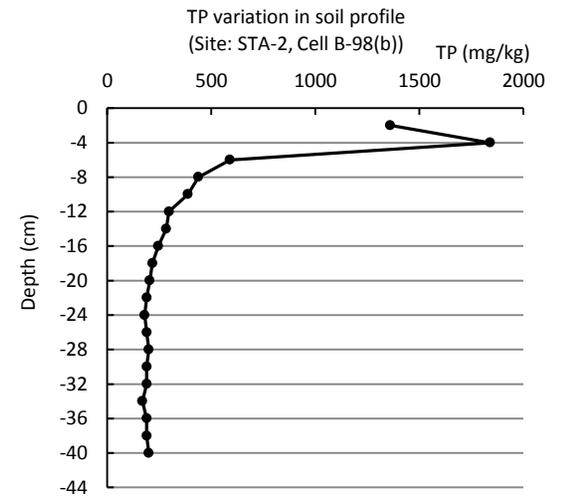
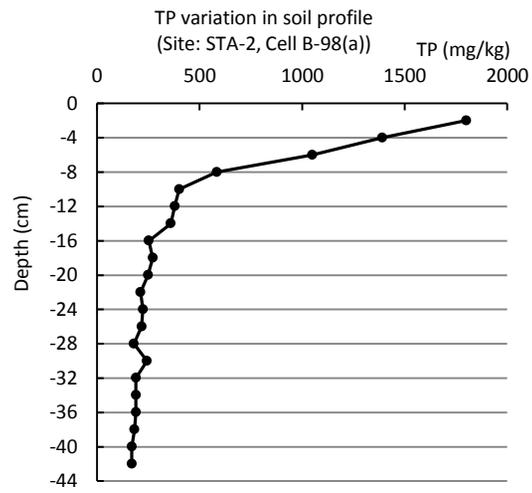
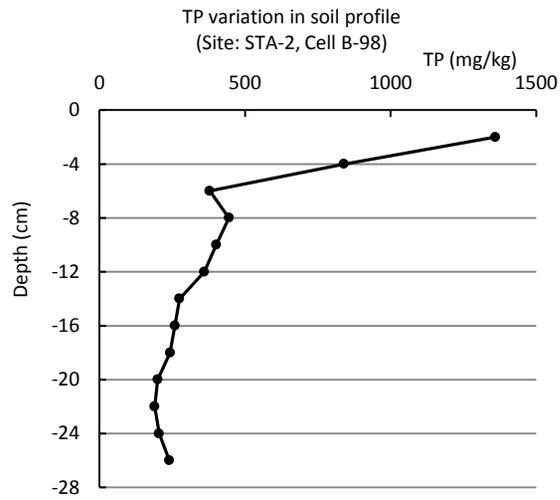
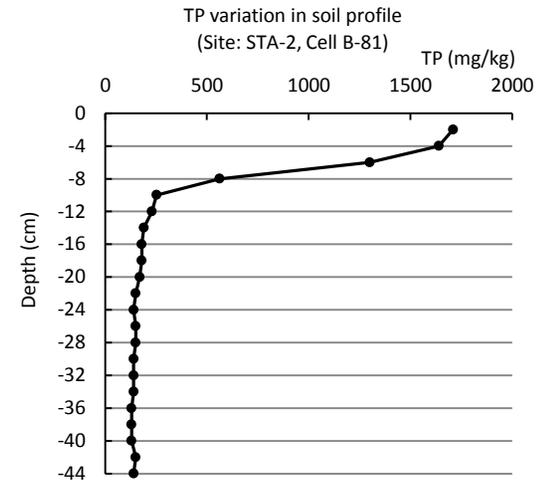
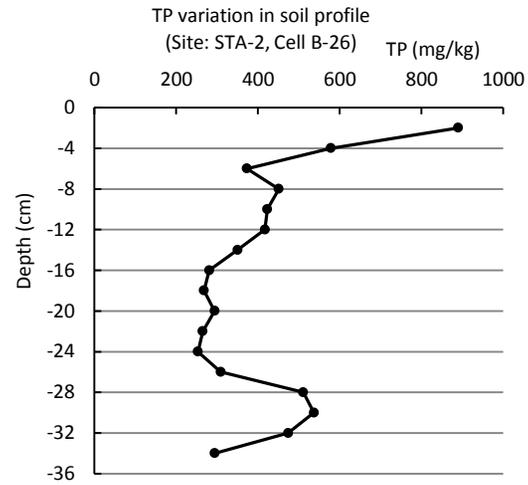
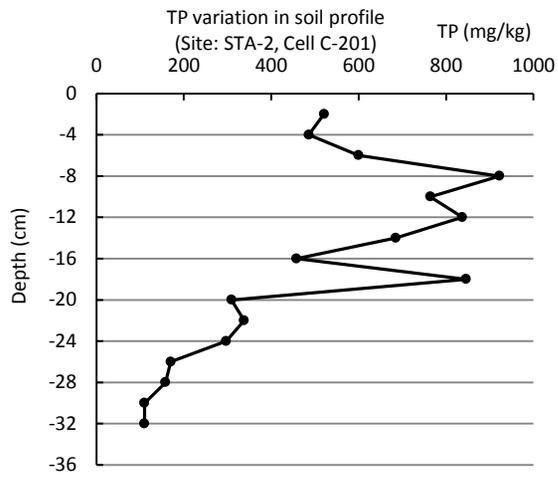


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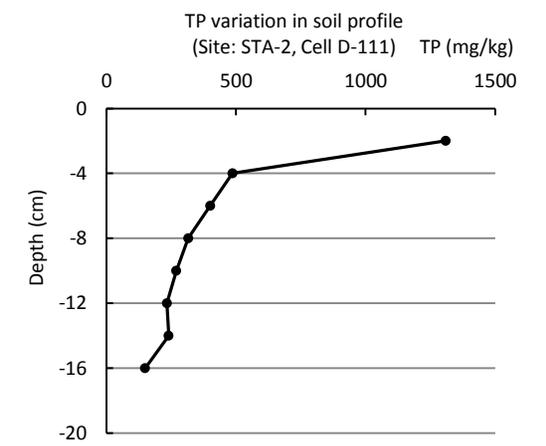
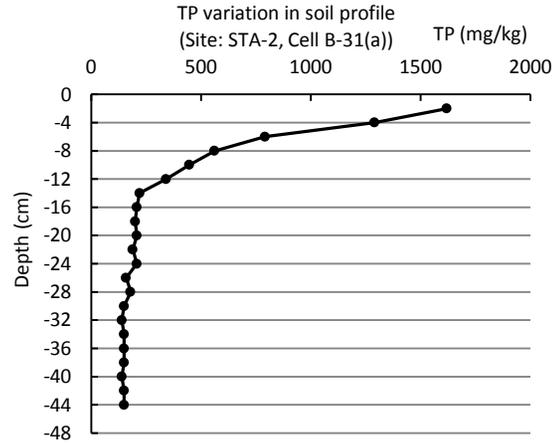
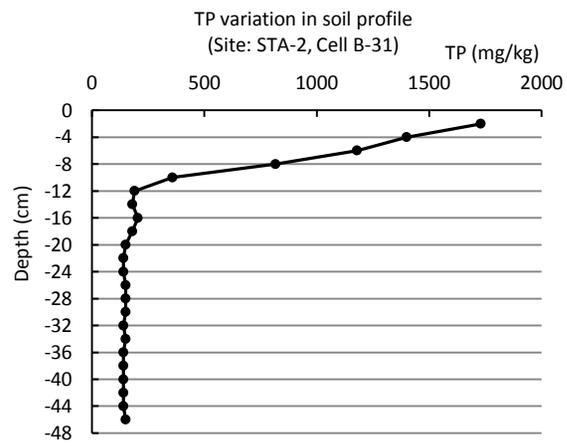
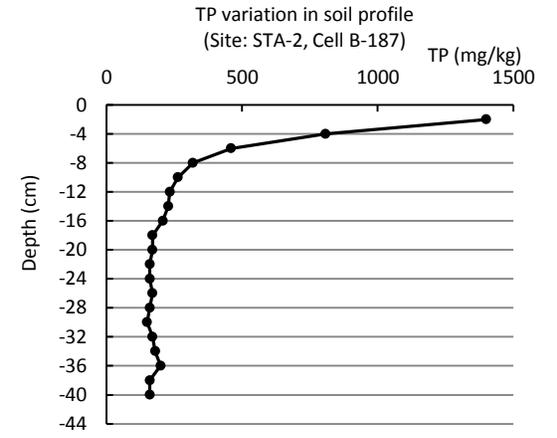
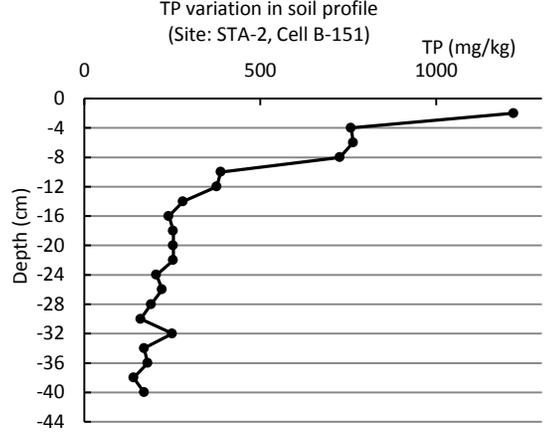
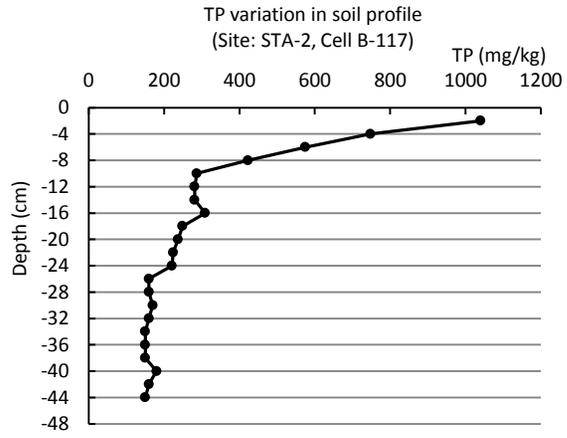


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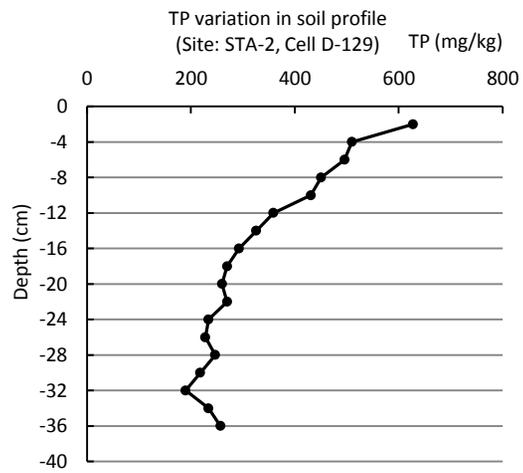
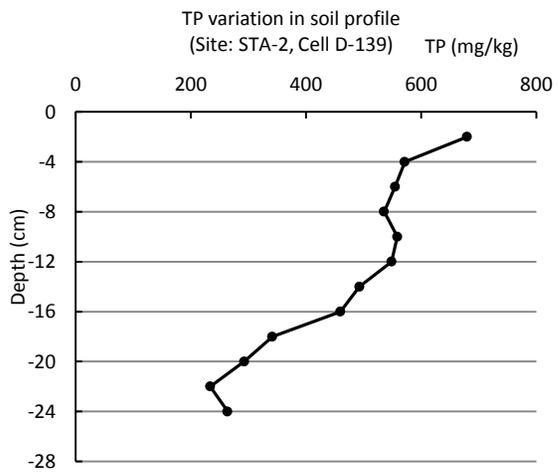
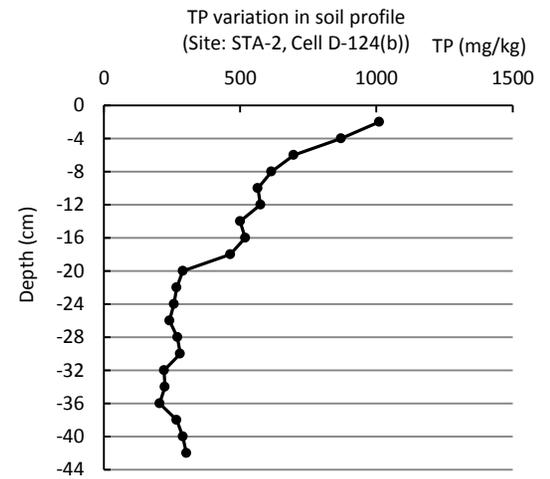
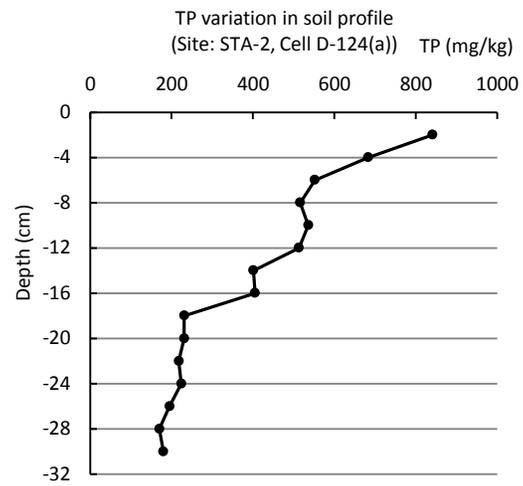
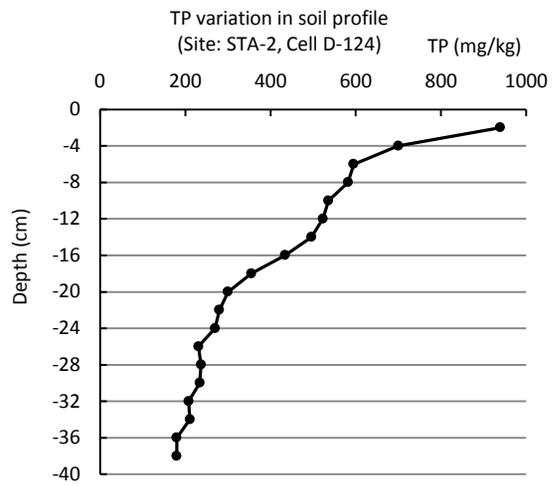
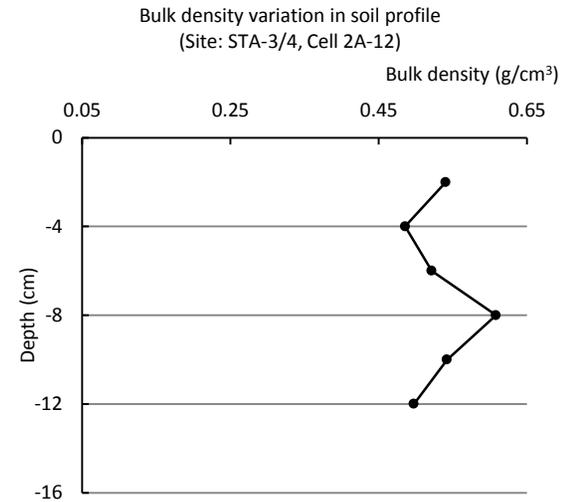
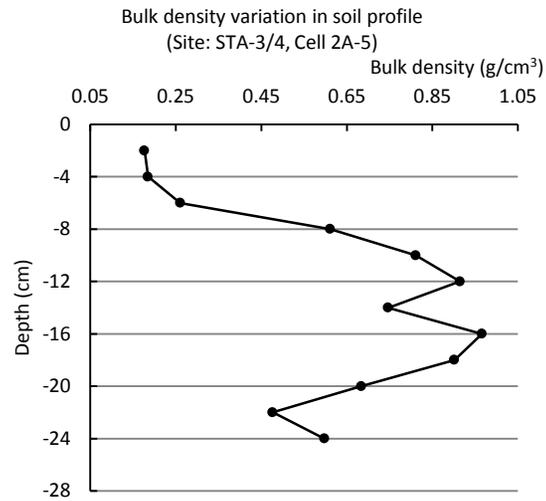
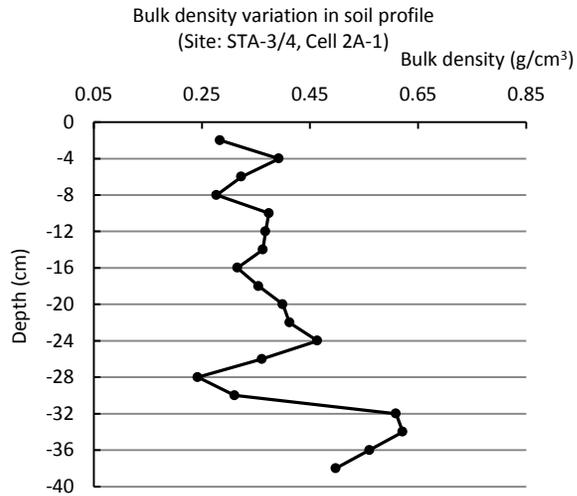
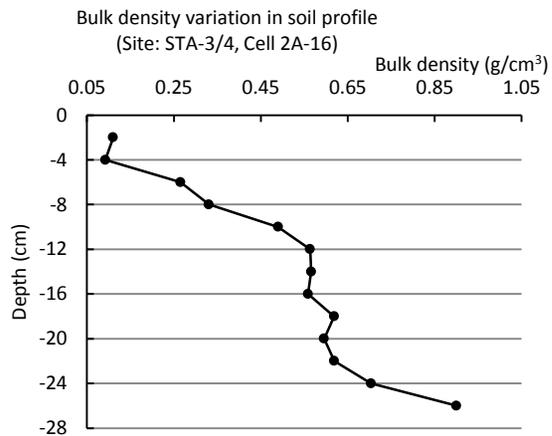


Figure D-7. Continued

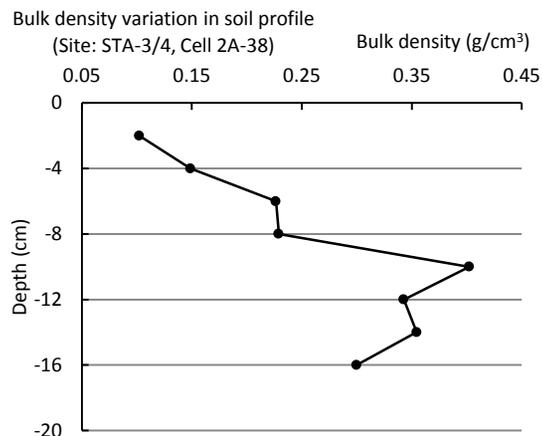


EAV cell



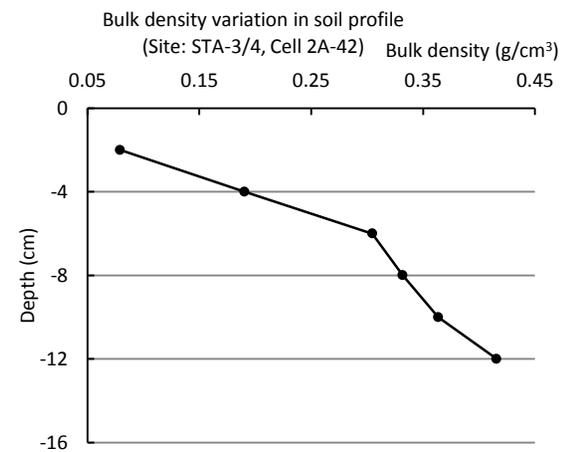
EAV cell

EAV cell



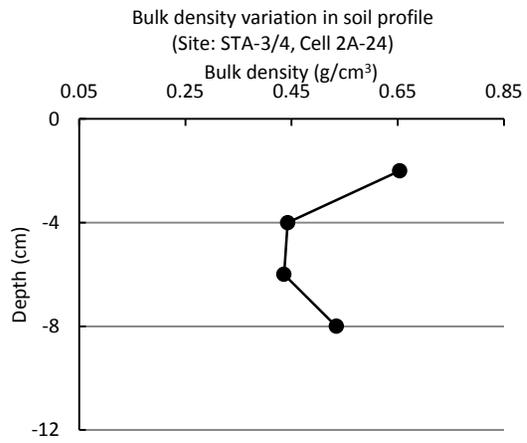
EAV cell

EAV cell

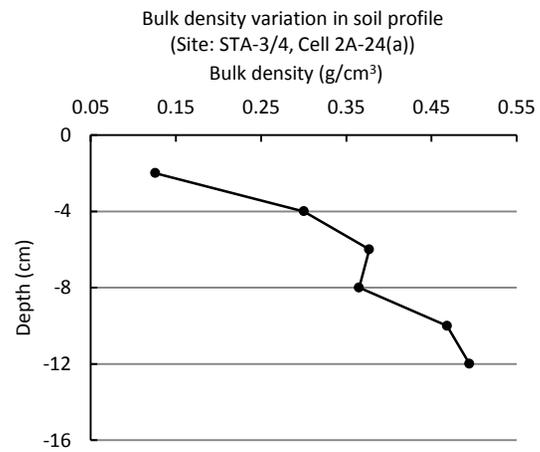


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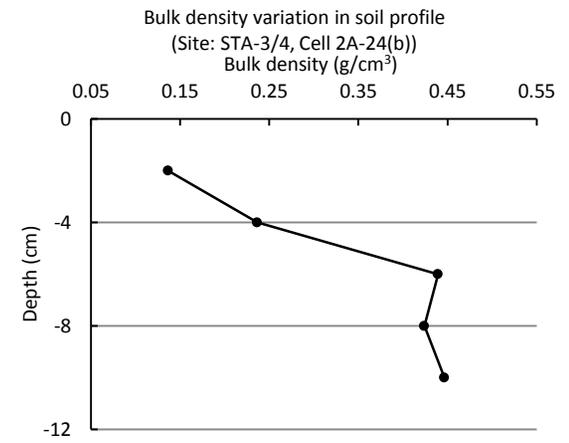
Figure D-8. Bulk density profile in each soil core collected from STA-3/4.



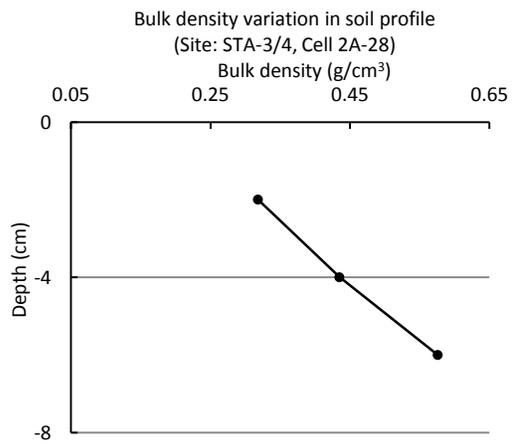
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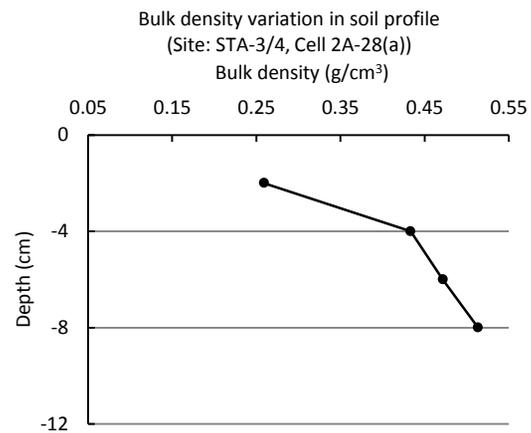
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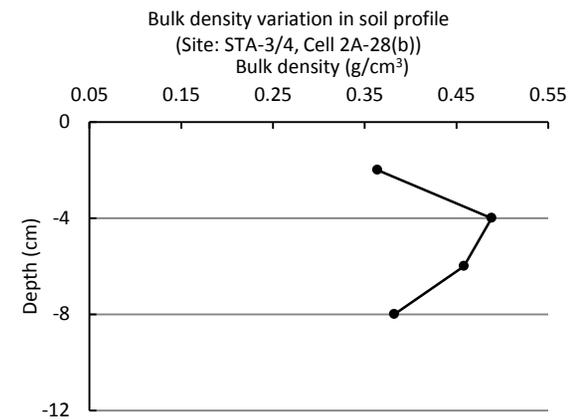
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EAV cell

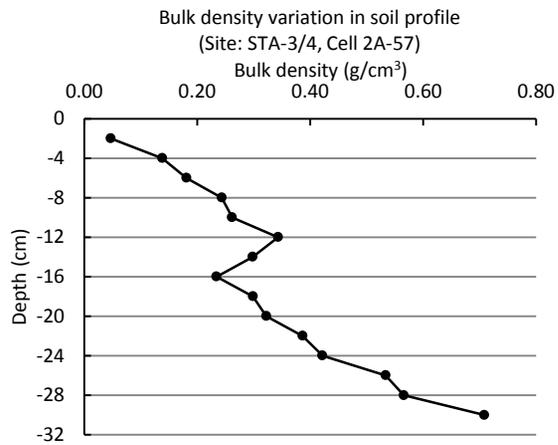


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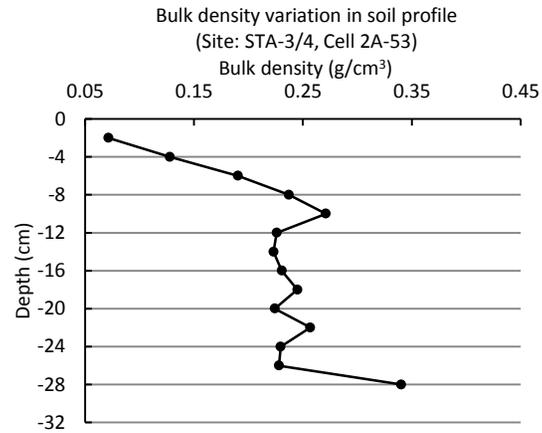


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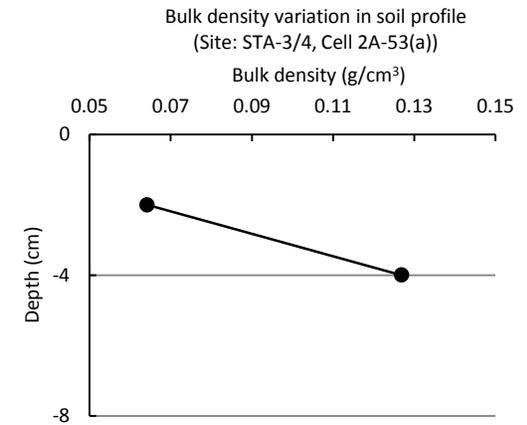
Figure D-8. Continued



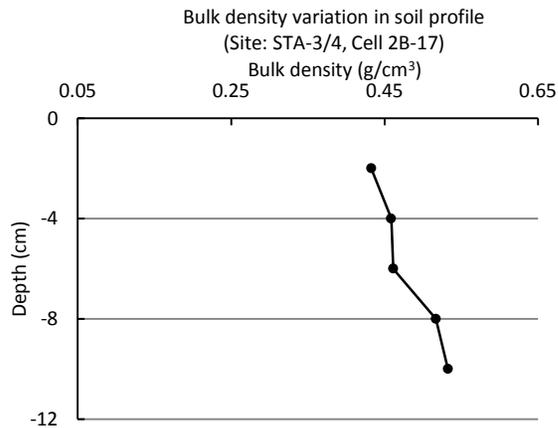
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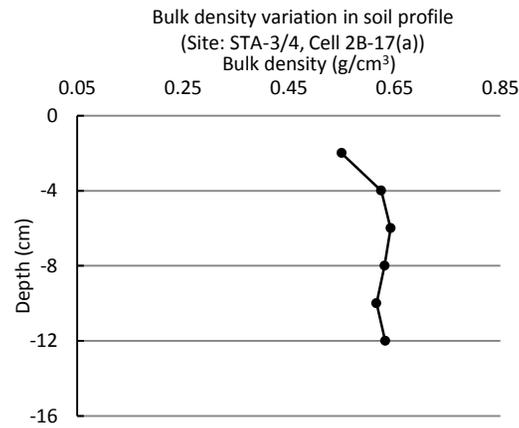
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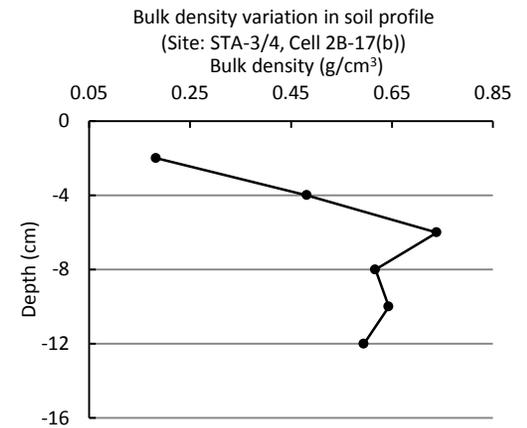
EAV cell



SAV cell

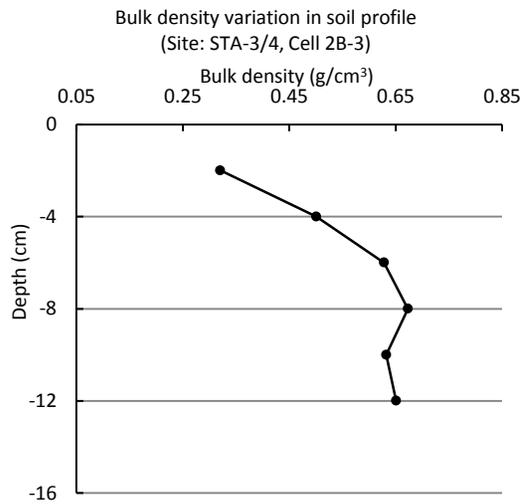


SAV cell

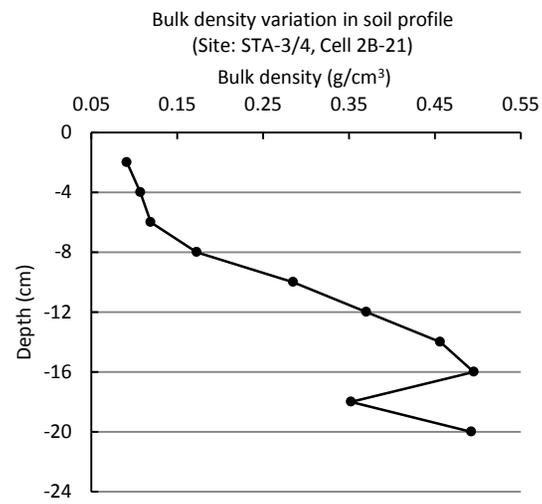


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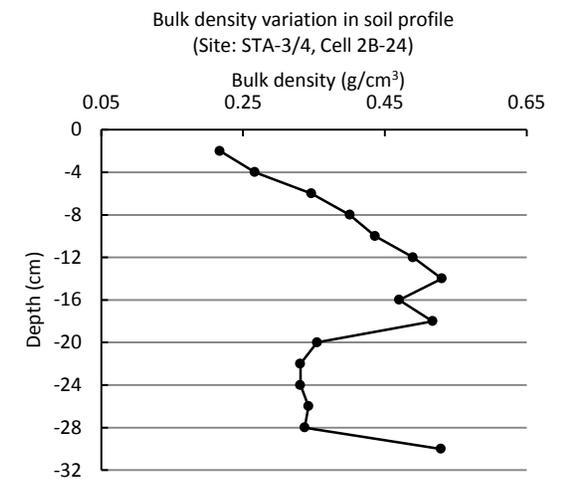
Figure D-8. Continued



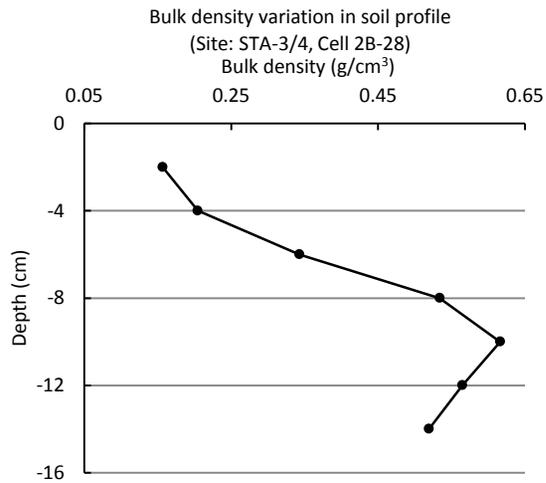
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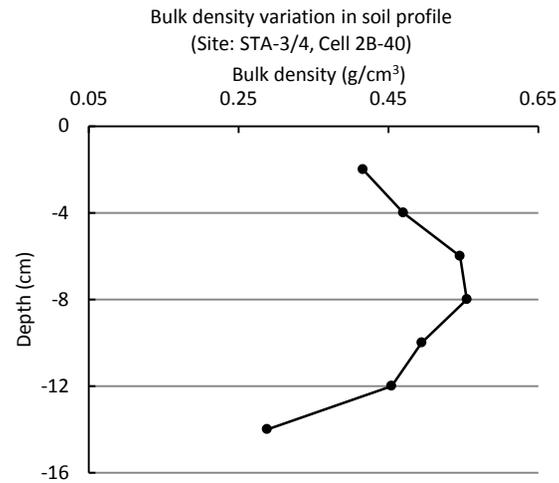
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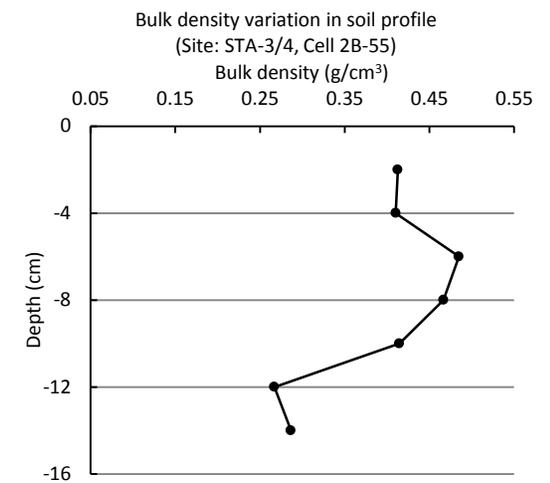
SAV cell



SAV cell

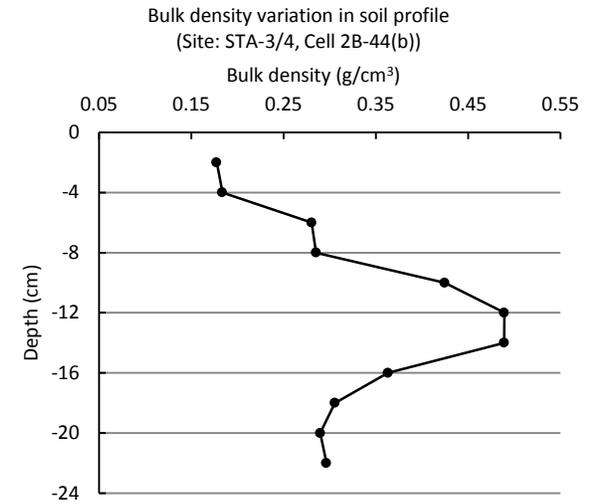
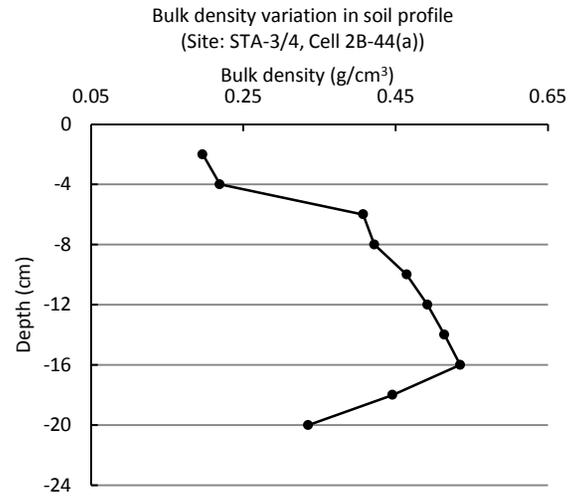
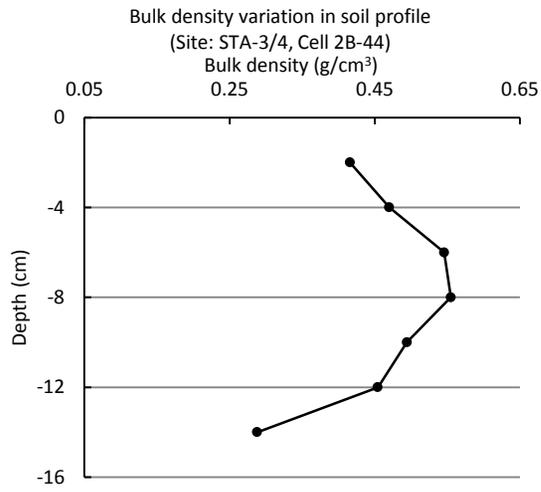


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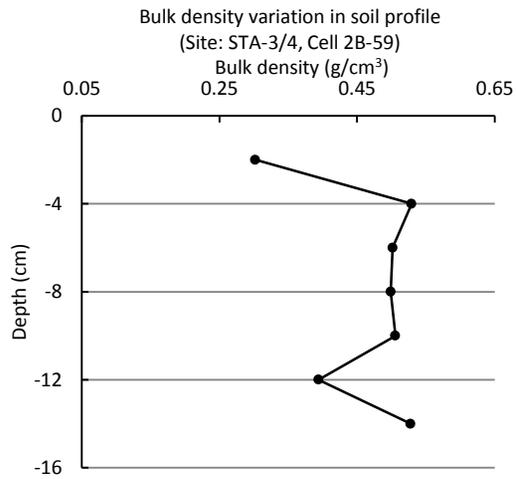


SAV cell

Figure D-8. Continued

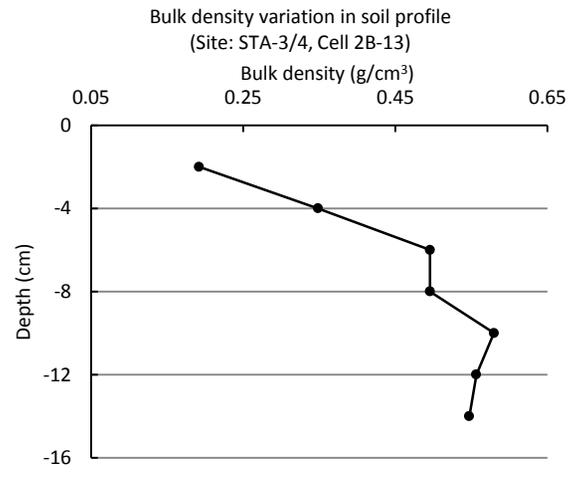


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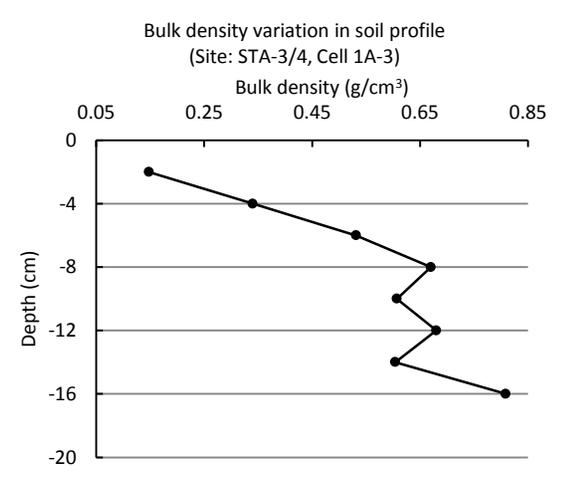
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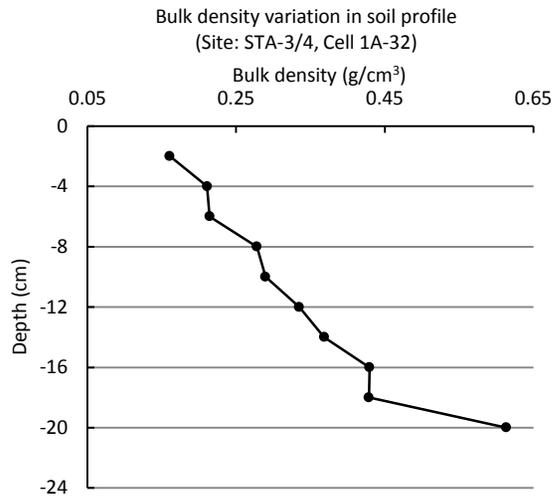
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SAV cell

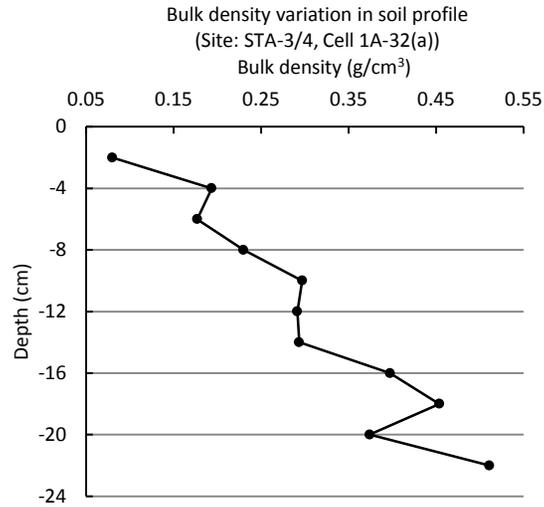


EAV cell

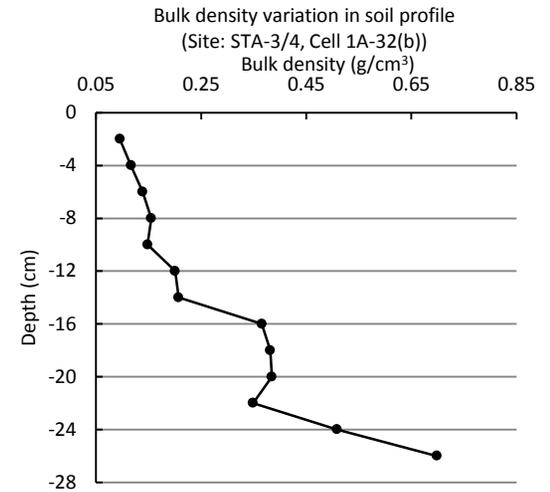
Figure D-8. Continued



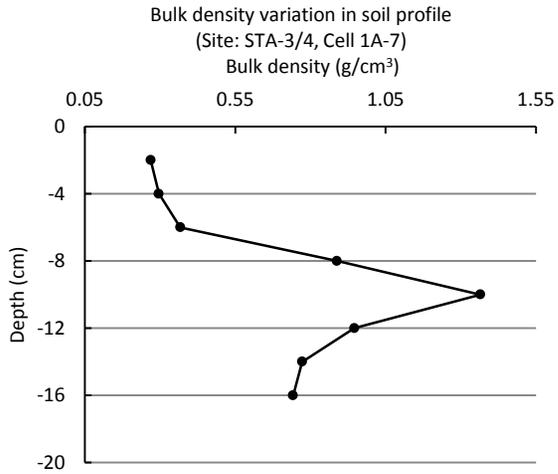
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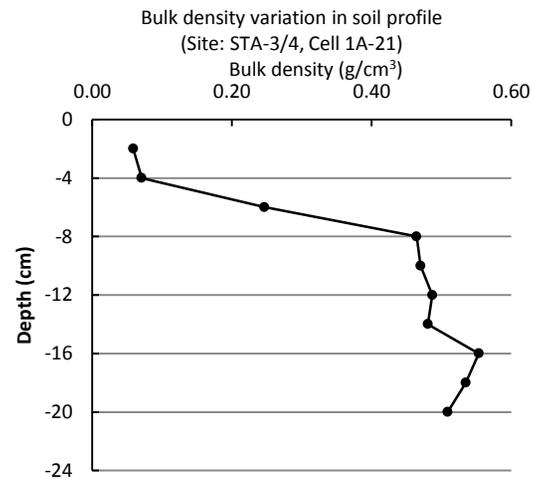
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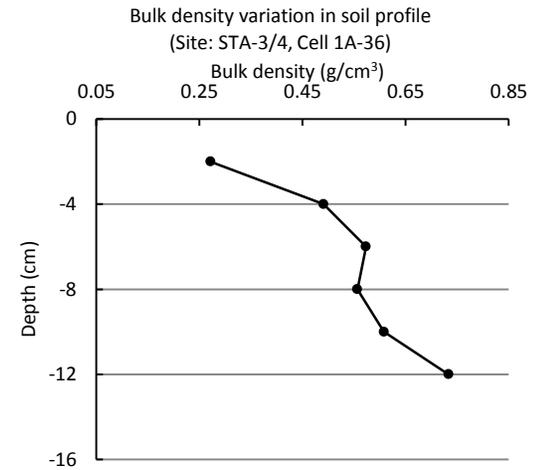
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EAV cell

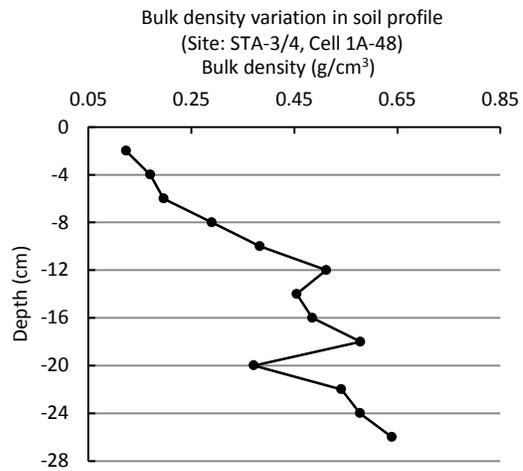


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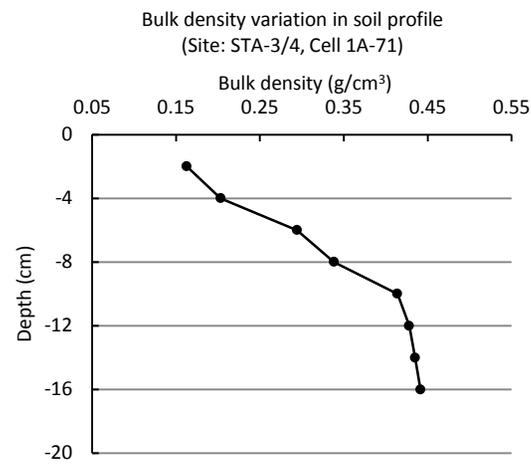


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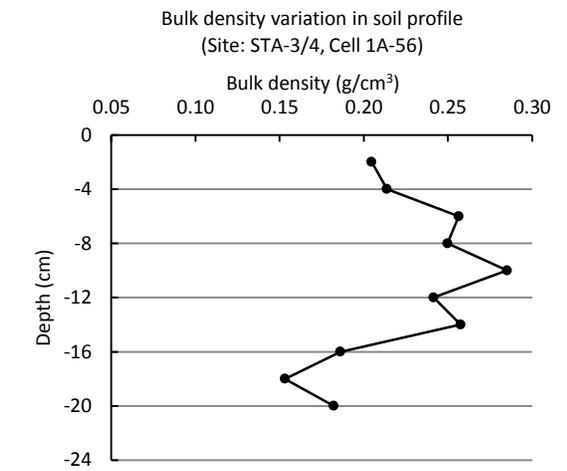
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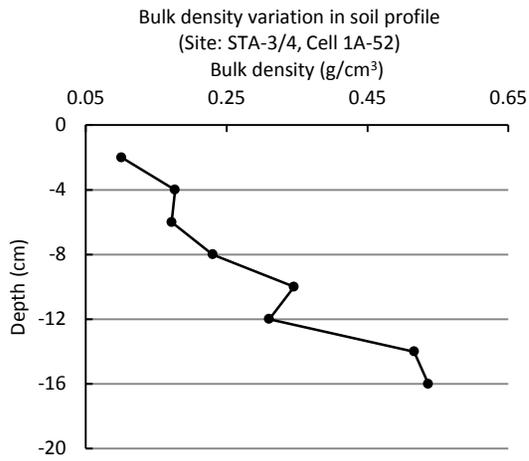
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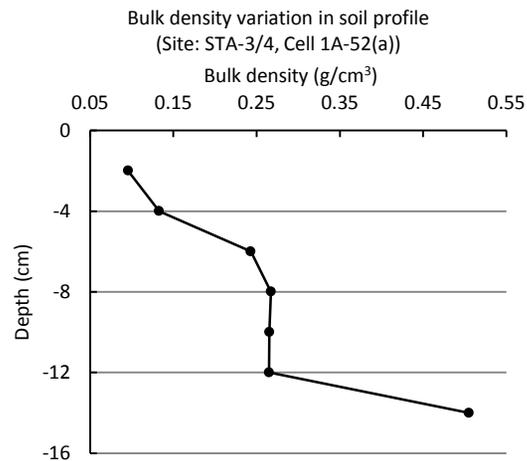
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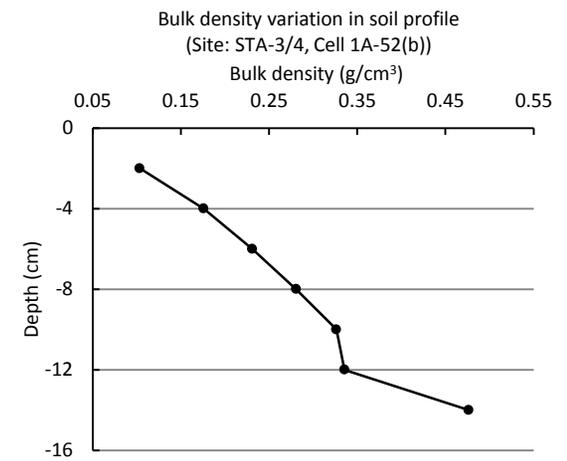
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EAV cell

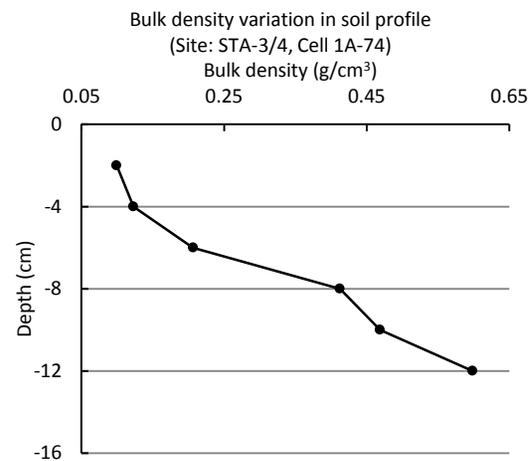


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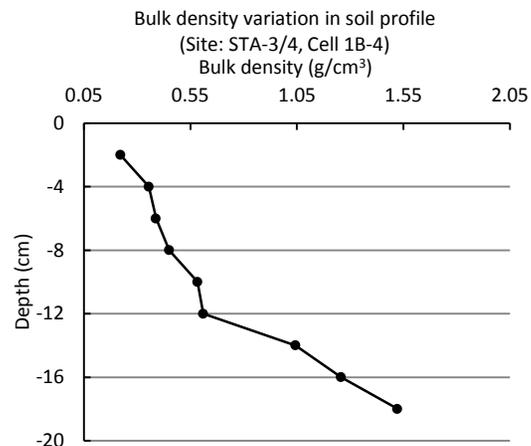


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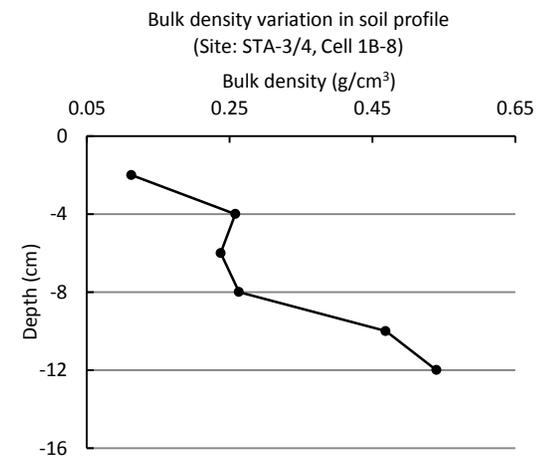
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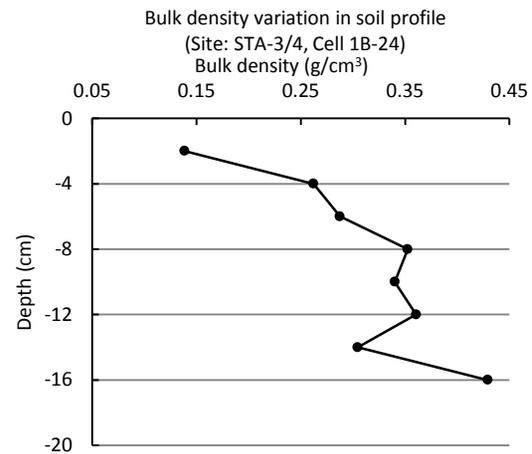
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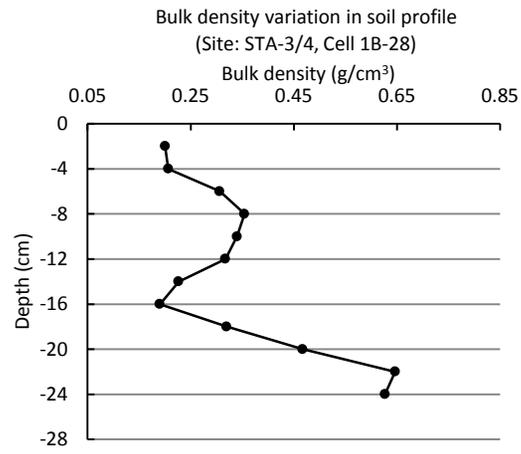
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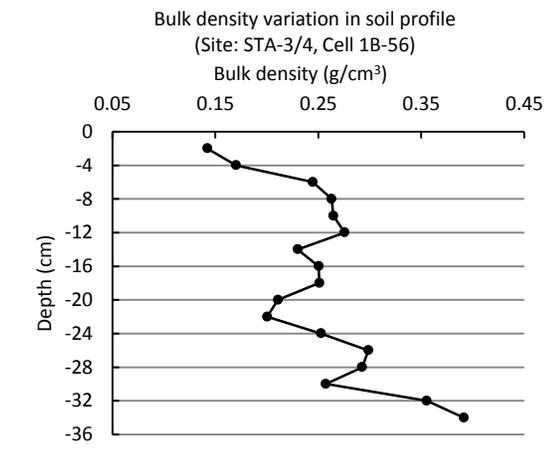
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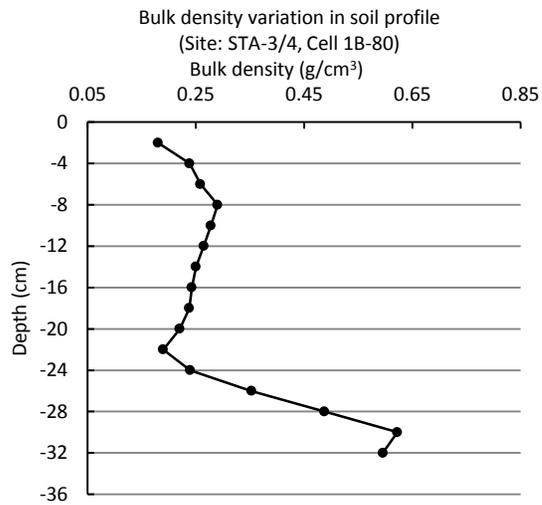


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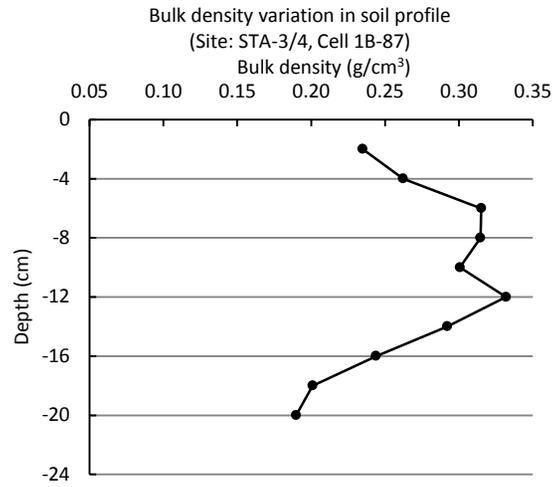


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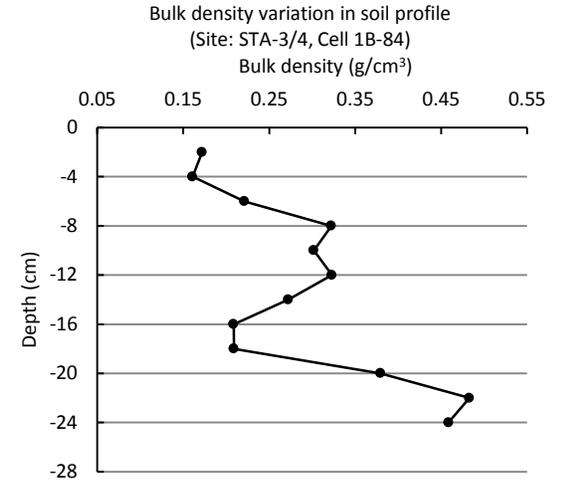
Figure D-8. Continued



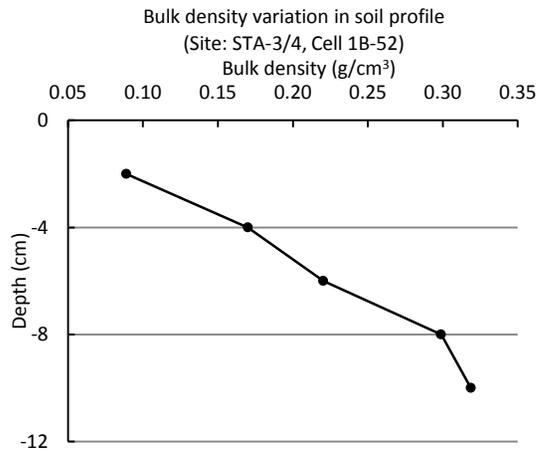
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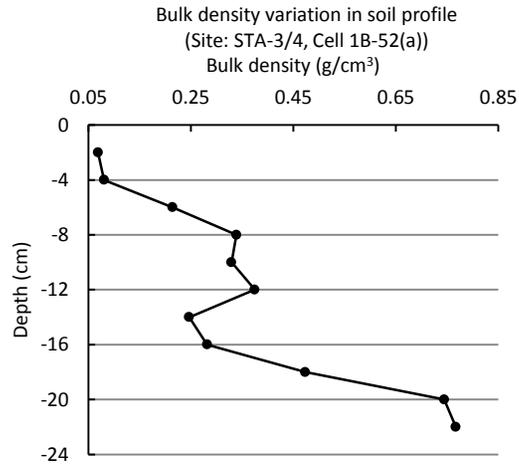
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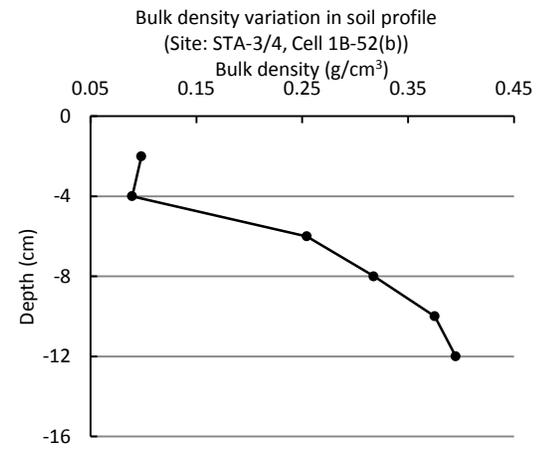
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EAV cell

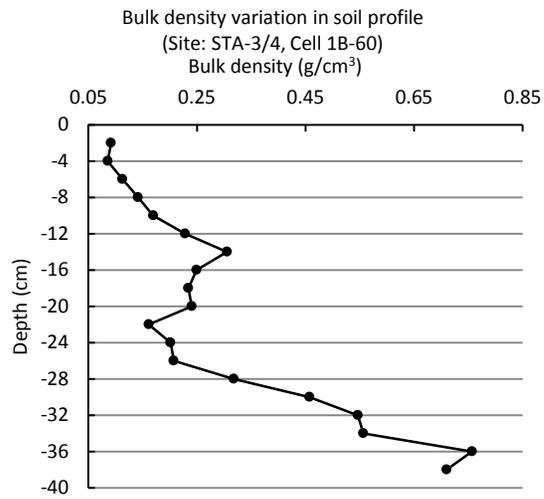


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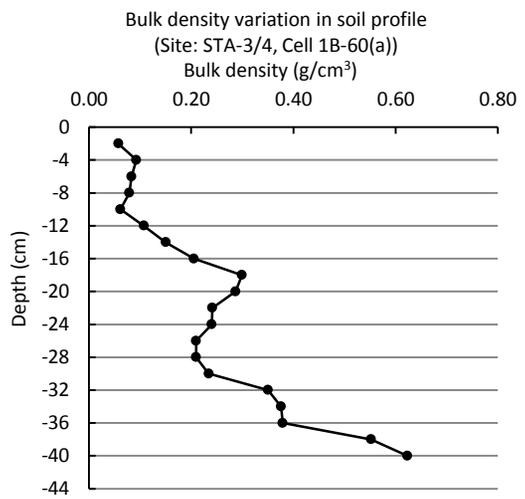


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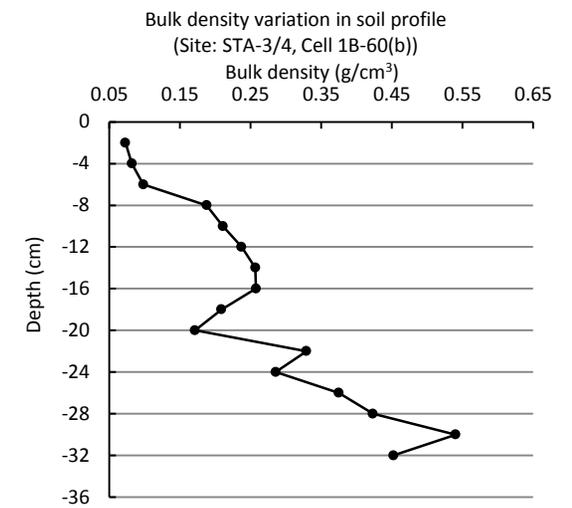
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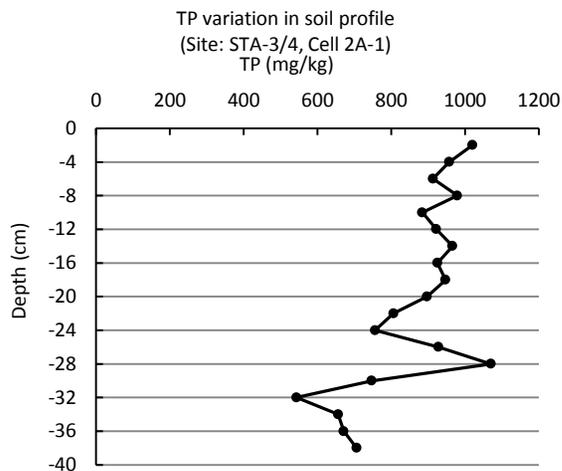


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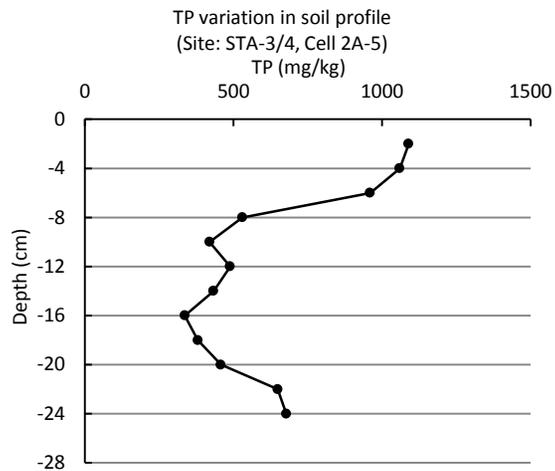


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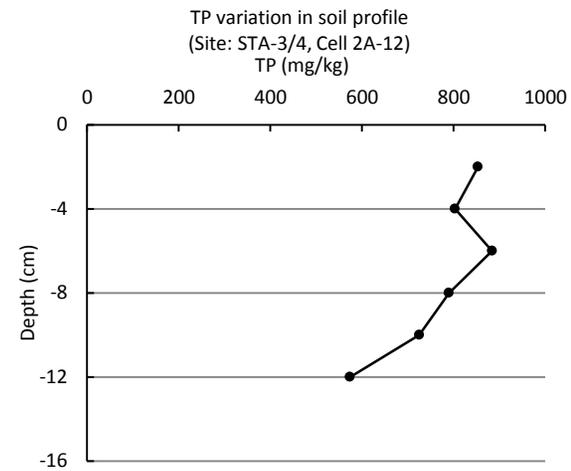
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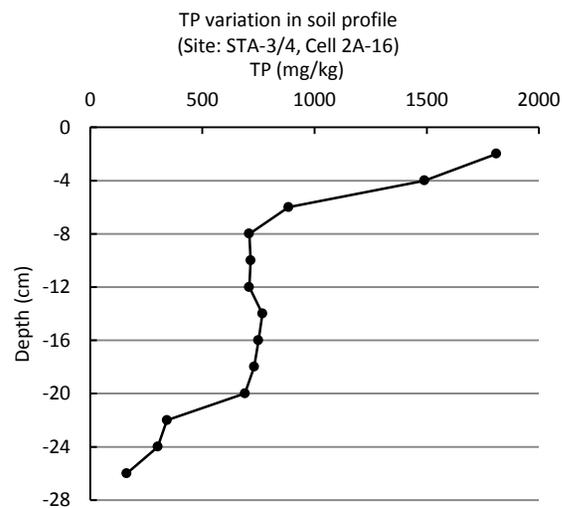
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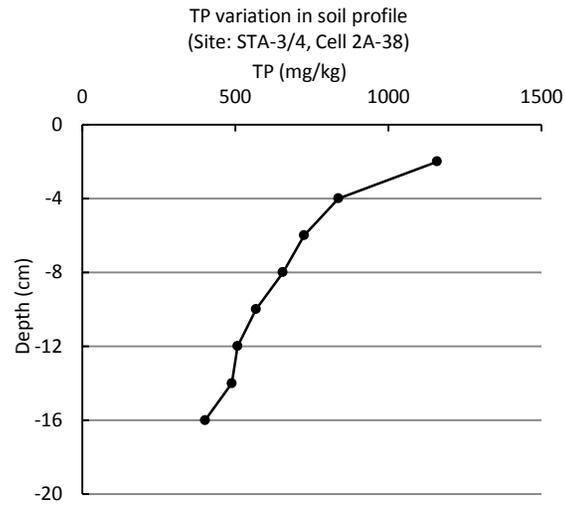
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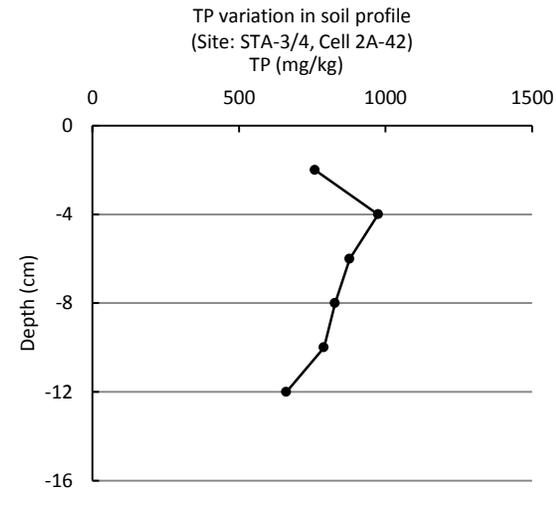
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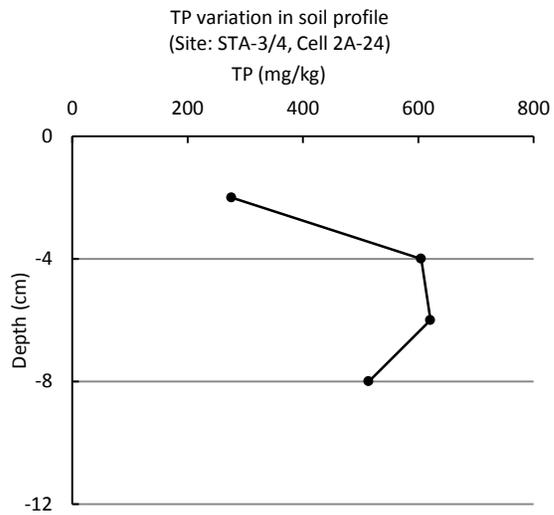


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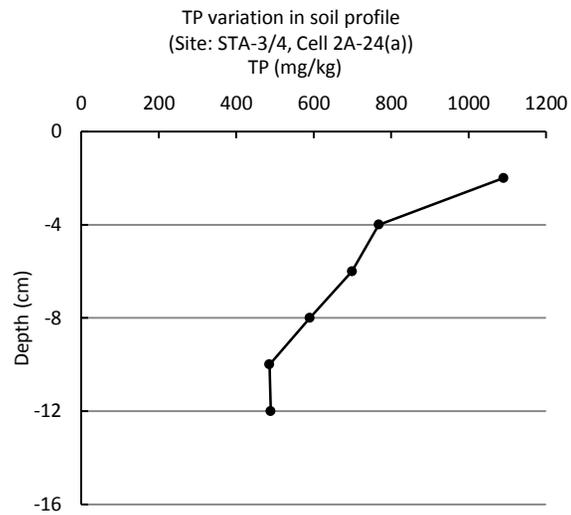


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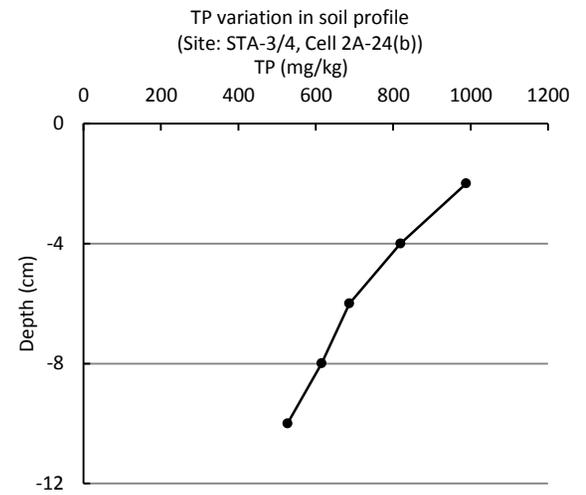
Figure D-9. Total phosphorus profile in each soil core collected from STA-3/4.



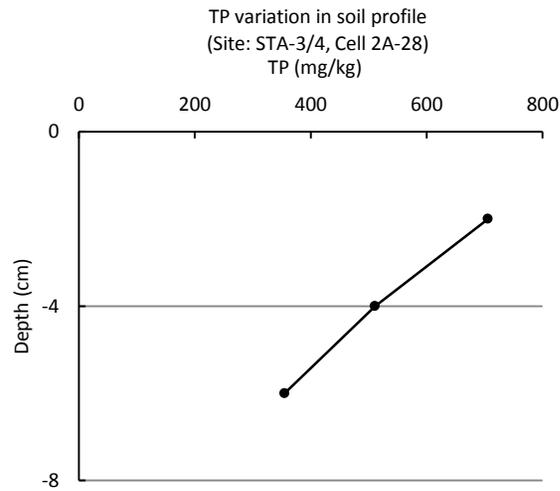
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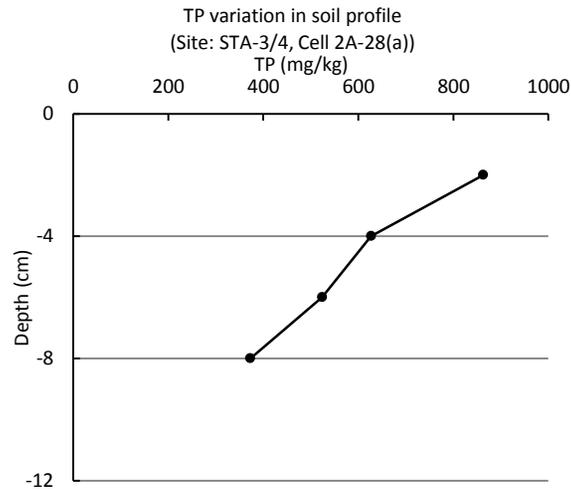
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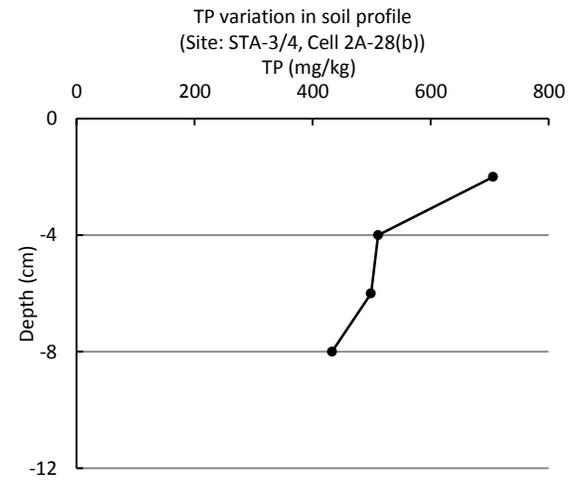
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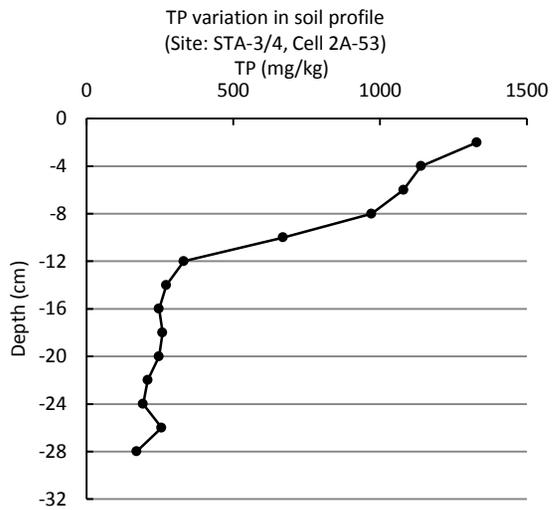


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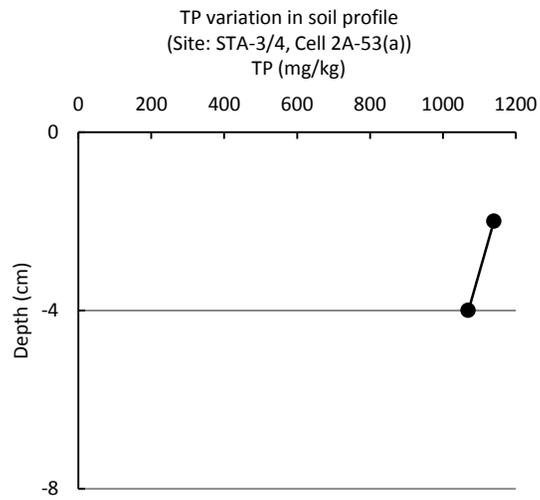


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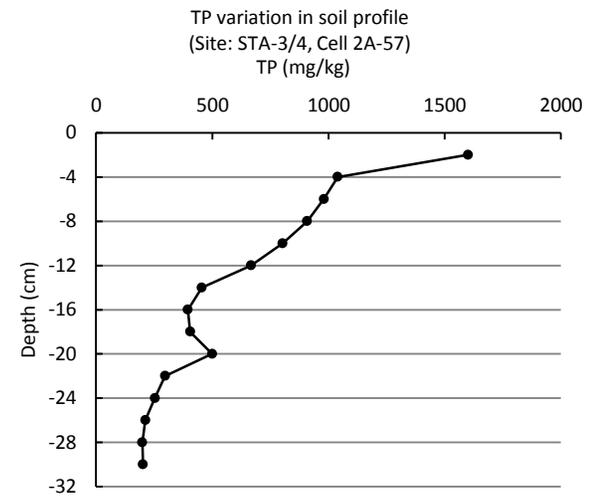
Figure D-9. Continued



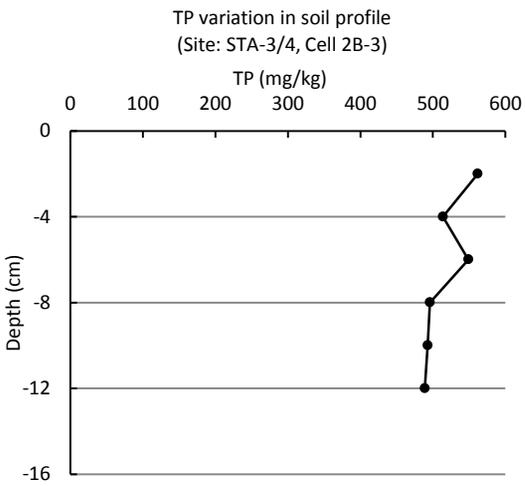
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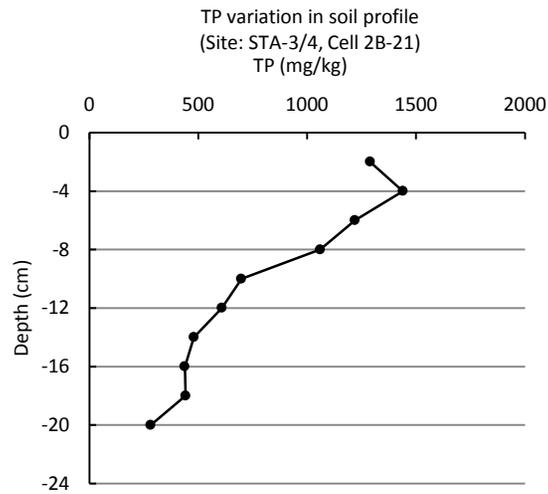
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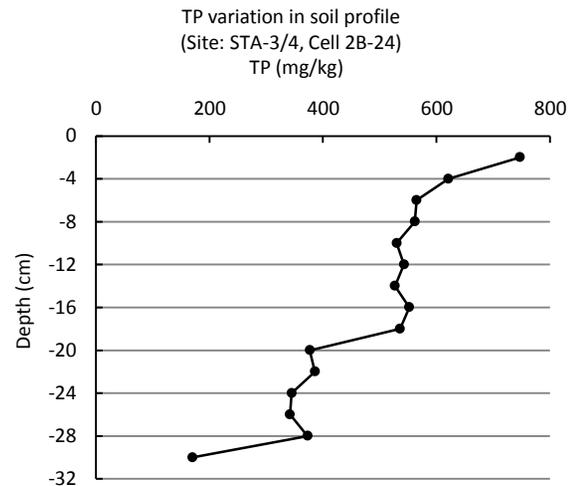
EAV cell



SAV cell

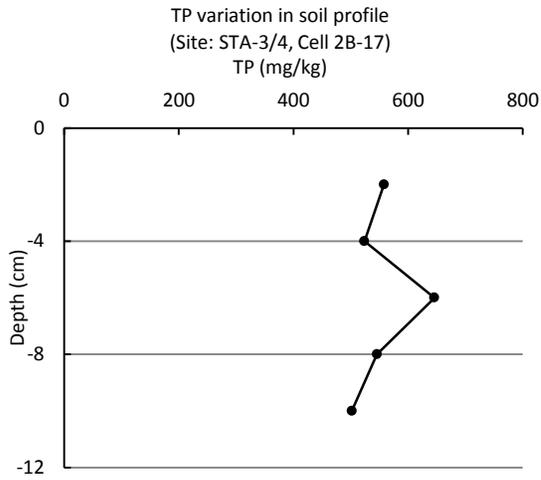


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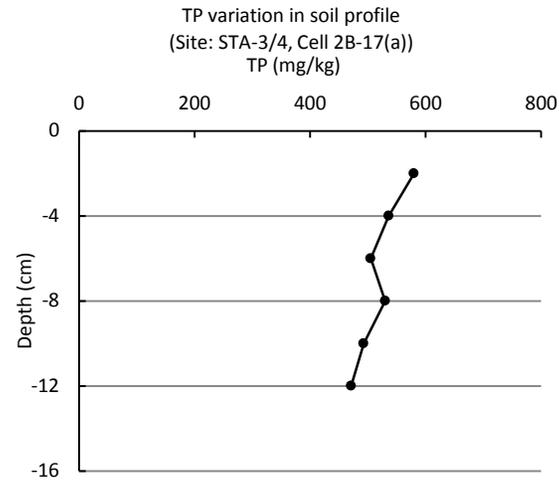


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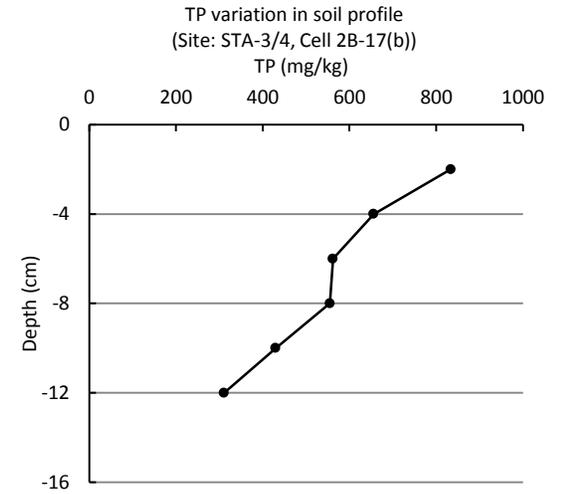
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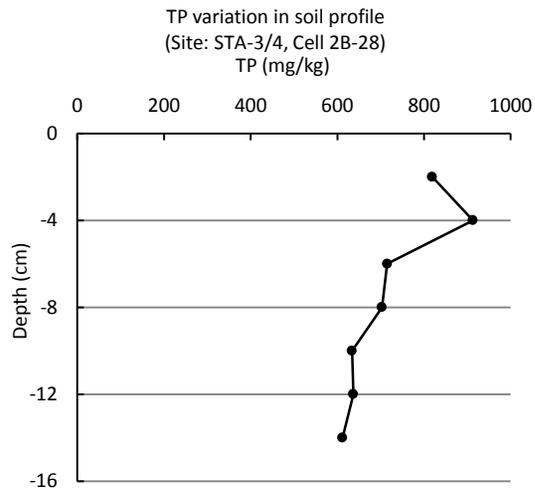
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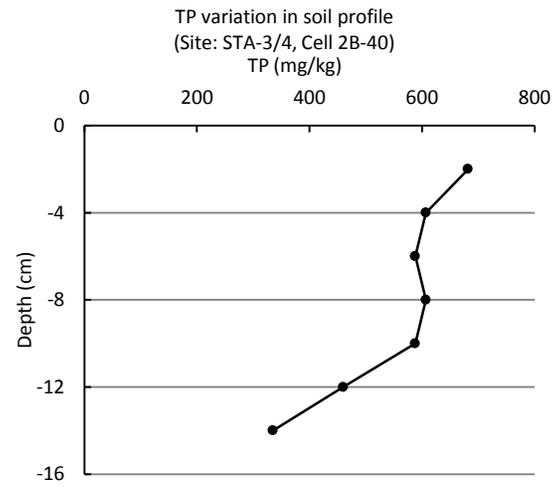
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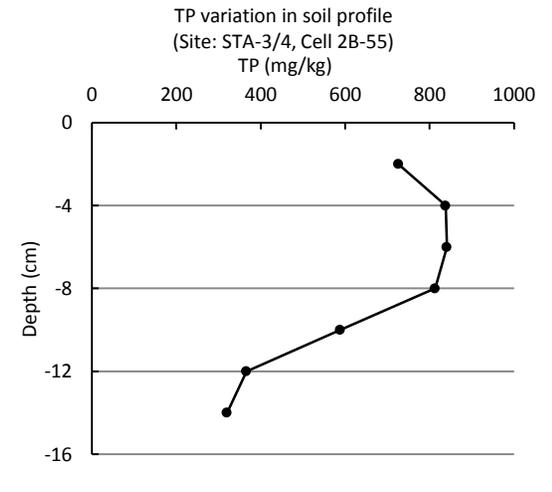
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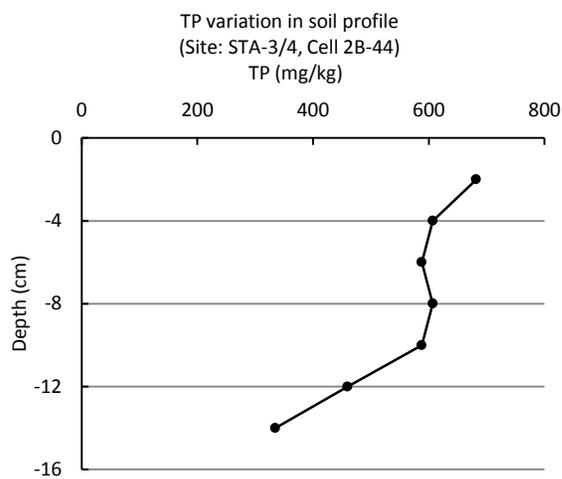


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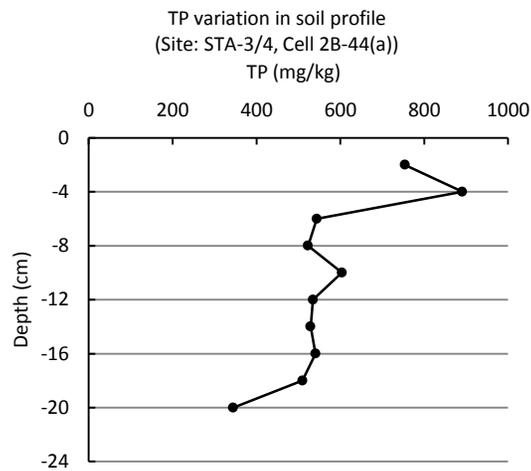


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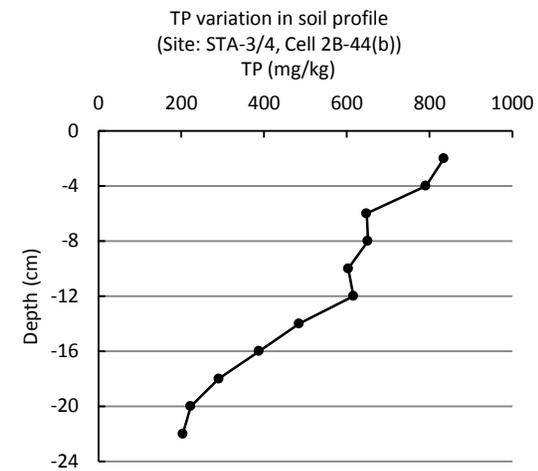
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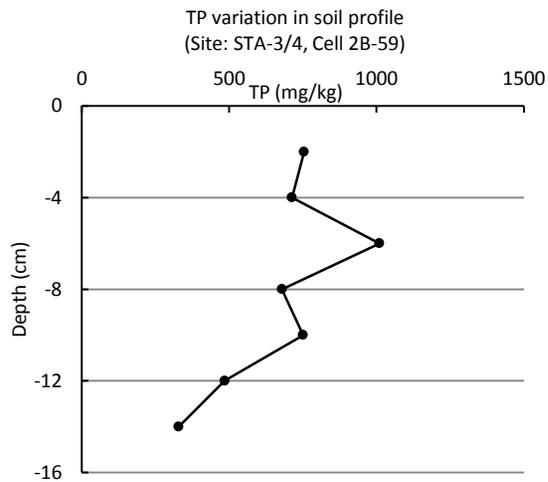
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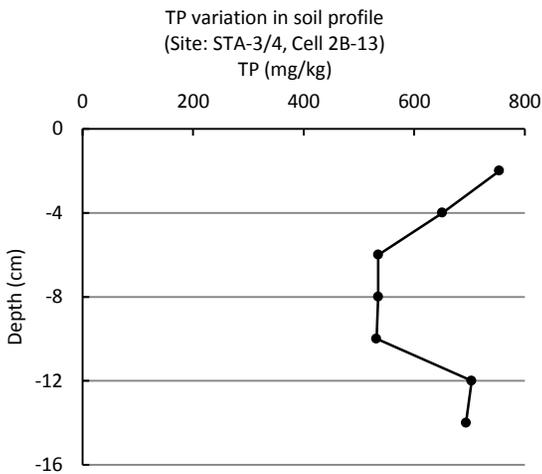
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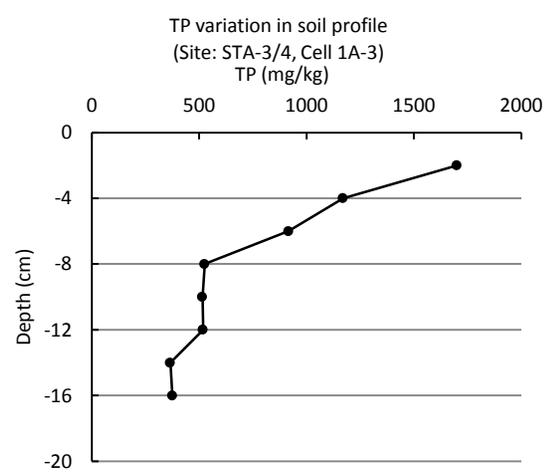
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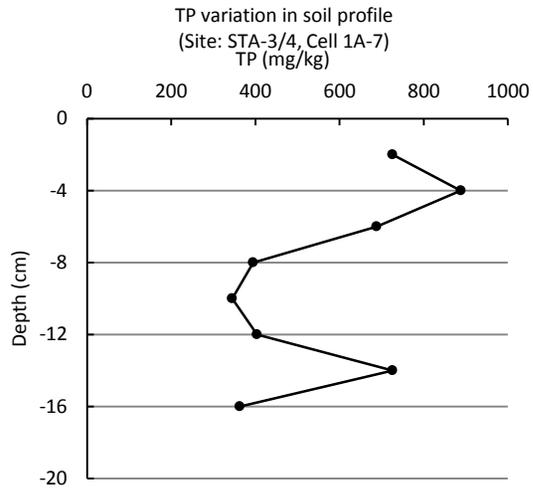


SAV cell

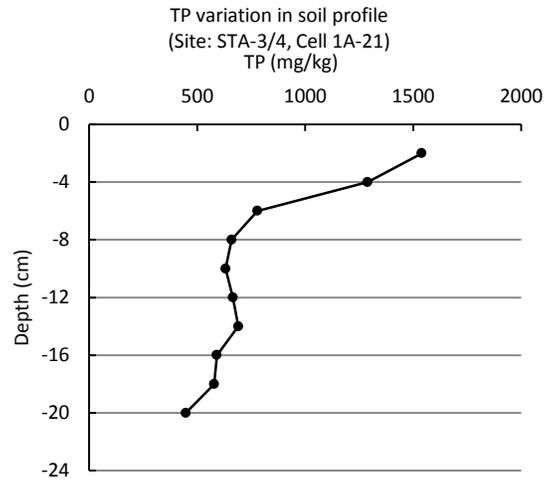


EAV cell

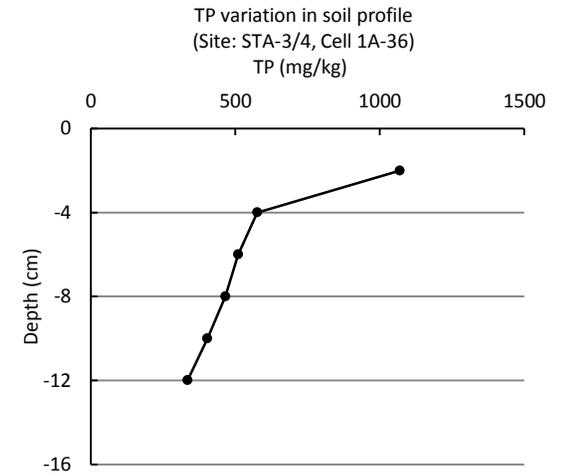
Figure D-9. Continued



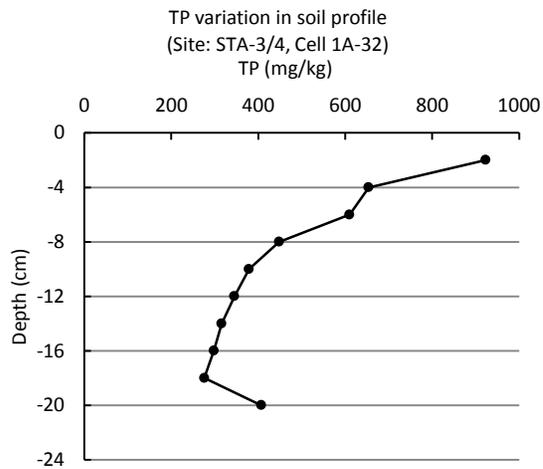
EAV cell



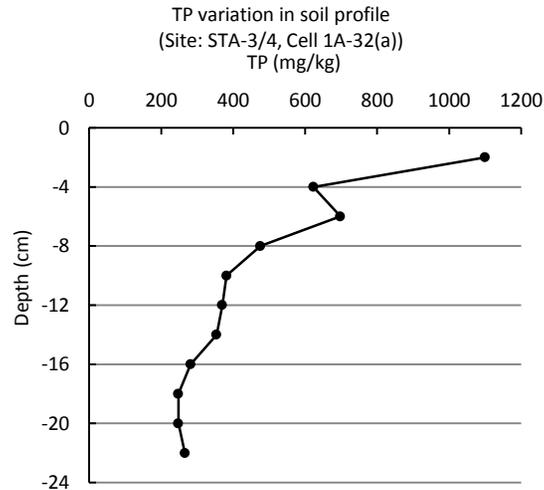
EAV cell



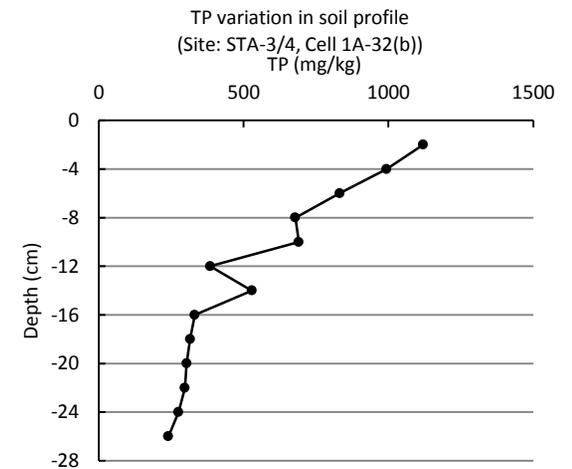
EAV cell



EAV cell

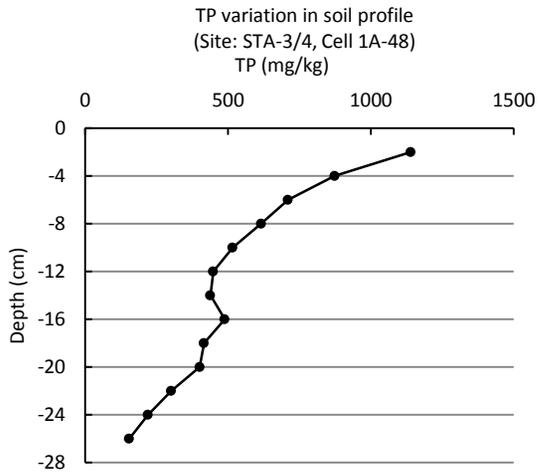


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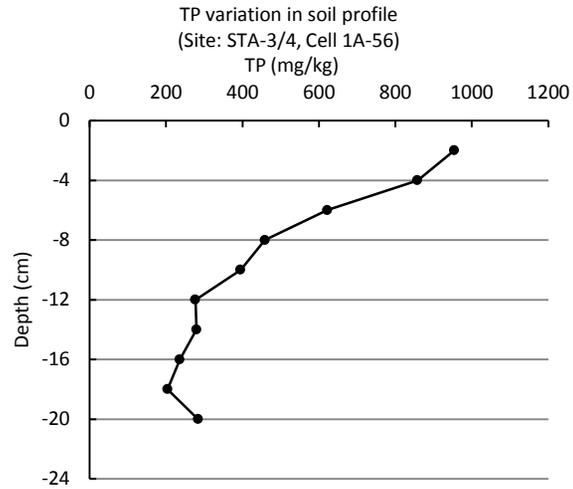


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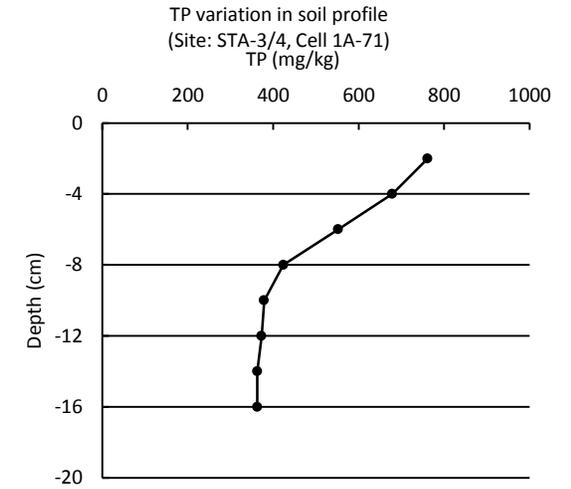
Figure D-9. Continued



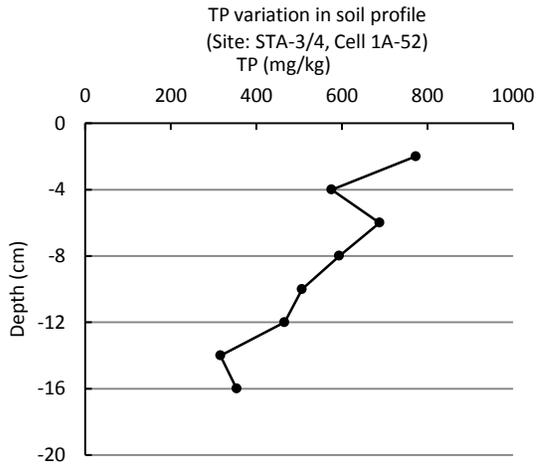
EAV cell



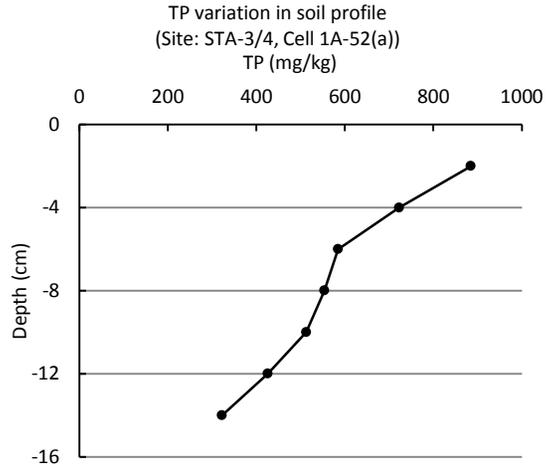
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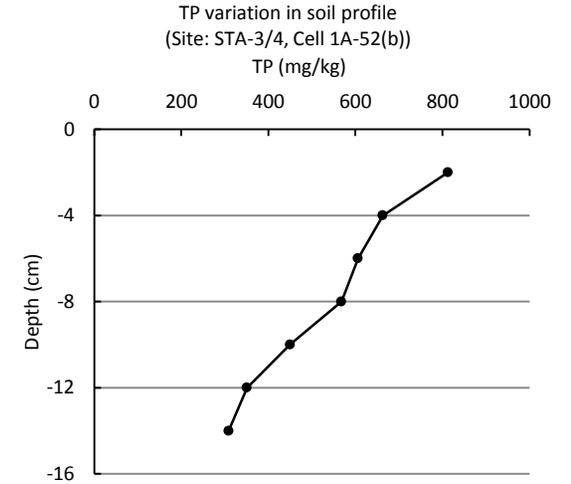
EAV cell



EAV cell

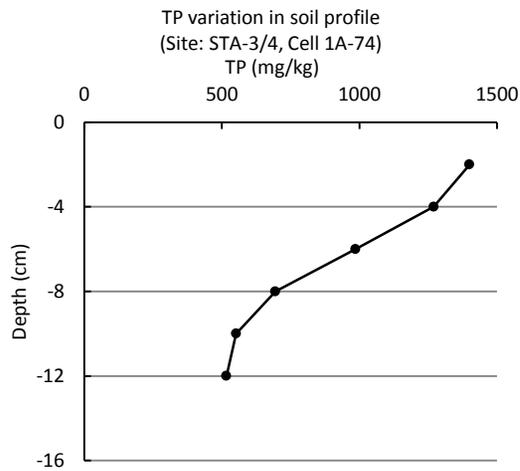


EAV cell

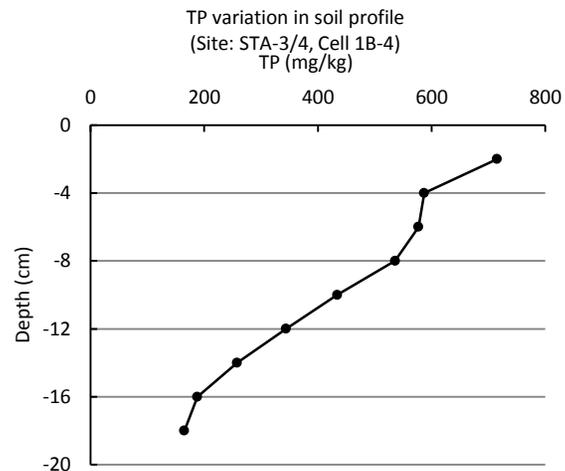


EAV cell

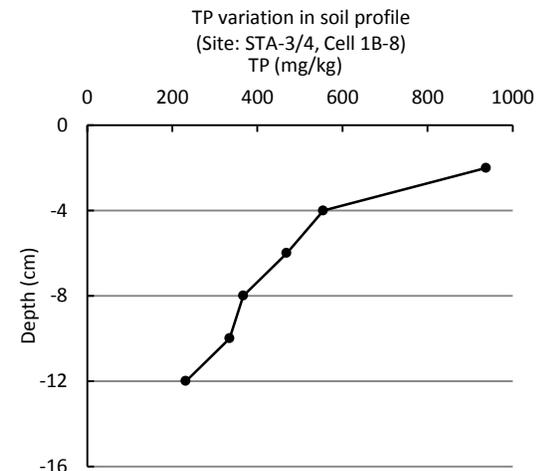
Figure D-9. Continued



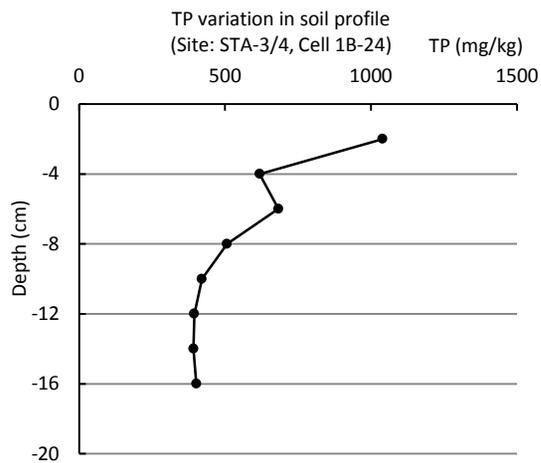
EAV cell



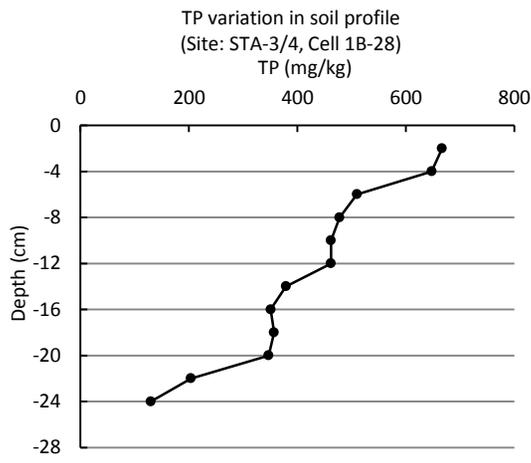
EAV cell



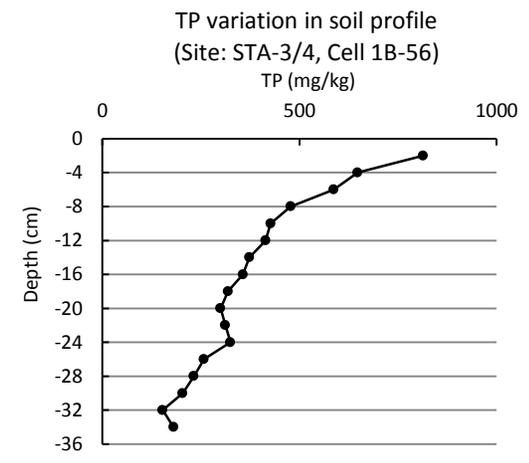
EAV cell



EAV cell

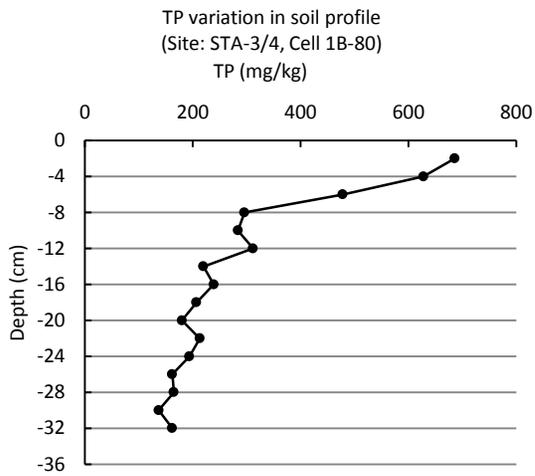


EAV cell

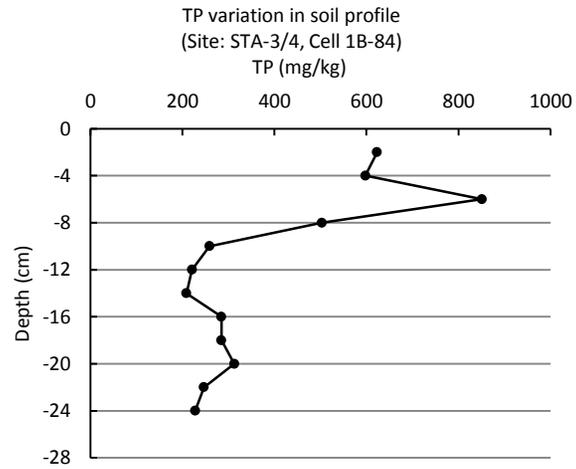


EAV cell

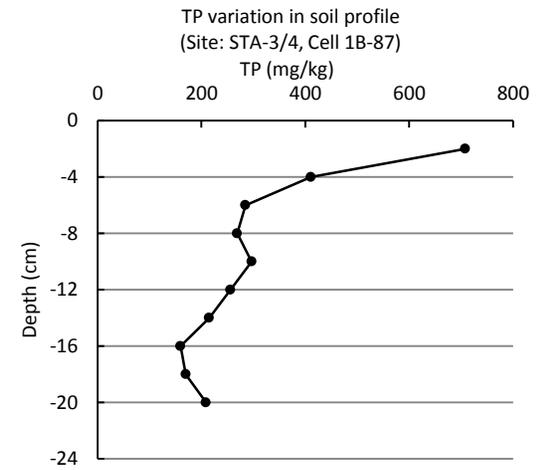
Figure D-9. Continued



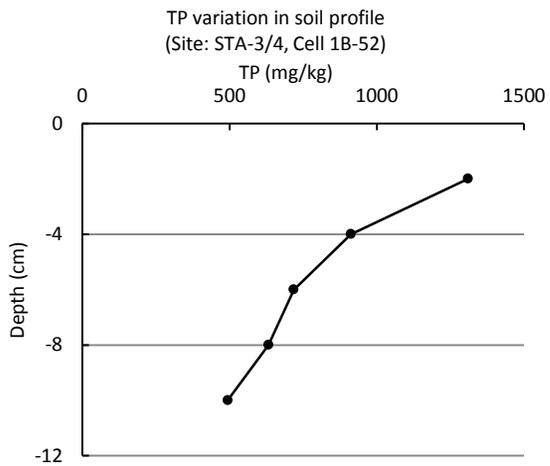
EAV cell



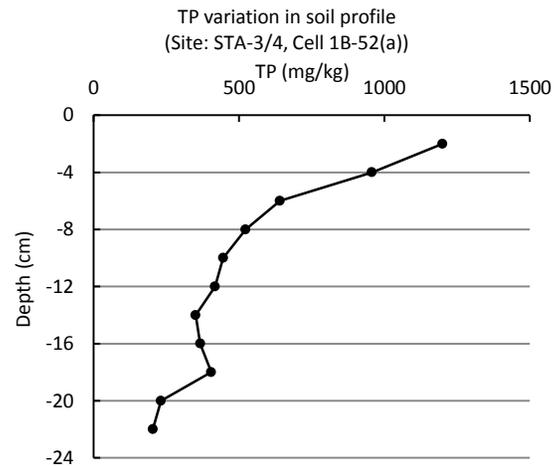
EAV cell



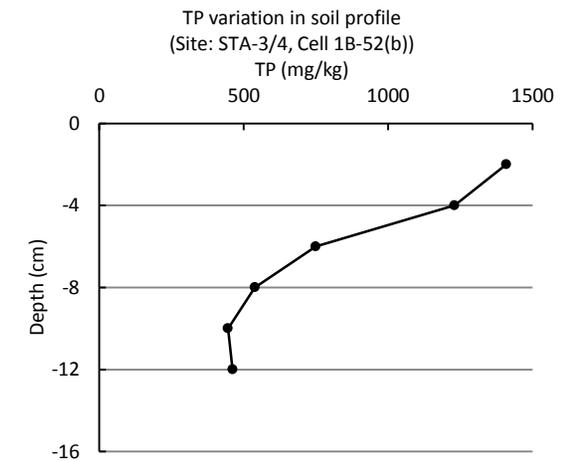
EAV cell



EAV cell

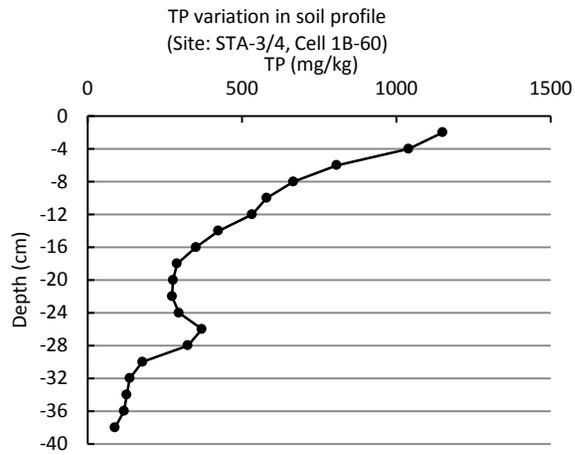


EAV cell

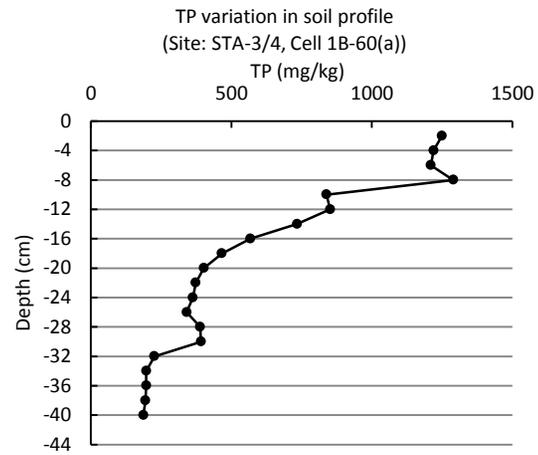


EAV cell

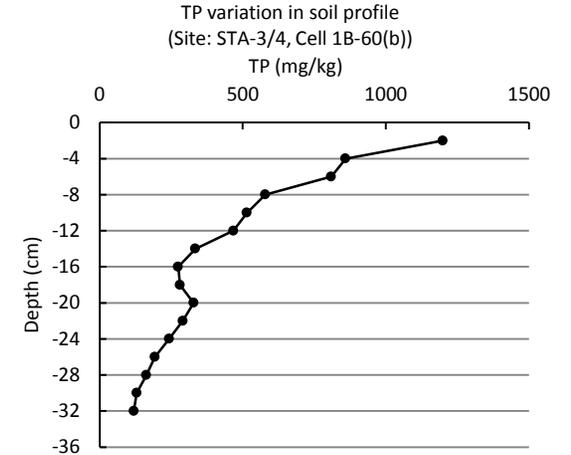
Figure D-9. Continued



EAV cell



EAV cell



EAV cell

Figure D-9. Continued

APPENDIX E
 ADDITIONAL DATA AND INFORMATION PERTAINING TO CHAPTER 5

Table E-1. STA-1W and STA-2 soil core collection sites by vegetation type and cell. A total 44 soil cores were collected from these locations.

Soil core sampling locations							
		EAV		SAV		EAV conversion	
STA- 1W	Cell 5A		Cell 5B		Cell 3		
		5A112	5A150	5B108	5B202	3I	3P
		5A112(a)	5A74	5B125	5B83	3I(a)	3B
		5A112(b)	--	5B125(a)	5B162	3I(b)	--
		--	--	5B125(b)	--	--	--
		EAV		SAV			
STA-2	Cell 1	Cell 2	Cell 3	Cell 4	--	--	
	A103	B117	C129	D111	--	--	
	A103(a)	B151	C165	D124	--	--	
	A103(b)	B187	C201	D124(a)	--	--	
	A138	B26	C21	D124(b)	--	--	
	A172	B81	C75	D129	--	--	
	A51	B98	C75(a)	D139	--	--	
	--	B98(a)	C75(b)	--	--	--	
	--	B98(b)	--	--	--	--	

Table E-2. Mean depth of RAS at STA-1W sampling sites used for separating RAS from pre-STA soil.

STA-1W					
EAV Cell 5A		SAV Cell 5B		EAV conversion Cell 3	
Site	Depth (cm)	Site	Depth (cm)	Site	Depth (cm)
5A112	8	5B108	8	3I	12
5A112(a)	8	5B125	8	3I(a)	10
5A112(b)	8	5B125(a)	8	3I(b)	10
5A150	10	5B125(b)	12	3P	10
5A74	16	5B202	8	3B	12
--	--	5B83	10	--	--
--	--	5B162	12	--	--

Table E-3. Mean depth of RAS at STA-2 sampling sites used for separating RAS from pre-STA soil.

STA-2							
EAV				SAV			
Cell 1		Cell 2		Cell 3		Cell 4	
Site	Depth (cm)	Site	Depth (cm)	Site	Depth (cm)	Site	Depth (cm)
A103	8	B117	10	C129	8	D111	6
A103(a)*	12	B151	12	C165	12	D124	8
A103(b)*	8	B187	14	C201	10	D124(a)	12
A138	10	B26	8	C21	8	D124(b)	12
A172	8	B81	12	C75	8	D129	12
A51	8	B98	8	C75(a)	12	D139	12
--	-	B98(a)	8	C75(b)	4	--	-
--	-	B98(b)	8	--	--	--	-

Table E-4. Depth of soil fraction, bulk density, total phosphorus concentration and TP storage for each soil fraction at sampling sites in STA-1W.

STA-1W		Floc			RAS				Pre-STA soil			
EAV	Depth	Bulk density	TP Conc.	TP Storage	Depth	Bulk density	TP Conc.	TP Storage	Depth	Bulk density	TP Conc.	TP Storage
	cm	g cm ⁻³	mg Pkg ⁻¹	g P m ⁻²	cm	g cm ⁻³	mg P kg ⁻¹	g P m ⁻²	cm	g cm ⁻³	mg Pkg ⁻¹	g Pm ⁻²
Cell-5A												
5A-112	8	0.11	1219	11.2	8	0.29	461	10.5	15	0.35	369	19.5
5A-112(a)	5	0.12	1080	6.5	8	0.31	444	11.0	15	0.34	428	21.8
5A-112(b)	8	0.08	1340	8.8	8	0.29	827	19.0	15	0.39	443	25.6
5A-150	16	0.05	1339	10.9	10	0.32	245	7.9	15	0.23	182	6.4
5A-74	--	--	--	--	16	0.37	684	40.5	15	0.34	497	25.3
SAV												
Cell-3												
3B	8	0.18	334	4.7	12	0.31	226	8.4	15	0.33	222	10.9
3I	8	0.08	1094	7.3	12	0.23	446	12.5	15	0.26	186	7.2
3I(a)	6	0.05	1460	4.3	10	0.17	1045	17.9	15	0.26	210	8.3
3I(b)	8	0.06	940	4.5	10	0.22	789	17.2	15	0.28	198	8.3
3P	14	0.09	660	8.3	10	0.21	384	8.1	15	0.29	202	8.9
Cell-5B												
5B-108	6	0.21	1002	12.8	8	0.35	426	12.0	15	0.19	255	7.3
5B-125	5	0.14	1199	8.1	8	0.26	568	12.0	15	0.28	322	13.4
5B-125(a)	6	0.13	986	8.0	8	0.28	353	7.9	15	0.28	298	12.3
5B-125(b)	5	0.10	778	3.8	12	0.33	426	17.0	15	0.32	364	17.6
5B-162	8	0.17	1011	13.7	12	0.28	508	17.2	15	0.27	396	16.2
5B-202	4	0.20	798	6.5	8	0.31	552	13.9	15	0.28	326	13.5
5B-83	6	0.09	690	3.9	10	0.39	733	28.6	15	0.32	588	28.2

*For pre-STA soil, TP storages were calculated only for a 15-cm deep soil layer, assuming constant bulk density throughout the layer.

Table E-5. Depth of soil fraction, bulk density, total phosphorus concentration and TP storage for each soil fraction at sampling sites in STA-2.

STA-2		Floc			RAS				Pre-STA soil			
EAV	Depth	Bulk density	TP Conc.	TP Storage	Depth	Bulk density	TP Conc.	TP Storage	Depth	Bulk density	TP Conc.	TP Storage*
	cm	g cm ⁻³	mg Pkg ⁻¹	g P m ⁻²	cm	g cm ⁻³	mg P kg ⁻¹	g P m ⁻²	cm	g cm ⁻³	mg Pkg ⁻¹	g Pm ⁻²
Cell 1												
A103	10	0.08	1014	7.7	8	0.18	255	3.7	15	0.14	178	3.8
A103 (a)	10	0.08	1098	8.3	12	0.16	275	5.3	15	0.13	162	3.1
A103 (b)	12	0.07	1031	8.9	8	0.14	297	3.3	15	0.14	174	3.6
A138	8	0.07	760	4.2	10	0.21	276	5.7	15	0.11	172	2.9
A172	8	0.04	1009	3.1	8	0.31	302	7.5	15	0.12	186	3.3
A51	9	0.04	1444	5.3	8	0.17	636	8.5	15	0.17	192	5.0
Cell 2												
B117	7	0.08	644	3.6	10	0.25	317	8.1	15	0.13	181	3.6
B151	5	0.02	1455	1.5	12	0.15	554	10.2	15	0.18	220	5.8
B187	12	0.03	1117	3.8	14	0.19	455	12.3	15	0.41	199	12.2
B26	4	0.02	798	0.6	8	0.38	482	14.7	15	0.39	330	19.2
B81	7	0.12	1293	10.7	12	0.27	380	12.5	15	0.15	170	3.8
B98	10	0.04	1361	5.0	8	0.26	395	8.2	15	0.11	249	4.1
B98(a)	6	0.07	1116	4.8	8	0.20	406	6.4	15	0.12	174	3.1
B98(b)	10	0.07	1218	8.1	8	0.21	340	5.8	15	0.09	176	2.3

For pre-STA soil fraction, mass P storages were calculated only for 15 cm depth, assuming constant bulk density for the entire 15 cm depth.

Table E-5 Continued

STA-2		Floc			RAS				Pre-STA soil			
SAV	Depth	Bulk density	TP Conc.	TP Storage	Depth	Bulk density	TP Conc.	TP Storage	Depth	Bulk density	TP Conc.	TP Storage
	cm	g cm ⁻³	mg Pkg ⁻¹	g P m ⁻²	cm	g cm ⁻³	mg P kg ⁻¹	g P m ⁻²	cm	g cm ⁻³	mg Pkg ⁻¹	g Pm ⁻²
Cell 3												
C129	8	0.12	523	5.2	8	0.25	370	7.5	15	0.26	280	10.7
C165	7	0.10	506	3.5	12	0.30	389	14.2	15	0.22	242	8.0
C201	11	0.12	362	4.9	10	0.32	513	16.4	15	0.39	236	13.8
C21	5	0.13	886	5.9	8	0.46	399	14.6	15	0.39	431	25.3
C75	10	0.12	1083	12.8	8	0.23	777	14.5	15	0.14	284	6.2
C75 (a)	10	0.13	1020	13.2	12	0.24	753	21.9	15	0.20	278	8.3
C75 (b)	7	0.10	979	7.0	4	0.27	525	5.7	15	0.18	297	8.0
Cell 4												
D111	--	--	--	--	6	0.25	967	14.6	15	0.25	294	10.8
D124	--	--	--	--	8	0.18	751	10.6	15	0.35	75	3.9
D124 (a)	--	--	--	--	12	0.24	655	19.1	15	0.32	405	19.4
D124 (b)	--	--	--	--	12	0.29	585	20.5	15	0.26	363	14.2
D129	--	--	--	--	12	0.31	610	22.8	15	0.39	414	24.0
D139	--	--	--	--	12	0.34	607	25.1	15	0.38	534	30.3

*For pre-STA soil, TP storages were calculated only for a 15 cm deep soil layer, assuming constant bulk density throughout the layer.

Table E-6. Depth of soil fraction, bulk density, total nitrogen concentration and TN storage for each soil fraction at sampling sites in STA-1W.

STA-1W		Floc			RAS				Pre-STA soil			
EAV	Depth	Bulk density	TN Conc.	TN Storage	Depth	Bulk density	TN Conc.	TN Storage	Depth	Bulk density	TN Conc.	TN*
	cm	g cm ⁻³	g Nkg ⁻¹	kg N m ⁻²	cm	g cm ⁻³	g Nkg ⁻¹	kg N m ⁻²	cm	g cm ⁻³	g Nkg ⁻¹	kg N m ⁻²
Cell-5A												
5A-112	8	0.11	29.0	0.27	8.0	0.3	28.1	0.64	15	0.4	28.6	1.51
5A-112(a)	5	0.12	28.3	0.17	8.0	0.3	27.6	0.69	15	0.3	28.7	1.47
5A-112(b)	8	0.08	27.7	0.18	8.0	0.3	24.6	0.56	15	0.4	28.9	1.67
5A-150	16	0.05	33.9	0.28	10.0	0.3	35.6	1.15	15	0.2	38.8	1.36
5A-74	--	--	--	--	16.0	0.4	28.6	1.69	15	0.3	34.0	1.73
SAV												
Cell-3												
3B	8	0.18	33.5	0.47	12.0	0.3	35.8	1.34	15	0.3	35.7	1.75
3I	8	0.08	33.2	0.22	12.0	0.2	31.4	0.88	15	0.3	32.3	1.25
3I(a)	6	0.05	32.6	0.10	10.0	0.2	48.9	0.84	15	0.3	31.8	1.25
3I(b)	8	0.06	34.2	0.16	10.0	0.2	33.5	0.73	15	0.3	33.0	1.37
3P	14	0.09	30.4	0.38	10.0	0.2	31.4	0.66	15	0.3	30.3	1.34
Cell-5B												
5B-108	6	0.21	29.6	0.38	8.0	0.4	37.1	1.05	15	0.2	38.1	1.08
5B-125	5	0.14	23.9	0.16	8.0	0.3	28.9	0.61	15	0.3	32.5	1.36
5B-125(a)	6	0.13	24.9	0.20	8.0	0.3	30.3	0.68	15	0.3	31.4	1.30
5B-125(b)	5	0.10	25.5	0.12	12.0	0.3	29.8	1.19	15	0.3	31.8	1.54
5B-162	8	0.17	27.9	0.38	12.0	0.3	34.7	1.17	15	0.3	34.8	1.42
5B-202	4	0.20	30.2	0.25	8.0	0.3	33.2	0.83	15	0.3	32.6	1.35
5B-83	6	0.09	32.2	0.18	10.0	0.4	35.8	1.40	15	0.3	36.8	1.76

*For pre-STA soil, TN storages were calculated only for a 15-cm deep soil layer, assuming constant bulk density throughout the layer.

Table E-7. Depth of soil fraction, bulk density, total nitrogen concentration and TN storage for each soil fraction at sampling sites in STA-2.

STA-2		Floc			RAS				Pre-STA soil			
EAV	Depth	Bulk density	TN Conc.	TN Storage	Depth	Bulk density	TN Conc.	TN Storage	Depth	Bulk density	TN Conc.	TN* Storage
	cm	g cm ⁻³	g Nkg ⁻¹	kg N m ⁻²	cm	g cm ⁻³	g Nkg ⁻¹	kg N m ⁻²	cm	g cm ⁻³	g Nkg ⁻¹	kg N m ⁻²
Cell 1												
A103	10	0.08	25.9	0.20	8.0	0.2	29.2	0.43	15	0.1	26.7	0.56
A103 (a)	10	0.08	29.2	0.22	12.0	0.2	30.4	0.58	15	0.1	26.1	0.51
A103 (b)	12	0.07	27.3	0.24	8.0	0.1	31.8	0.36	15	0.1	28.3	0.58
A138	8	0.07	26.8	0.15	10.0	0.2	31.4	0.65	15	0.1	29.4	0.50
A172	8	0.04	28.6	0.09	8.0	0.3	31.8	0.79	15	0.1	29.9	0.54
A51	9	0.04	28.2	0.10	8.0	0.2	29.0	0.39	15	0.2	28.7	0.75
Cell 2												
B117	7	0.08	30.3	0.17	10.0	0.3	30.1	0.76	15	0.1	26.1	0.52
B151	5	0.02	28.3	0.03	12.0	0.2	29.3	0.54	15	0.2	28.5	0.75
B187	12	0.03	26.9	0.09	14.0	0.2	30.9	0.83	15	0.4	26.8	1.63
B26	4	0.02	13.2	0.01	8.0	0.4	24.5	0.75	15	0.4	27.9	1.63
B81	7	0.12	24.3	0.20	12.0	0.3	29.9	0.98	15	0.1	27.9	0.62
B98	10	0.04	24.3	0.09	8.0	0.3	29.2	0.60	15	0.1	28.9	0.47
B98(a)	6	0.07	29.2	0.13	8.0	0.2	31.3	0.50	15	0.1	27.9	0.50
B98(b)	10	0.07	28.0	0.19	8.0	0.2	29.9	0.51	15	0.1	26.8	0.35

*For pre-STA soil, TN storages were calculated only for a 15-cm deep soil layer, assuming constant bulk density throughout the layer.

Table E-7 Continued

STA-2		Floc			RAS				Pre-STA soil			
SAV	Depth	Bulk density	TN Conc.	TN Storage	Depth	Bulk density	TN Conc.	TN Storage	Depth	Bulk density	TN Conc.	TN Storage
	cm	g cm ⁻³	g Nkg ⁻¹	kg N m ⁻²	cm	g cm ⁻³	g Nkg ⁻¹	kg N m ⁻²	cm	g cm ⁻³	g Nkg ⁻¹	kg N m ⁻²
Cell 3												
C129	8	0.12	10.1	0.10	8.0	0.3	22.0	0.45	15	0.3	28.7	1.10
C165	7	0.10	16.1	0.11	12.0	0.3	30.9	1.13	15	0.2	37.8	1.25
C201	11	0.12	11.9	0.16	10.0	0.3	32.2	1.03	15	0.4	19.0	1.11
C21	5	0.13	12.0	0.08	8.0	0.5	28.5	1.04	15	0.4	19.0	1.12
C75	10	0.12	11.9	0.14	8.0	0.2	16.2	0.30	15	0.1	32.6	0.71
C75 (a)	10	0.13	11.4	0.15	12.0	0.2	17.5	0.51	15	0.2	28.1	0.84
C75 (b)	7	0.10	13.2	0.09	4.0	0.3	23.5	0.26	15	0.2	31.1	0.84
Cell 4												
D111	--	--	--	--	6.0	0.3	25.5	0.38	15	0.2	34.9	1.29
D124	--	--	--	--	8.0	0.2	30.7	0.43	15	0.3	30.5	1.59
D124 (a)	--	--	--	--	12.0	0.2	30.5	0.89	15	0.3	29.0	1.39
D124 (b)	--	--	--	--	12.0	0.3	30.2	1.06	15	0.3	30.3	1.19
D129	--	--	--	--	12.0	0.3	27.4	1.03	15	0.4	30.9	1.79
D139	--	--	--	--	12.0	0.3	28.0	1.16	15	0.4	32.2	1.82

For pre-STA soil fraction, mass N storages were calculated only for 15 cm depth, assuming constant bulk density for the entire 15 cm depth.

Table E-8. Depth of soil fraction, bulk density, total carbon concentration and TC storage for each soil fraction at sampling sites in STA-1W.

STA-1W		Floc			RAS				Pre-STA soil			
EAV	Depth	Bulk density	TC Conc.	TC Storage	Depth	Bulk density	TC Conc.	TC Storage	Depth	Bulk density	TC Conc.	TC*
Cell-5A	cm	g cm ⁻³	g Ckg ⁻¹	kg C m ⁻²	cm	g cm ⁻³	g Ckg ⁻¹	kg C m ⁻²	cm	g cm ⁻³	g Ckg ⁻¹	kg C m ⁻²
5A-112	8	0.11	3.8	412.5	8.0	0.3	10.2	448.1	15	0.4	25.3	478.5
5A-112(a)	5	0.12	2.4	399.7	8.0	0.3	11.2	450.9	15	0.3	24.3	475.2
5A-112(b)	8	0.08	2.6	391.1	8.0	0.3	8.9	385.9	15	0.4	27.4	473.3
5A-150	16	0.05	3.2	397.0	10.0	0.3	15.7	483.8	15	0.2	17.5	499.4
5A-74					16.0	0.4	23.2	391.5	15	0.3	23.6	464.1
SAV												
Cell-3												
3B	8	0.18	6.7	476.2	12.0	0.3	19.0	509.3	15	0.3	25.3	516.6
3I	8	0.08	2.8	416.7	12.0	0.2	12.7	454.5	15	0.3	18.8	483.0
3I(a)	6	0.05	1.1	368.4	10.0	0.2	11.3	661.4	15	0.3	18.9	479.2
3I(b)	8	0.06	2.0	426.3	10.0	0.2	9.6	440.9	15	0.3	20.1	483.3
3P	14	0.09	5.7	458.5	10.0	0.2	10.2	482.7	15	0.3	21.9	496.4
Cell-5B												
5B-108	6	0.21	4.8	377.5	8.0	0.4	13.0	460.8	15	0.2	13.9	488.7
5B-125	5	0.14	2.0	296.6	8.0	0.3	8.7	411.8	15	0.3	19.6	470.7
5B-125(a)	6	0.13	2.6	328.3	8.0	0.3	10.2	454.5	15	0.3	19.7	474.4
5B-125(b)	5	0.10	1.8	379.1	12.0	0.3	18.6	464.3	15	0.3	23.1	476.0
5B-162	8	0.17	4.5	334.9	12.0	0.3	15.9	469.7	15	0.3	19.7	483.9
5B-202	4	0.20	3.3	398.8	8.0	0.3	11.9	472.8	15	0.3	20.6	496.1
5B-83	6	0.09	2.1	379.3	10.0	0.4	17.4	446.2	15	0.3	21.5	448.9

*For pre-STA soil, TC storages were calculated only for a 15-cm deep soil layer, assuming constant bulk density throughout the layer.

Table E-9. Depth of soil fraction, bulk density, total carbon concentration and TC storage for each soil fraction at sampling sites in STA-2.

STA-2		Floc			RAS				Pre-STA soil			
EAV	Depth	Bulk density	TC Conc.	TC Storage	Depth	Bulk density	TC Conc.	TC Storage	Depth	Bulk density	TC Conc.	TC*
Cell1	cm	g cm ⁻³	g Ckg ⁻¹	kg C m ⁻²	cm	g cm ⁻³	g Ckg ⁻¹	kg C m ⁻²	cm	g cm ⁻³	g Ckg ⁻¹	kg C m ⁻²
A103	10	0.08	2.6	342.8	8.0	0.2	6.5	445.8	15	0.1	9.5	453.6
A103 (a)	10	0.08	2.9	377.2	12.0	0.2	8.4	441.2	15	0.1	8.9	458.6
A103 (b)	12	0.07	3.0	354.0	8.0	0.1	4.9	436.4	15	0.1	9.6	469.2
A138	8	0.07	2.3	411.6	10.0	0.2	9.3	450.3	15	0.1	8.3	484.6
A172	8	0.04	1.2	379.6	8.0	0.3	11.0	442.8	15	0.1	8.5	473.4
A51	9	0.04	1.4	377.0	8.0	0.2	5.7	426.1	15	0.2	12.5	478.7
Cell 2												
B117	7	0.08	2.4	429.8	10.0	0.3	11.6	457.1	15	0.1	9.6	481.4
B151	5	0.02	0.4	406.9	12.0	0.2	8.3	448.2	15	0.2	12.5	475.5
B187	12	0.03	1.4	401.6	14.0	0.2	12.3	457.1	15	0.4	29.1	476.4
B26	4	0.02	0.2	223.2	8.0	0.4	12.6	415.3	15	0.4	27.6	474.4
B81	7	0.12	2.9	345.9	12.0	0.3	15.0	456.8	15	0.1	11.0	494.0
B98	10	0.04	1.3	343.0	8.0	0.3	9.1	441.0	15	0.1	7.5	457.2
B98(a)	6	0.07	1.7	384.5	8.0	0.2	6.9	435.8	15	0.1	8.5	472.0
B98(b)	10	0.07	2.5	382.9	8.0	0.2	7.5	444.5	15	0.1	6.0	465.0

*For pre-STA soil, TC storages were calculated only for a 15-cm deep soil layer, assuming constant bulk density throughout the layer.

Table E-9 continued.

STA-2		Floc			RAS				Pre-STA soil			
SAV	Depth	Bulk density	TC Conc.	TC Storage	Depth	Bulk density	TC Conc.	TC Storage	Depth	Bulk density	TC Conc.	TC*
Cell 3	cm	g cm ⁻³	g Ckg ⁻¹	kg C m ⁻²	cm	g cm ⁻³	g Ckg ⁻¹	kg C m ⁻²	cm	g cm ⁻³	g Ckg ⁻¹	kg C m ⁻²
C129	8	0.12	1.7	175.8	8.0	0.3	7.5	368.7	15	0.3	16.0	416.6
C165	7	0.10	1.6	237.3	12.0	0.3	16.0	438.8	15	0.2	14.4	436.3
C201	11	0.12	2.7	199.3	10.0	0.3	14.6	456.8	15	0.4	14.0	239.1
C21	5	0.13	1.4	205.6	8.0	0.5	16.3	446.4	15	0.4	15.5	264.2
C75	10	0.12	2.1	181.0	8.0	0.2	4.9	263.0	15	0.1	10.1	465.1
C75 (a)	10	0.13	2.3	178.5	12.0	0.2	8.2	281.1	15	0.2	13.5	452.2
C75 (b)	7	0.10	1.4	195.7	4.0	0.3	4.1	375.3	15	0.2	12.3	455.0
Cell 4												
D111	--	--	--	--	6.0	0.3	4.8	318.6	15	0.2	17.9	486.8
D124	--	--	--	--	8.0	0.2	5.9	416.9	15	0.3	23.4	449.5
D124 (a)	--	--	--	--	12.0	0.2	12.5	429.8	15	0.3	21.4	447.3
D124 (b)	--	--	--	--	12.0	0.3	15.2	433.6	15	0.3	18.1	461.0
D129	--	--	--	--	12.0	0.3	14.3	380.6	15	0.4	25.8	445.6
D139	--	--	--	--	12.0	0.3	15.7	378.8	15	0.4	25.7	452.8

*For pre-STA soil, TC storages were calculated only for a 15-cm deep soil layer, assuming constant bulk density throughout the layer.

Table E-10. Average total phosphorus concentration and TP storage for each soil fraction over all sampling sites in EAV and SAV cells of STA-1W. [Mean \pm 1 SD; N= number of samples]

STA-1W		Floc		RAS		Pre-STA soil			
	N	TP Conc. mg P kg ⁻¹	TP Storage g P m ⁻²	N	TP Conc. mg P kg ⁻¹	TP Storage g P m ⁻²	N	TP Conc. mg P kg ⁻¹	TP Storage g P m ⁻²
EAV									
Cell-5A	4	1244 \pm 123	9.3 \pm 2.2	5	532 \pm 227	17.8 \pm 13.3	5	384 \pm 122	19.7 \pm 7.9
SAV									
Cell-3	5	898 \pm 427	5.8 \pm 1.8	5	578 \pm 332	12.8 \pm 4.6	5	204 \pm 13	8.7 \pm 1.3
Cell-5B	7	924 \pm 176	8.1 \pm 3.9	7	509 \pm 125	15.5 \pm 6.6	7	364 \pm 108	15.5 \pm 6.5

Table E-11. Average total phosphorus concentration and TP storage for each soil fraction over all sampling sites in EAV and SAV cells of STA-2 [Mean \pm SD; N= number of samples]

STA-2		Floc		RAS		Pre-STA soil			
	N	TP Conc. mg P kg ⁻¹	TP Storage g P m ⁻²	N	TP Conc. mg P kg ⁻¹	TP Storage g P m ⁻²	N	TP Conc. mg P kg ⁻¹	TP Storage g P m ⁻²
EAV									
Cell 1	6	1059 \pm 221	6.2 \pm 2.4	6	340 \pm 146	5.7 \pm 2	6	177 \pm 11	3.6 \pm 0.7
Cell 2	8	1125 \pm 278	4.7 \pm 3.3	8	416 \pm 78	9.8 \pm 3.2	8	212 \pm 55	6.8 \pm 5.9
SAV									
Cell 3	7	766 \pm 293	7.5 \pm 3.9	7	532 \pm 170	13.5 \pm 5.4	7	292 \pm 65	11.5 \pm 6.6
Cell 4	--	--	--	6	696 \pm 146	18.8 \pm 5.4	6	347 \pm 155	17.1 \pm 9.5

Table E-12. Average total nitrogen concentration and TN storage for each soil fraction over all sampling sites in EAV and SAV cells of STA-1W. [Mean \pm SD; N= number of samples]

STA-1W		Floc		RAS		Pre-STA			
		TN Conc.	TN Storage		TN Conc.	TN Storage		TN Conc.	TN Storage
EAV	N	g Nkg ⁻¹	kg N m ⁻²	N	g Nkg ⁻¹	kg N m ⁻²	N	g Nkg ⁻¹	kg N m ⁻²
Cell-5A	4	29.7 \pm 2.8	0.22 \pm 0.05	5	28.9 \pm 4.1	0.95 \pm 0.48	5	31.8 \pm 4.5	1.55 \pm 0.15
SAV									
Cell-3	5	32.8 \pm 1.4	0.27 \pm 0.16	5	36.2 \pm 7.3	0.89 \pm 0.27	5	32.6 \pm 2	1.39 \pm 0.21
Cell-5B	7	27.7 \pm 3.1	0.24 \pm 0.1	7	32.8 \pm 3.2	0.99 \pm 0.29	7	34 \pm 2.6	1.4 \pm 0.21

Table E-13. Total nitrogen concentration and TN storage for each soil fraction over all sampling sites in EAV and SAV cells of STA-2. [Mean \pm SD; N= number of samples]

STA-2		Floc		RAS		Pre-STA			
		TN Conc.	TN Storage		TN Conc.	TN Storage		TN Conc.	TN Storage
EAV	N	g Nkg ⁻¹	kg N m ⁻²	N	g Nkg ⁻¹	kg N m ⁻²	N	g Nkg ⁻¹	kg N m ⁻²
Cell 1	6	27.7 \pm 1.2	0.17 \pm 0.06	6	30.6 \pm 1.3	0.53 \pm 0.17	6	28.2 \pm 1.5	0.57 \pm 0.09
Cell 2	8	25.6 \pm 5.4	0.11 \pm 0.07	8	29.4 \pm 2.1	0.68 \pm 0.18	8	27.6 \pm 0.9	0.81 \pm 0.52
SAV									
Cell 3	7	12.4 \pm 1.9	0.12 \pm 0.03	7	24.4 \pm 6.3	0.67 \pm 0.38	7	28 \pm 6.9	0.99 \pm 0.2
Cell 4		--	--	6	28.7 \pm 2.1	0.82 \pm 0.33	6	31.3 \pm 2	1.51 \pm 0.27

Table E-14. Total carbon concentration and TC storage for each soil fraction over all sampling sites in EAV and SAV cells of STA-1W. [Mean \pm SD; N= number of samples]

STA-1W		Floc		RAS		Pre-STA			
		TC Conc.	TC Storage		TC Conc.	TC Storage		TC Conc.	TC Storage
	N	g C kg ⁻¹	kg C m ⁻²	N	g C kg ⁻¹	kg C m ⁻²	N	g C kg ⁻¹	kg C m ⁻²
EAV	N			N			N		
Cell-5A	4	400 \pm 9	3 \pm 0.6	5	432 \pm 42	13.8 \pm 5.8	5	478 \pm 13	23.6 \pm 3.7
SAV									
Cell-3	5	429 \pm 42	3.7 \pm 2.4	5	510 \pm 89	12.6 \pm 3.8	5	492 \pm 15	21 \pm 2.7
Cell-5B	7	356 \pm 37	3 \pm 1.2	7	454 \pm 21	13.7 \pm 3.7	7	477 \pm 15	19.7 \pm 2.9

Table E-15. Total carbon concentration TC and storage for each soil fraction over all sampling sites in EAV and SAV cells of STA-2. [Mean \pm SD; N= number of samples]

STA-2		Floc		RAS		Pre-STA			
		TC Conc.	TC Storage		TC Conc.	TC Storage		TC Conc.	TC Storage
	N	g C kg ⁻¹	kg C m ⁻²	N	g C kg ⁻¹	kg C m ⁻²	N	g C kg ⁻¹	kg C m ⁻²
EAV	N			N			N		
Cell 1	6	374 \pm 24	2.2 \pm 0.8	6	440 \pm 8	7.6 \pm 2.3	6	470 \pm 12	9.6 \pm 1.6
Cell 2	8	365 \pm 64	1.6 \pm 1	8	444 \pm 14	10.4 \pm 2.9	8	474 \pm 11	14 \pm 9.1
SAV									
Cell 3	7	196 \pm 21	1.9 \pm 0.5	7	376 \pm 79	10.2 \pm 5.3	7	390 \pm 96	13.7 \pm 2
Cell 4	--	--	--	6	393 \pm 44	11.4 \pm 4.8	6	457 \pm 16	22.1 \pm 3.5

Table E-16. Pearson correlation coefficients for select parameters measured in soil cores from EAV cells of STA-1W. All correlations were evaluated at $\alpha=0.05$ (N=14). ns= not significant.

STA-1W EAV	Bulk density	TP	Ca	Mg	Fe	Al	Pi	TN	TC	Po	LOI
TP	-0.86										
Ca	ns	ns									
Mg	ns	ns	0.93								
Fe	0.77	-0.62	ns	ns							
Al	0.88	-0.64	ns	ns	0.77						
Pi	-0.50	0.73	0.61	0.56	ns	ns					
TN	ns	ns	-0.81	-0.91	ns	ns	-0.51				
TC	0.64	-0.86	-0.73	-0.64	0.51	ns	-0.81	0.53			
Po	-0.88	0.89	ns	ns	-0.66	-0.76	ns	ns	-0.61		
LOI	ns	-0.69	-0.82	-0.70	ns	ns	-0.71	0.51	0.94	-0.45	
Pr	-0.80	0.79	ns	ns	-0.59	-0.72	0.54	ns	-0.67	0.68	-0.48

Table E-17. Pearson correlation coefficients for select parameters measured in soil cores from SAV cells of STA-1W. All correlations were evaluated at $\alpha=0.05$ (N=36). ns= not significant.

STA-1W SAV	Bulk density	TP	Ca	Mg	Fe	Al	Pi	TN	TC	Po	LOI
TP	-0.65										
Ca	ns	0.53									
Mg	ns	ns	0.52								
Fe	0.74	-0.71	-0.43	-0.46							
Al	0.66	-0.57	ns	ns	0.73						
Pi	-0.43	0.90	0.79	0.38	-0.62	-0.37					
TN	ns	ns	-0.42	-0.35	ns	ns	-0.35				
TC	0.30	-0.56	-0.67	-0.32	0.46	0.32	-0.72	0.79			
Po	-0.62	0.77	ns	ns	-0.48	-0.42	0.53	ns	-0.29		
LOI	0.40	-0.78	-0.90	-0.48	0.67	0.47	-0.92	0.45	0.78	-0.30	
Residual P	-0.52	0.86	0.40	ns	-0.54	-0.58	0.73	ns	-0.49	0.67	-0.65

Table E-18. Pearson correlation coefficients for select parameters measured in soil cores from EAV cells of STA-2. All correlations were evaluated at $\alpha=0.05$ (N=42). ns= not significant.

STA-2	EAV	Bulk density	TP	Ca	Mg	Fe	Al	Pi	TN	TC	Po	LOI
	TP	-0.48										
	Ca	ns	0.37									
	Mg	ns	ns	0.58								
	Fe	0.32	-0.67	ns	0.38							
	Al	0.37	-0.47	ns	0.36	0.47						
	Pi	-0.33	0.83	0.56	ns	-0.41	ns					
	TN	ns	-0.27	-0.61	-0.67	ns	ns	-0.54				
	TC	0.44	-0.77	-0.73	-0.41	0.42	0.28	-0.83	0.65			
	Po	-0.49	0.92	ns	-0.40	-0.69	-0.52	0.63	ns	-0.55		
	LOI	0.33	-0.64	-0.84	-0.55	0.27	ns	-0.80	0.76	0.95	-0.37	
	Residual P	-0.36	0.81	0.51	ns	-0.49	ns	0.74	-0.26	-0.73	0.69	-0.65

Table E-19. Pearson correlation coefficients for select parameters measured in soil cores from SAV cells of STA-2. All correlations were evaluated at $\alpha=0.05$ (N=33). ns= not significant.

STA-2	SAV	Bulk density	TP	Ca	Mg	Fe	Al	Pi	TN	TC	Po	LOI
	TP	-0.45										
	Ca	-0.62	0.65									
	Mg	-0.34	0.56	0.65								
	Fe	0.65	-0.39	-0.69	-0.49							
	Al	0.69	-0.40	-0.64	-0.47	0.69						
	Pi	-0.37	0.86	0.69	0.43	-0.37	ns					
	TN	0.48	-0.55	-0.82	-0.47	0.64	0.35	-0.70				
	TC	0.48	-0.59	-0.77	-0.49	0.60	ns	-0.71	0.96			
	Po	ns	ns	ns	ns	0.33	ns	ns	0.32	ns		
	LOI	0.38	-0.40	-0.72	-0.43	0.46	0.34	-0.59	0.85	0.86	ns	
	Residual P	-0.41	0.76	0.44	0.40	ns	-0.30	0.57	-0.39	-0.44	0.50	-0.36

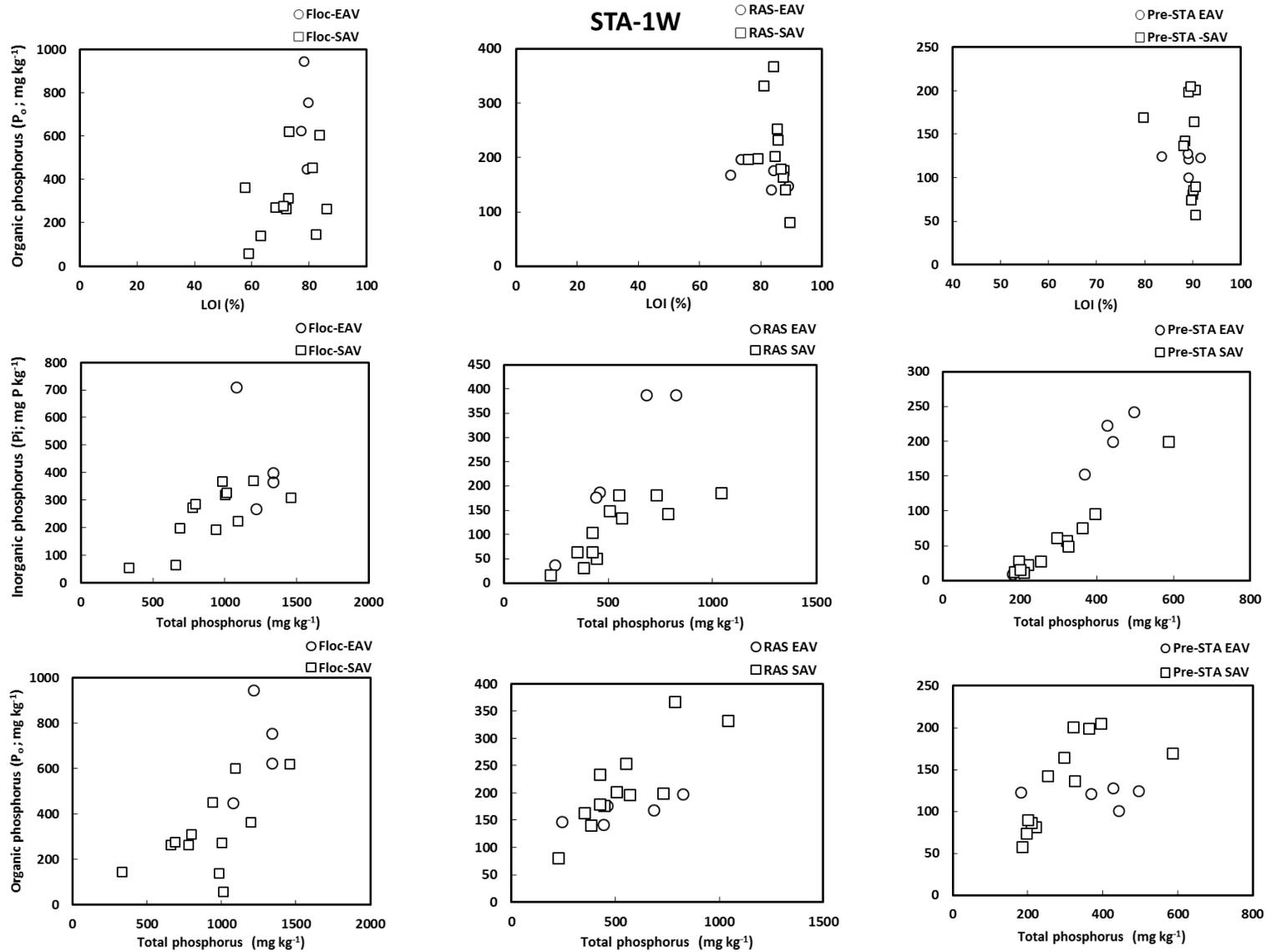


Figure E-1. Relation of TP with P_o and P_i and LOI with P_o in floc, RAS and pre-STA soil from EAV and SAV cells of STA-1W.

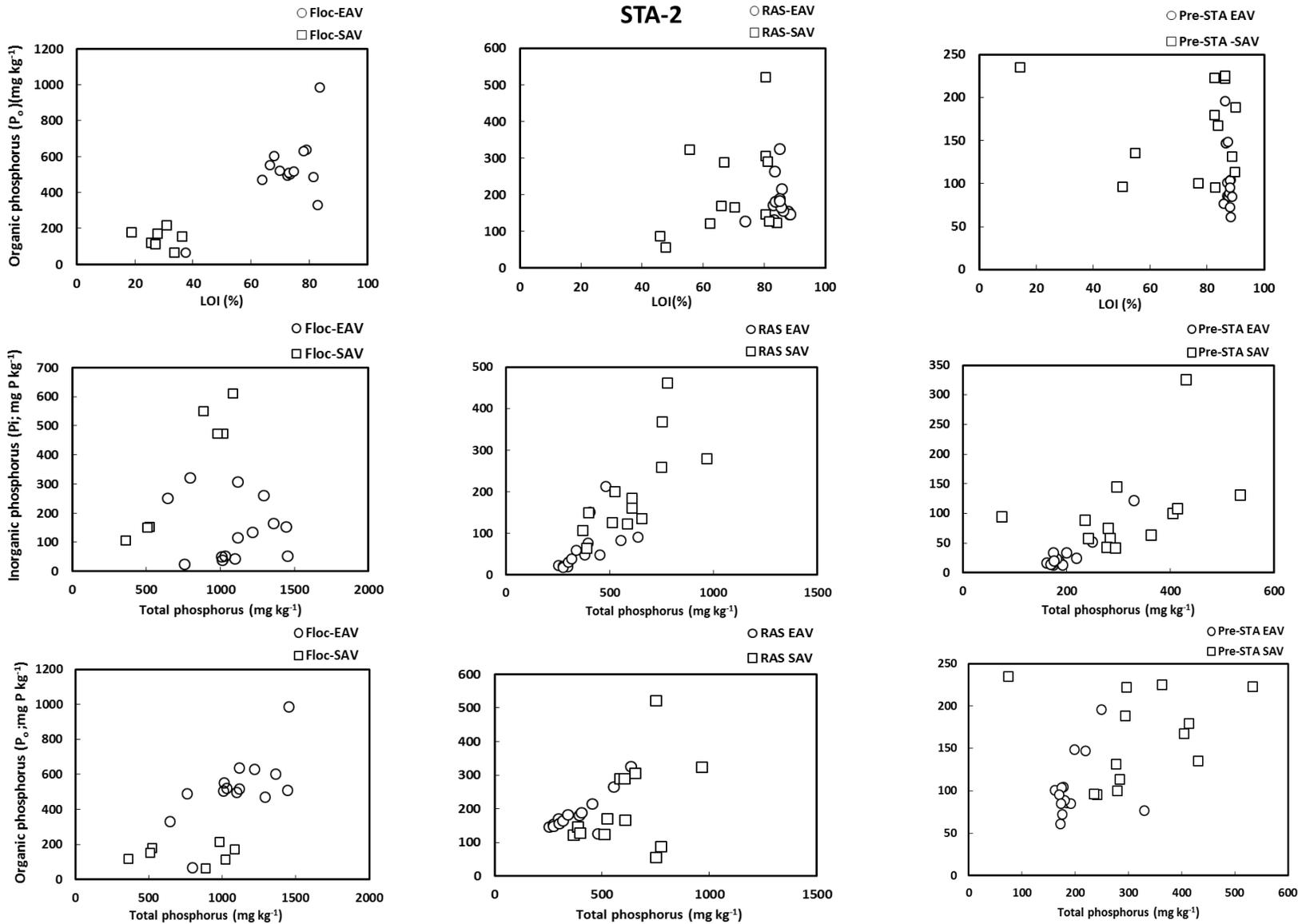


Figure E-2. Relation of TP with P_o and P_i and LOI with P_o in floc, RAS and pre-STA soil from EAV and SAV cells of STA-2.

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BIOGRAPHICAL SKETCH

Rupesh Kumar Bhomia was born in a small town – Pilani, in the state of Rajasthan, India. His early childhood and education was spread across various locations in northern India as his father's changed jobs from one paper manufacturing unit to another. Those paper mills were generally located in the rural-forested regions of the country and growing in the shadow of those tall smoke stacks, Rupesh developed a curious desire to study-learn more about natural environment at an early age. That desire was officially fulfilled in 2001 when he enrolled for a M.Sc. program at the School of Environmental Sciences, Jawaharlal Nehru University, New Delhi. He then had the privilege to attend Worcester College, Oxford University; graduating in 2004 with M.Sc. in Biodiversity, Conservation and Management. He returned to India and was employed at the Indian Institute of Forest Management (IIFM), Bhopal where he managed a project on Sustainable Forest Management. In mid-2005, he joined a non-governmental organization - WWF-India based in New Delhi. While at the Forests Division of WWF-India, he managed multiple projects on Protected Area management, ecotourism and sustainable livelihoods, and conducted forest officers training workshops. In 2008, he was recruited by Dr. K. R. Reddy in the Wetlands Biogeochemistry Laboratory, at the University of Florida. This dissertation is the centerpiece of his rewarding academic journey since then!