Impacts of Soil Heavy Metal Contamination on Methane Flux and the Primary Production of Phragmites australis

Adam G. Piombino

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Abstract: Liberty State Park in Jersey City, NJ, a mixed landscape encompassing areas of freshwater wetlands, was the site of an abandoned train yard and contains several areas in which soil concentrations of As, Cr, Cu, Pb, V and Zn occur above ambient levels of New Jersey soil. Human population growth and expanding urbanization are both placing an increased amount of stress on wetland environments. Methane, a greenhouse gas is both produced and consumed by the respiration of microorganisms in the soil. The methane flux rate and direction might be impacted by soil metal contamination. This variation could have broad implications for climate change. A field study and a laboratory study were conducted to study the effect of metal contamination on soil methane flux. Five study sites with varying levels of heavy metal pollution dominated with the common reed Phragmites australis were examined. The field study used portable air chambers to collect gas samples for a comparative analysis. For the laboratory study, sections of soil and Phragmites australis from each site were also transported to a MSU greenhouse to study the metals contamination’s effects in a controlled setting. Air samples from the greenhouse study were taken using the same gas chamber technique. Methane concentrations are examined using gas chromatography with a flame ionization detector. Methane flux was found to be high with methane being emitted from the soil to the atmosphere at the wetland sites with low soil metal contamination. Methane flux was lower with methane being taken in to the soil from the atmosphere at the upland sites with high soil metal load. Metal concentrations distressing soil microbes and the site hydrology may have produced these outcomes. The primary production and energy allocation of Phragmites australis was also examined at the five Liberty State Park study sites. The primary production of Phragmites australis was decreased at sites with higher metal load with more energy being allocated to below ground biomass production.
IMPACTS OF SOIL HEAVY METAL CONTAMINATION ON METHANE FLUX AND THE PRIMARY PRODUCTION OF *PHRAGMITES AUSTRALIS*

A THESIS

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For the degree of Environmental Studies, Master of Arts

by

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Montclair, NJ

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Chapter 1
Introduction

Methane Flux

Atmospheric trace gas concentrations (H₂, CO, CH₄, N₂O, NO, etc.) have been increasing over the last century, affecting the global climate (USEPA 2012, Hanson 1996). Sources of trace gases or “greenhouse gasses” can be both natural and anthropogenic (Sishra 1999, Saari 1994). Methane is a significant greenhouse gas, for which soil processes have been identified as major sources and occasional sinks (Solomon et al., 2007). Anthropogenic impacts on soils and wetlands may be affecting the rate and direction of gas flux. Land modification by human development and contamination from point and non-point sources, has driven changes to soil chemistry and the biosphere (Mishra et al. 1998). These land-use changes affect the surface sources and uptake of climatically active atmospheric trace gases, as well as other surface-based climate processes, biodiversity, food security and carbon storage in soils (Brasseur et al., 2003, Solomon et al., 2007).

Methane gas, which is known to contribute to global climate change, is both produced and consumed by the respiration and assimilation of microorganisms in the soil. Microorganisms break-down organic carbon to inorganic end products (Sutton-Grier et al. 2011). Aerobic methanotrophic microbial communities in aerated soils are the planets largest biological sink for atmospheric methane. Wetland soils tend to be anoxic and support the production of trace gases by anaerobic bacteria such as fermenters, methanogens, acetogens, sulfate reducers, and denitrifiers (USEPA 2010). While most other gasses are typically intermediates, methane is the dominant gaseous product of anaerobic degradation of organic matter by soil microbes (Conrad 1996). Metabotropic microbes consume one-carbon compounds as an energy and carbon source.
Methane that is created in anaerobic environments which is not oxidized by methanotrophs, releases into the atmosphere (Hanson 1996).

Soil to atmospheric methane flux can be summarized as the result of the balance between two offsetting processes; methanogenesis (microbial production under anaerobic conditions) and methanotrophy (aerobic microbial consumption) (Kim, Dong-Gil, et al., 2010). Biogenic methane is the end product of anaerobic methanogen microbial activity (Berestovskaya 2003). Methane uptake in soils occurs through aerobic methanotrophic microorganisms that are able to utilize methane as a source of both energy and carbon (Le Mer et al. 2001). Methanotrophy has been identified as the dominant process in upland soils, where oxidation generally exceeds production with a resulting net uptake of atmospheric methane by soil (Le Mar et al. 2001).

In wetland environments there are two major physiological groups of methanogens based on substrate utilization; acetoclastic methanogens convert acetate into CH₄ and CO₂, while hydrogenotrophic methanogens convert CO₂ and hydrogen (H₂) into CH₄ and water (Godin et al. 2012). A “significant percentage of the produced methane is oxidized by methanotrophic bacteria at anoxic-oxic interfaces such as the soil surface and the root surface of aquatic plants that serve as conduits for O₂ transport into and CH₄ transport out of the wetland soils” (Conrad 1996). In anaerobic soils, methanogenesis occurs as the final step of anoxic organic matter decomposition and its rate is dependent on substrate availability, soil pH, temperature, water table position, soil redox potential, and vegetation type and density (Mohanty 2000, Singh 2000). Methanogenesis also varies seasonally due to fluctuations in the water table and soil temperature (Bloom et al. 2012). Vegetation coverage is shown to increase methane output compared with similar un-vegetated sites (Singh et al. 2000).
Several studies have focused on the difference in methane flux between varying landscapes. Forest soils are the most active sink of methane, followed by grass lands and cultivated soils, and the methane uptake potential of many upland soils is reduced by cultivation and application of ammonium N fertilizer (Kim, Dong-Gil, et al. 2010). Laboratory studies of potential oxidation rates measured in soil slurries usually exceed the rates of potential methanogenesis and it is generally assumed that most methane produced is recycled and does not reach the atmosphere (Segers 1998). Soils with high methane oxidation actively serve as methane sink (Freitag, et al. 2010). Nevertheless, individual site-to-site specific estimates of the proportion of methane produced that escapes oxidation and is released into the atmosphere vary widely. This causes of this variation is still unknown however, vegetation type and hydrological conditions are known to be major controlling factors (Freitag, et al. 2010). Diurnal methane flux patterns are not as plainly observable, however one study suggest that higher methane flux occurs during the day time due to differences in the physical processes of gas transport because of atmospheric instability (Lai et al. 2012). Methane flux rates are higher in the warmer months then during the colder periods (Singh et al. 2000).

Portable and static trace gas chambers have been widely used to measure gas fluxes. Chamber methods measure gas concentrations in a head space resulting from small, well defined areas (Lai et al. 2012). Manual chambers have been used more extensively than automated chamber designs in trace gas flux analysis (Lai et al. 2012). Static chambers can be flooded during high precipitation events or irrigation and can also easily facilitate algal growth on the soil surface due to high humidity within the chamber (Sainju et al. 2012). Ambient windy conditions have been shown to underestimate calculated methane flux rates during short deployment times, however with deployments over 13 min or longer the effects were abated (Lai
et al. 2012). Manual chambers must be moved to and from the location site for every sampling event leading to shorter deployment periods. Shorter chamber deployment period can increase the uncertainty of flux calculation and the difficulty of obtaining a detectable flux (Lai et al. 2012). Monthly sampling and sampling periods of 30 min have been shown to accurately access methane flux rates (Singh et al. 2000, Sha, et al 2011).

Soil Metal Contamination

Wetlands and natural areas along the east coast of the United States have been exploited for commercial gains and altered by man for over 200 years. The New York- New Jersey area is part of a highly urbanized estuary system developed to maximize economic production in the densely developed areas along the Hudson River, New York Bight, and Newark Bay. Although lakeshore wetland ecosystems can perform a string of ecological functions, such as wildlife habitat, water purification and filtration, buffer zone, erosion protection, and so on, most of them have been reclaimed or occupied by humans for economic benefits (Bai et al. 2009).

In many areas urban soils contain trace metals, typically cadmium (Cd), copper (Cu), zinc (Zn), lead (Pb) and others, above established screening criteria (Gallagher et al 2008). The concentrations and the form of heavy metals in soils and the behavior of their free ions in soils solution are influenced by soil pH, organic matter content (TOC), cation exchange capacity (CEC), and clay mineralogy (Pavel et al. 2012). Many urban brownfields display heterogeneous distribution of soil metal contamination with localized areas containing high loading (Gallagher et al 2008).
Soil microorganisms play many important roles within an ecosystem. They are critical to soil productiveness, primary production, nutrient cycling, and decomposition (Oliveira 2006). Some heavy metals, deemed micronutrients, are essential for growth and are required by microorganisms at low concentrations. These include cobalt, chromium, nickel, iron, manganese, zinc, etc. (Pavel et al. 2012). Toxic effects of heavy metals on microorganisms have also been observed since the early twentieth century (Lipman and Burgess 1914). High concentrations of micronutrient metals are toxic to microbes and can inhibit metabolism and change growth characteristics (Giller et al. 1998). Other heavy metals such as arsenic, cadmium, mercury, and lead have little or no biological role and can be detrimental even at low concentrations (Pavel et al. 2012).

Soil heavy metal contamination has been shown to impact the growth and morphology of soil microbes (Giller et al. 1998; Pavel et al. 2012). Decreases in soil microbial biomass linked to changes in group make-up all result from metal toxicity (Giller et al 2009). Bioavailability and the sensitivity of microbes are the two main factors that contribute to the chronic toxicity effects of heavy metals to soil microbes (Giller et al. 2009). Bioavailability can be influenced by pH and soil textural properties, which impact the soil effective cation exchange capacity (eCEC) (Smolders et al. 2009). Increases in the eCEC cause a linear decrease in the toxicity of heavy metals on soil microbes (Giller et al. 2009).

Arsenic toxicity is the result of its similarity to phosphorus and its capability to bond with sulfur covalently (Tamaki 1992). This can lead to the interference of protein phosphorylation, and an interference with protein synthesis. Arsenic detoxification is closely linked to the biological processes of methanogenic bacteria within anaerobic environments (Tamaki 1992).
Arsenate may be reduced to arsenite, and then transformed to dimethylarsine through methylation (Tamaki 1992).

Chromium mostly exists within soil systems as insoluble Cr(OH)$_3$.aq or as soil absorbable Cr(III). In these forms Chromium uptake by plants and leaching does not occur. The toxic effects of Chromium on microorganisms are resultant from its ability to diffuse through the cell membrane and powerful oxidation potential. Chromium can inhibit microbial activity, and soil microbial transformations such as nitrification.

Lead contamination is widely found in heavy populated and industrial areas due to its historical use in fuels, paints and many other products (USEPA 2013). Lead is known to have very toxic effects on animals, however less is known about its effects on microorganisms. Lead contamination has been shown to reduce soil microbial biomass (USEPA 2013).

Zinc is commonly found within many contaminated systems due to its high solubility over a large pH range (Moberly, et al 2010). It is a micronutrient that is a significant structural element for many proteins (Berg et al 1996). Toxic effects are thought to result from the replacement by Zinc of other crucial ions from cellular sites, and also from the blocking of other important molecules (Moberly, et al. 2010). Zinc speciation has a large impact on its toxicity (Moberly, et al. 2010; Morton, et al. 2000).

Copper is an essential element to all life but can inhibit microbial activity at higher concentrations. Copper ions have the ability to chelate sulfhydryl groups, affecting a cells proteins or enzymes (Ochoa-Herrera, et al. 2011). Studies have shown significant variation in the inhibitory levels of copper to methanogens ranging from 2.2 mg L$^{-1}$ to as much as 400 mg L$^{-1}$ (Ahring et al. 1985; Mori et al. 2000; Karri et al. 2006).
Plants within urban brownfield can absorb heavy metals through root tissue which can be transported through the plant by its xylem systems. (Pilon-Smith 2005). Uptake of As, Cr, Cu, and Zn has been shown at Liberty State Park (Qian et al. 2012). Heavy metals in soils are generally toxic to most plants, affecting their metabolism and growth when the heavy metal concentrations exceed the maximum permissible limit (Melo et al. 2011). In a study done at Liberty State Park, primary production of *Betula populifolia* (gray birch) was inhibited by Zn (Gallagher et al 2008).

**Invasive Species and *Phragmites australis***

The USEPA defines an invasive species as an “alien species whose introduction does or is likely to cause economic or environmental harm or harm to human health” (USEPA 2013). Many alien species will become just part of the background flora and fauna or die off but other species due to their adaptive nature will become invasive and spread (Bax 2003). Invasive species have been accidentally and purposely introduced to the United States throughout history. Invasive aquatic plants can have many negative effects on aquatic ecosystems such as reducing native populations, altering the hydrology, and changing runoff characteristics (USEPA 2013). Native plant species provide many important services, when they are replaced by invasive species these services become altered, usually diminishing.

*Phragmites australis* known as the common reed is a perennial shrub that has propagates throughout the entire United States of America, and much of Canada (USDA 2012). It is classified as a noxious weed and invasive species. *Phragmites australis* can grow to over 3 meters in height. The plant is made up of a long stem with elongated leaves and a bushy flower
at the top of the stem. *Phragmites australis* grows in dense stands spreading horizontally through a network of rhizomes. The plants can quickly take over native wetland species, altering marsh hydrology and wildlife habitat (USNPS 2010). Alterations to wetland habitat caused by *Phragmites australis* can increase the potential for wild fires as well as reducing the productivity of wetland environments for other wildlife (US National Park Service 2010).

*Phragmites australis* has a wide range of tolerances to environmental conditions. It can thrive in fresh or brackish water and can tolerate high salinity and a pH range of 4.8-8.2 (Robinson 2002). *Phragmites australis* prefers a water table ranging from 15cm above to 15cm below ground level, and calm water over faster flowing water. It can also tolerate poorly aerated waters because of the air spaces in its above ground sections of its roots and rhizomes with allow for the transport of air down to the roots. Invasive non-native European strains of *Phragmites australis* which were first introduced in the late 1700’s or early 1800’s have been replacing *Typha* spp and *Spartina alterniflora* in the Atlantic Region of the United States causing ecological change (Kerrie et al. 2003, US National Park Service 2010). *Phragmites australis* monoculture stands are may be a major source of trace gas emissions, and may be more important in that respect than other vegetation types because of its high rates of internal convective flow (Brix et al. 1996).
Chapter 2

Liberty State Park Study Area

Liberty State Park

This study was conducted at Liberty State Park (LSP), Jersey City, New Jersey (Figure 1). The site is located on the west bank of Upper New York Bay (centered at 40°42'14"N; 74°03'14"W) (Figure 1) (Gallagher et al. 2011). LSP has a rich history, neighboring The Statue of Liberty and Ellis Island. Prior to its development the area was an intertidal mud flat and salt marsh (Gallagher et al. 2011). The site was filled using refuse and construction debris from New York City (Figure 2). The surface was stabilized for use as a rail yard with cinder and ash as was typical in the time (Gallagher et al. 2011). The Central Railroad of New Jersey used the land as a railroad yard for over a century until they closed in 1969. Industrial goods such as coal were stored and transported at the site.

Due to its history total soil metal load (TSML) shows significant local variation throughout the site (Figure 4). In many areas metal concentration are below the minimum detectable limit while in other places metal concentrations exceed the USEPA: Maximum Acceptable Toxic Concentration. The specific sites chosen for this study contain different types of vegetative assemblage and varying levels of TSML. A survey of the TSML at Liberty State Park was conducted in 2005 (Gallagher et al. 2008.) Since the rail yard closed in 1967 the site has remained inaccessible and mostly untouched. The 251 acre LSP study site is a fenced off undeveloped section surrounded by approximately 1100 acres of NJ State Park land that is open to the public. The study section is unevenly comprised by early successional forest, shrub lands,
and wetlands dominated by *Phragmites australis* (Figure 3). The complete vegetative assemblage of the area was surveyed by the United States Army Corps of Engineers in 2004.

Several studies have been conducted on Liberty State Park. Soil metal concentrations were assessed and found to be above ambient conditions in several areas unevenly spread across the study area (Gallagher et al. 2008). The translocation of heavy metals into the vegetation was also studied. Several tree species *Betula populifolia* and *Populus deltoids*, were found to be accumulating Zn in leaf tissue at high levels, while *B. populifolia*, *P. deltoides* and *Rhus copallinum* were found to accumulate Cr in the root tissue (Gallagher et al. 2008). A comparison of soil metal load and vegetation assemblage showed that areas with higher metal load were dominated by sessional northern hardwood, while semi-emergent marshes containing mostly endemic species were limited largely to areas of low soil metal load (Gallagher et al. 2008).

The impact of soil metal contamination on the plant productivity of the tree species *Betula populifolia* was analyzed. The study showed that growth was inhibited in areas with high soil metal load, and that ecosystems functions were impaired in the areas with the highest soil metal load. (Gallagher et al. 2008*). The impact of soil metal contaminations on the vegetative assembly of Liberty State Park was examined on a coarse scale. The study demonstrated that an urban brownfield with variable soil metal load can produce a stress gradient leading to distinct vegetative assemblages with varying guild trajectories (Gallagher et al 2011).

The uptake of heavy metals by plants within Liberty State Park was examined further. The study showed higher metal accumulation in the root systems than in the areal sections with uptake varying between plant and metal species. It also demonstrated how environmental factors such as oxidation-reduction potential, pH, and organic content may impact metal uptake (Qian, et
al. 2012). Synchrotron X-ray technology was then used to examine lead and iron accumulation in the root and rhizome of Typha latifolia. Higher concentrations were found within the epidermis while lower concentrations were found within the vascular tissues. These results suggested that Typha latifolia could be used as a low cost bioremediation method to sequester metals within its root systems (Feng et al 2012).
Figure 1: Aerial Map of Liberty State Park, Jersey City, New Jersey and surrounding New York City Metropolitan area (Google Maps)
Figure 2: Aerial Map of Liberty State Park and Upper New York Bay (Google Maps)
Figure 3: Map of Liberty State Park, New Jersey with the vegetation assembling patterns for each sampling site. SNH, successional northern hardwood; SSB, successional shrub land; SOF, successional old field; MS, maritime shrub land; MG, maritime grasslands; CRM, common reed/mugwort; FFW, floodplain forested wetlands; SSW, shrub swamp wetland; SEM, shallow emergent marsh; CRW, common-reed-dominated wetland. (United States Army Corps of Engineers in 2004)
Figure 4: Soil Metal Loading at Liberty State Park with study site locations (Gallagher et al. 2011)
Data from the 2005 sampling of TMLS at liberty state park was used for this study (Gallagher et al 2008). Samples were taken in triplicate at one meter intervals at 35 different sampling sites spread around the fenced off section of LSP using a GPS mapping system. Samples were taken at the depth showing the greatest root concentrations with gravel and plant material was removed from the samples.

Arsenic (As) was found to be present in the soil at concentrations below the minimum detectable limit (0.005 µg/g⁻¹) and at concentrations up to 977.6 ± 44.3 µg/g⁻¹, (mean ± S.D.) (Gallagher et al. 2011). Chromium (Cr) was found to be present in the soil at concentrations as low as 9.7 ± 2.5 µg/g⁻¹, and as elevated as 208.8 ± 10.4 µg/g⁻¹. Copper (Cu) was found to occur in the soil at concentrations as low as 44.0 ± 2.5 µg/g⁻¹ and as high as 1870.0 ± 3155 µg/g⁻¹.

Mercury was discovered to occur at some sites in concentrations below the MDL (0.002 µg/g⁻¹) and at concentration as high as 3.6 ± 6.0 µg/g⁻¹. Lead (Pb) was found in concentrations from 86.0 ± 11.1 µg/g⁻¹ to 4640 ± 1799 µg/g⁻¹. Vanadium (v) was found to occur in the soil at concentrations below the MDL (.01 µg/g⁻¹) and at concentrations up to 193.2 ± 112.6 µg/g⁻¹.

Zinc (Zn) was present in the soil at concentrations from 80.0 ± 12.9 µg/g⁻¹ to 6501.0 ± 1491 µg/g⁻¹. (Gallagher et al 2011) More information on the TMSL is available in Table 1.

A soil metal rank (Table 1) was calculated to compare the TSML of the study sites at LSP (Gallagher et al 2008). The soil metal rank uses the concentrations of five selected metals, As, Cr, Cu, Pb, and Zn in the soil to come up with an overall rank of soil heavy metal contamination. The soil metal rank allows for a single quantity to be used to compare the metal contamination levels for each of the study sites. The log transformations of the soil metal concentration in µg/g were calculated for each metal of the five metals. These were then ranked
in ascending order. The rank was then divided by the total number to calculate the standardized rank. The standardized rank orders for each metal at a site were then added up to create the soil metal rank for each site. (Wu, et al 2006)
Table 1 - Soil Metal Load at selected study site at LSP (Gallagher et al. 2008)

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil All Metal Rank</th>
<th>As (µg/g)</th>
<th>Cr (µg/g)</th>
<th>Cu (µg/g)</th>
<th>Pb (µg/g)</th>
<th>Zn (µg/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.97</td>
<td>14</td>
<td>61</td>
<td>135</td>
<td>492</td>
<td>338</td>
</tr>
<tr>
<td>43</td>
<td>1.64</td>
<td>29</td>
<td>19</td>
<td>230</td>
<td>460</td>
<td>89</td>
</tr>
<tr>
<td>7/8</td>
<td>4.00</td>
<td>117</td>
<td>140</td>
<td>406</td>
<td>835</td>
<td>444</td>
</tr>
<tr>
<td>16</td>
<td>3.46</td>
<td>17</td>
<td>244</td>
<td>170</td>
<td>3542</td>
<td>4218</td>
</tr>
<tr>
<td>25</td>
<td>4.31</td>
<td>384</td>
<td>66</td>
<td>2200</td>
<td>6673</td>
<td>2327</td>
</tr>
</tbody>
</table>
Study Sites

The five selected sites vary in soil metal load and in hydrology (Figure 5). They all contain *Phragmites australis* stands. Site 1 had some of the lowest TSML of the five study sites. It was located in the north-western section of the study area, along the edge of the research zone adjacent to Phillip Street and across from the Liberty Science Center. The site was classified as common reed dominated and successional old field. It was dominated by areas of monoculture *Phragmites australis*. Several areas within this site contain surface water. The site slopes down towards Philip Street ending at the fence and a water filled ditch which runs parallel to the street.

Site 43 was a wetland site with standing water on the site under typical climatic conditions. Site 43 was classified as successional northern hardwood, containing area where *Phragmites australis* was the predominant species. The site was located in the south-western section of the enclosed study area. Gravel and waste such as old timbers and scrap metal are strewn around the site. An industrial area was located to the south-west on the other side of the fence from LSP. Site 7/8 was located in the north western section of the study area along Phillip Street at the edge of the fenced in section of LSP. Similarly to Site 1, Site 7/8 it slopes down towards the border fence and Philip Street. The water filled ditch running parallel to Philip Street was also present. *Phragmites australis* grows in monoculture in the wetter area near the road and fence. The site was classified as common reed dominated, maritime shrub land, and maritime grassland.

Site 16 was located in the interior of the fenced in study area at LSP. It was an upland site with no surface water present. The site was classified as successional northern hardwood, and shallow emergent marsh land. The TSML was comparatively low. Within the site there are areas where *Phragmites australis* grows in monoculture. Refuse such a scrap metal, glass bottles, and charcoal are visible throughout the site. The soil metal concentrations used for Site 16 are
from the samples taken at Site 16 W which was the exact location of study site. For the purposes of this study it will be referred to as Site 16. Site 25 had the highest TMSL of the five study sites. It was centrally located within the study area. This was an upland site that does not have standing water. Site 25 was classified as successional northern hardwood, containing area where *Phragmites australis* was the predominant species. There was an abundance of scrap metal and charcoal pieces throughout the site. It also contains areas which appear to have once been paved with asphalt or gravel and are disintegrating.

**Soil Survey Methods**

A soil survey was performed at each sampling site on April 14, 2012 (Table 3). Soils cores were taken using the stainless steel soil probe to depths of at least 0.75 m. Soil was removed intact from the soil probe and analyzed for color and texture using a *Munsell® Soil-Color Chart*. Texture was determined by using the “soil ribbon test”. A moistened ball of soil was squeezed between the thumb and fingers. The resulting ribbon was compared to a textural flow chart.

Soil was also collected in September of 2011 for pH analysis from each site using a stainless steel sampling shovel (Table 2). Soil was collected at a depth between 14 and 16 cm below surface level. Soil pH was analyzed in triplicate for each site. Soil samples with a mass of 20g were placed in a 50ml beaker to which 20 ml of reagent water was added. This was continuously stirred for five minutes. The suspension was then left to stand for one hour to allow the suspended clay to settle out. Soil pH analysis was done using a pH meter with a three point
calibration using pH buffers of 4, 6, and 8 and the pH electrode was then lowered in to the beaker just far enough to be submerged in the liquid but not touching the soil at the bottom. The pH was recorded once the pH meter had a stable reading.

Soil nutrient levels were also analyzed, with samples taken in September of 2012 (Table 4). Samples were analyzed by the soil testing laboratory at Rutgers State University. Soil was collect for organic content analysis in May of 2011 and in September of 2011 (Table 2). In the May only Site 1, 43, 7/8, and 25 were sampled. In September soil samples were taken at all five study sites. Soil samples were taken using a stainless steel hand shovel and places in to plastic bags. The samples were taken at uniform depths of 14-16 cm below surface level. The soil was stored in a refrigerator until analysis. To begin the analysis crucible were first weighed empty and then filled to just below the top with soil from selected site. Crucible plus soil were then weighed. Crucibles were then placed into the muffle furnace at 550°C for four hours. Once cooled in a desiccator, crucibles plus ash were weighed. The weight of the empty crucible was subtracted out, and the ash weight was subtracted from the dry weight to determine loss by ignition.

The percent carbon of the soil was calculated by the following equation;

\[
% \text{ Organic} = \frac{(\text{Dry weight- crucible}) - (\text{ash weight-crucible})}{(\text{dry weight-crucible})} \times 100
\]
Table 2 - Soil Characteristics

<table>
<thead>
<tr>
<th>Soil Characteristic</th>
<th>Site 1</th>
<th>Site 43</th>
<th>Site 7/8</th>
<th>Site 16</th>
<th>Site 25</th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>5.76 ± 0.037</td>
<td>5.42 ± 0.18</td>
<td>6.42 ± 0.073</td>
<td>5.98 ± 0.066</td>
<td>6.01 ± 0.026</td>
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<tr>
<td>% organic</td>
<td>2.21 ± 0.76</td>
<td>30.6 ± 1.65</td>
<td>10.99 ± 2.94</td>
<td>17.19</td>
<td>19.89 ± 3.62</td>
</tr>
<tr>
<td>Site 1</td>
<td>Site 43</td>
<td>Site 7/8</td>
<td>Site 16</td>
<td>Site 25</td>
<td></td>
</tr>
<tr>
<td>----------------</td>
<td>------------------</td>
<td>-------------------</td>
<td>------------------</td>
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<td></td>
</tr>
<tr>
<td>0-17cm</td>
<td>0-6 cm</td>
<td>0-8 cm</td>
<td>0-8 cm</td>
<td>0-60cm</td>
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<tr>
<td>Silty loam</td>
<td>Sandy loam</td>
<td>Silty clay loam</td>
<td>Sandy clay loam</td>
<td>Sandy Loam</td>
<td></td>
</tr>
<tr>
<td>2.5 YR 3/3</td>
<td>5 YR 3/2</td>
<td>5 YR 2.5/2</td>
<td>2.5 YR 3/2</td>
<td>10 R 2.5/1</td>
<td></td>
</tr>
<tr>
<td>&quot;Reddish brown&quot;</td>
<td>&quot;Dark reddish</td>
<td>&quot;Dark reddish</td>
<td>&quot;Dusky Red&quot;</td>
<td>&quot;Reddish black&quot;</td>
<td></td>
</tr>
<tr>
<td></td>
<td>brown&quot;</td>
<td>brown&quot;</td>
<td></td>
<td>40% medium to</td>
<td></td>
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<tr>
<td></td>
<td>30-40% organic</td>
<td></td>
<td></td>
<td>coarse charcoal,</td>
<td></td>
</tr>
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<td></td>
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<td></td>
<td></td>
<td>gravel, brick,</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>asphalt and tar</td>
<td></td>
</tr>
</tbody>
</table>

| 18-75cm        | 6-18 cm          | 8-75 cm           | 8-17 cm          | 17-35 cm         |
| Sandy clay loam| Loam             | Sandy clay loam   | Silty clay loam  | Sandy loam       |
| 2.5 YR 3/2     | 5 YR 2.5/1       | 5 YR 3/3          | Stripes .5-1.5cm | 5 YR 3/1         |
| "Dusky Red"    | "Black"          | "Dark reddish     | wide             | "Very dark grey" |
| 15% Fine to very fine gravel | 40% Fine to very fine gravel and charcoal | 30% medium to coarse gravel, very fine to medium pieces of charcoal, very fine red brick pieces, very fine to medium asphalt | 5 YR 2.5/1 “Black” | 5 YR 7/3 “Pink” |
|                | Oily sheen       |                   | 5 YR 6/8 “Reddish yellow” | 10% Coarse asphalt |

| 18-100 cm      | 18-100 cm        | 17-35 cm          |                  |                  |
| 7.5 YR 2.5/1   | 7.5 YR 2.5/1     |                  |                  |                  |
| "Black"        | "Black"          |                  |                  |                  |
| 50% Fine to very fine gravel and charcoal | 50% Fine to very fine gravel and charcoal | 5 YR 3/1 | 5 YR 5/6 |
| Oily sheen     | Oily sheen       |                  | "Very dark grey" |

| 35-100 cm      |                  |                  |                  |                  |
| Loamy sand     |                  |                  |                  |                  |
| 5 YR 5/6       |                  |                  | "Yellowish red"  |                  |
Table 4- Soil Nutrients at LSP Study Sites

<table>
<thead>
<tr>
<th>Macronutrient (Pounds per acre)</th>
<th>Site 1</th>
<th>Site 43</th>
<th>Site 7/8</th>
<th>Site 16</th>
<th>Site 25</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phosphorus</td>
<td>44 (below optimum)</td>
<td>11 (below optimum)</td>
<td>36 (below optimum)</td>
<td>21 (below optimum)</td>
<td>31 (below optimum)</td>
</tr>
<tr>
<td>Potassium</td>
<td>105 (below optimum)</td>
<td>48 (below optimum)</td>
<td>115 (below optimum)</td>
<td>189 (optimum)</td>
<td>182 (optimum)</td>
</tr>
<tr>
<td>Magnesium</td>
<td>305 (Above optimum)</td>
<td>77 (below optimum)</td>
<td>408 (Above optimum)</td>
<td>197 (optimum)</td>
<td>108 (below optimum)</td>
</tr>
<tr>
<td>Calcium</td>
<td>3147 (Above optimum)</td>
<td>696 (below optimum)</td>
<td>4717 (above optimum)</td>
<td>2674 (above optimum)</td>
<td>1203(below optimum)</td>
</tr>
</tbody>
</table>
Figure 5- Liberty State Park Water Table Level by Study Site
Chapter 3

The Impacts of Soil Heavy Metal Contamination on the Primary Production on *Phragmites australis*

Field Study

Materials and Methods

This study was designed to analyze the effects of high soil metal contamination on the growth, and energy allocation of *Phragmites australis*. A field study and a laboratory study were created to track the growth of *Phragmites australis*. This study will test the hypothesis that sites with higher levels of metal contamination will have decreased growth and will show signs of stress in its energy allocation.

Field Sampling for primary production analysis was accomplished in September, and November of 2011. Plant heights and density were measured at each site using the sampling square and meter stick. Next intact *Phragmites australis* were dug out by hand shovel with rhizomes intact. These plants were placed in plastic bags for transport to MSU. *Phragmites australis* plant density for each site was measured using the 1m sampling square in September and November of 2011 (Table 5).

*Phragmites australis* plants were first measured plant height. The entire plant was then broken down in to stem, leaf, sheath, flower, root, and rhizome. Aluminum Foil bags were weighed empty and then with filled with a part from an individual plant. They were then placed in the *Thermo Scientific Precision drying oven* at 60-80°C for three days. Once dried, foil with plant inside was weighed again for a dry weight.
Dry mass of part “a” (g) = the mass of dried foil bag filled with part “a” (g) – the mass of the empty foil bag (g)

The root to shoot ratio was also calculated from these dry weights. The root to shoot ratio was calculated by dividing the below ground total dry mass (combined weights of fine root, rhizome) by the above ground total dry mass (combined weights of stem, sheath, leaf, flower).

The dry mass and lengths of the harvested plants were used to calculate biomass of the Phragmites australis growing in the field during methane flux measurement (Figure 6). The recorded heights (cm) of the *Phragmites australis* plants grown within the chamber anchors were plotted as the independent variable, x. The dry weights (g) from the field survey data were plotted as the dependent variable, y, and n = 100. A second degree polynomial regression line was computed to be;

\[ Y = 4.7865x^2 + 0.4006x + 1.2116 \quad (R^2 = 0.7627) \]
Table 5- *Phragmites australis* density per square meter at selected study sites at Liberty State Park at the end of summer and fall of 2011

<table>
<thead>
<tr>
<th>Study Site</th>
<th>Summer</th>
<th>Fall</th>
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<tbody>
<tr>
<td>1</td>
<td>42</td>
<td>27</td>
</tr>
<tr>
<td>43</td>
<td>76</td>
<td>27</td>
</tr>
<tr>
<td>7/8</td>
<td>36</td>
<td>73</td>
</tr>
<tr>
<td>16</td>
<td>17</td>
<td>43</td>
</tr>
<tr>
<td>25</td>
<td>32</td>
<td>57</td>
</tr>
</tbody>
</table>
Figure 6: Correlation between plant height and dry weight of *Phragmites australis* was used to estimate the dry mass of the *Phragmites australis* in the methane flux studies.
LSP Field Biomass Study Results

The energy allocations of *Phragmites australis* were calculated for each of the five study sites in the summer and in the fall (Figure 7, 8, 9). In the summer Sites 1 and 43, the least contaminated sites, have lower percent energy allocated to the below ground biomass; fine root and rhizome. At these two sites the *Phragmites australis* was putting more energy towards height and stem development than root development. This is a sign of growing in a less stressful soil environment.

Sites 7/8, 16 and 25 with high levels of soil contamination show increased rhizome production. Increased root production is a sign that a plant is under stressful soil conditions. Site 25 with the highest levels of contamination had the largest percentage make up of leaves and rhizome, and the smallest percentage of stem and flowers. This could be due to the forested environment at Site 25. The *Phragmites australis* at Site 25 had to compete with the taller trees for sunlight, and had put more energy into leaf production instead of reproduction.

In the fall sampling there are similar trends. Sites 1 and 43 have the lowest percentage of rhizome, again a sign of low stress soil conditions and healthy plants. Sites 7/8, 16, and 25 have increased rhizome production that is a sign of stressful soil conditions. Site 25 again had the highest percentage of leaves and the lowest percentage of flowers, due most likely to its forested habitat.

The root to shoot ratio further quantifies the relationship between stressful soil metal concentrations and altered growth patterns (Figure 10). Site 1 had the lowest average root to shoot ratio in the summer and in the fall studies. The low levels of soil metals are not hindering the growth at Site 1. Site 43 and Site 16 have similar root to shoot ratios. Site 43 had low levels
of soil metals but had a very gravely soil. This may have had an influence on the *Phragmites australis* to slightly increase root production at Site 43. At Site 16 the high levels of soil contamination may have influenced the increase in root production.

The *Phragmites australis* at site 7/8 had a relatively high root to shoot ratio. Site 7/8 had similar site characteristics and hydrology to Site 1, except it had high levels of soil contamination. The higher root to shoot ratio at site 7/8 could be a sign of stress caused by the high level of the soil metal contamination. Site 25 had the highest average root to shoot ratio. It showed the highest ratio recorded at any site during the summer sampling. In the fall sampling the ratio was one the second highest, just below the ratio at site 7/8.

The roots to shoot ratios of each site were plotted against that sites Soil Metal Rank (Figure 11). There was a positive sloping linear regression line with an insignificant $R^2$ for both the summer and the fall sampling. The data suggests that *Phragmites australis* growing at sites with higher soil metal loads may have increased root production as a response to environmental stress.
Figure 7 - *Phragmites australis* entire plant percent composition in summer and fall
Figure 8- *Phragmites australis* above ground percent composition in summer and fall
Figure 9 – Liberty State Park *Phragmites australis* Energy Allocation; summer and fall, above and below ground
Figure 10 - Root to Shoot Ratio of *Phragmites australis* in summer and fall
Figure 11 - Root to Shoot Ratio and Soil Metal Load
Growth of *Phragmites australis* within the chamber anchors at Liberty State Park varied greatly between the sites (Figure 12, 13). Site 1 grew much larger *Phragmites australis* plants than all the other sites. By day 40 of 211 Site 1 had a larger biomass than the other sites would have at the end of the study. Site 1 had the highest growth with a final biomass more than double that of the next highest site. The soil contained the lowest percent of organic matter at Site 1, Phosphorus and Potassium levels below optimum and Magnesium and Calcium levels above optimum. Site 43 was damaged by natural forces, possibly storms or wildlife, and thus had low production. The initial growth however was strong and could be used as the best possible estimate of how Site 43 may have ended up. The soil Site 43 had the highest percent of organic matter of any site, and also contains below optimum levels of all four soil nutrients studied.

Sites 7/8, 16, and 25 all showed poor primary production of *Phragmites australis*. There was a significant difference between the primary production at Site 1 and Site 7/8. These sites have very similar hydrology, with the soil at site 7/8 containing higher levels of Potassium, Magnesium, and Calcium, and higher levels of soil metal contamination. Site 7/8 also had the highest pH of the five study sites. Site 16 had poor primary production throughout the study. The site contains high levels of soil contamination, with relatively average soil pH and percent organic matter. Site 25 which contains the highest levels of soil contamination had the lowest biomass production of any site. Site 25 had below optimum levels of Phosphorus, Magnesium, and calcium, and optimum levels of Potassium.

Final biomass showed a negative trend with soil metal load (Figure 14). The plot of growth vs. Soil Metal Rank had a negatively sloping linear regression line with a low $R^2$. High heavy metal concentrations in the soil could be placing stress on the *Phragmites australis* causing decreased growth rates and smaller plant size.
A factor analysis statistical test was applied to the principle factors to determine the significance of the factors involved in determining the biomass of *Phragmites australis* at each of the study sites (Table 6). The program Systat 12 was used for this analysis and all data was standardized prior to the test. Varimax rotation was applied to the factor analysis to better assess the correlation between factors. The factors included final biomass production, soil concentrations of the individual metal species analyzed, soil nutrient levels, soil pH, soil percent organic, and water table height. The analysis explained 100 percent of the total variance using four factors.

There were two factors which included biomass as a significant factor; Factor 1 and Factor 4. Factor 1 which explained 32.2 percent of the total variance incorporated several significant factors with biomass. Three of the five soil metal contaminants were included in this factor; As, Cu, and Pb. These metals showed a negative relationship with biomass production as was previously demonstrated in Figure 13. The soil metal contamination seems to be a significant cause of stress to the *Phragmites australis*, causing decreased biomass production at the areas with high levels of contamination. The other soil metal contaminants, Zn and Cr, did not have a significant relationship to biomass. Soil metal rank also had a significant negative relationship with biomass production. It was a less substantial than individual metals because it took into account all five metal species.

Potassium was the only soil nutrients to have a significant correlation with biomass in Factor 1. It actually had a negative relationship with biomass suggesting that areas with higher levels of potassium produced less biomass.
Water table height had a positive correlation with *Phragmites australis* biomass. Areas with higher water table levels, the wetland sites, produced more biomass. This could be due to the fact that *Phragmites australis* prefers hydrologic conditions of wetland environments over upland and forested environments. In forested environments there is also more competition for sunlight and root space. Limited sunlight could have cause the *Phragmites australis* to develop a higher ratio of leaves to stem in order to capture the more sunlight. The *Phragmites australis* also had to compete with trees and other shrubs for root space in the soil. This would place stress on the plant possibly causing stunted growth. Wetland environments which had *Phragmites australis* growing in larger monoculture stands would be free of these problems.

The other factor that included biomass as significant was Factor 4. Factor 4 explained 18.4 percent of the total variance. In Factor 4 biomass had a positive relationship to levels of the soil nutrients magnesium and phosphorus. This suggests that sites with higher levels of these soil nutrients had healthier *Phragmites australis* with greater biomass production. Soil percentage organic matter had a negative relationship with *Phragmites australis* biomass in Factor 4. Site 1 which had much greater growth than the other sites had the lowest percentage of organic matter in its soil. The other sites had higher percentages of organic matter and produced less biomass. Factors 2 and 3 do not include biomass. They describe the similar distributions of some of the site characteristics.
Figure 12: *Phragmites australis* biomass over 211 day growth period within Liberty State Park
Figure 13: Liberty State Park *Phragmites australis* Average Final biomass
Figure 14: Liberty State Park Phragmites australis growth plotted against soil all metal rank

\[ y = -30.315x + 178.38 \]
\[ R^2 = 0.3462 \]
Rotated Loading Matrix (VARIMAX, Gamma = 1.000000)

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<td>AS</td>
<td>0.995</td>
<td>0.037</td>
<td>-0.019</td>
<td>0.089</td>
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<tr>
<td>CU</td>
<td>0.992</td>
<td>-0.109</td>
<td>0.03</td>
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</tr>
<tr>
<td>PB</td>
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<td>-0.166</td>
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<td>BIOMASS</td>
<td>-0.438</td>
<td>-0.135</td>
<td>-0.153</td>
<td>-0.876</td>
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Percent of Total Variance Explained

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<th>4</th>
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</thead>
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<td>Percent of Total Variance Explained</td>
<td>32.186</td>
<td>25.612</td>
<td>23.848</td>
<td>18.354</td>
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<tr>
<td>Cumulative Percent of Total Variance Explained</td>
<td>32.186</td>
<td>57.798</td>
<td>81.646</td>
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Table 6 – Factor analysis of the LSP field *Phragmites Australis* biomass study
Laboratory Greenhouse Biomass Study

Materials and Methods

A laboratory study similar to the field study was designed to conduct this testing in a controlled environment and to examine the impacts of soil heavy metal contaminations on the growth of *Phragmites australis* in a controlled environment. Sites 1, 43, 7/8, 16, and 25 are used in the laboratory study as in the field study. Soil and monoculture *Phragmites australis* were collected from each site and placed in five gallon buckets. *Phragmites australis* plants were removed in sections containing soil, rhizomes, and fine roots. These sections were disturbed as little as possible during extraction. Buckets were filled within three cm of the top rim. These were taken to the Montclair State University greenhouse for a controlled study. Four replicates from each site were created for this study.

*Phragmites australis* plants were trimmed down to soil level and will be re-grown in the laboratory greenhouse. Conditions in the greenhouse were set for optimal growth. The temperature was fixed at 35°C, and the lights are set for twelve hours of light and twelve hours of darkness. Buckets were placed on the south west side of the greenhouse along the windows. The buckets are aligned in two rows and will be rotated every week. *Phragmites australis* will be allowed to regrow so as to determine proper amounts of water and fertilizer needed, and to make sure that the plants are fit and hearty.

The *Phragmites* still in their five gallon buckets were then placed in five small pools measuring 17cm high with a diameter of 80cm. Each site was assigned its own pool in which its buckets were placed (Figure 15). The pools are filled with de-chlorinated water to 14 cm. When water evaporated from the pools they are refilled to 14 cm using de-chlorinated water. Pool locations were rotated every week within the greenhouse to correct any errors caused by
position. Buckets each had 8 holes drilled in to their sides to allow water from the pools to saturate the soil. \textit{Phragmites australis} was propagated in the buckets in monoculture.

The \textit{Phragmites australis} was then trimmed down to the soil level again. This will allow the study of primary production throughout the complete growth cycle of plants. \textit{Phragmites australis} heights were measured from soil level to highest stem point using a meter stick. Greenhouse sampling was conducted approximately every week. Sampling was begun at 10:00 am at every sampling event. Once this laboratory study was completed the soil and plants were returned to their respective sites at Liberty State Park.
Figure 15: *Phragmites australis* growing inside 5-gallon buckets within the pools in the greenhouse.
**Laboratory Greenhouse Biomass Study Results**

There was a large variation in the biomass production of the *Phragmites australis* grown within the chamber anchors in the greenhouse study (Figure 16, 17). Site 1 a wetland site with background levels of soil metal contamination produced the largest amount of *Phragmites australis* biomass over the 165 day growth period. Site 7/8, a wetland site with high soil metal contamination produced the second highest final biomass. The soil taken from Site 1 had the lowest percent organic carbon (~2%), and a pH of 5.76. Site 7/8 had a higher soil percent organic carbon (~11%) and higher pH of 6.42. This decreased production between these two sites could be due to stress caused by the soil metal contamination on the *Phragmites australis* or difference in organic material present in the soil.

Site 25 the most contaminated site produced the third highest amount of biomass. Site 16, an upland site with high levels of soil contamination, produced the second lowest final biomass and growth slope. Site 43 a wetland site with background levels of soil metal contaminations produced the lowest amount of biomass.

The trend between biomass production and soil metal load was weaker in the greenhouse study than in the field (Figure 18). Site 43 had the lowest final biomass despite having the lowest soil metal rank. Although Site 43 had low soil metal contamination, the soil was largely made up gravel and brick pieces and contained lower soil nutrients than the other sites. Site 43 had below optimum levels of magnesium, calcium, phosphorus and potassium. Site 43 also had the highest soil percent organic carbon (~30%) of all the sites. The soil at site 43 was also more rocky and contained more cobbles and brick pieces that the other sites.
The other difference was Site 25, an upland site with the highest soil metal rank of 4.31. Site 25 was a forested site in the field in which the *Phragmites australis* receives limited sunlight and grows in dryer soil conditions. The *Phragmites australis* growing on Site 25 in LSP shows signs of stress. They have a higher root to shoot ratio, and increased leaf production, and less flower production compared to the other sites. Due to the stressful environment, the *Phragmites australis* that was harvested from this site could have contained greater stored energy reserves in their roots and rhizomes. This then could give them an advantage when grown in the full sunlight and saturated soil conditions of the greenhouse.

Factor analysis was used to determine the influence of the site properties on the biomass production of *Phragmites australis* (Figure 14). The final biomass of *Phragmites australis* was included with the concentrations of the individual soil metal species, the levels of soil nutrients, the soil pH, and the percent of organic material in the soil. Four factors were computed that together explain 100 percent of the total variance.

Factor 1 was the only factor to significantly include biomass. Biomass had a negative relationship with the percent of organic material in the soil. The sites in the greenhouse study with less organic matter in their soil had greater biomass production. Biomass had a positive correlation to three of the four soil nutrients in Factor 1. Phosphorus, Magnesium, and Calcium had this positive relationship, while potassium was insignificant. Biomass production was greater at with increased level of these three nutrients in soil.

There was no significant correlation between *Phragmites australis* biomass production and soil metal load in this greenhouse study. Soil nutrient levels seemed to play a much more significant role in stimulating growth than metal concentrations did in biomass production.
Placing the plants in a controlled environment with steady levels of sunlight and water may have overcome any negative impacts of soil metal contamination. Their growth seems to have just been limited by the soil nutrients present in each sites.
Figure 16: Greenhouse study grown *Phragmites australis* biomass over 165 day growth period
Figure 17: Greenhouse *Phragmites australis* final biomass
Figure 18- Final biomass of *Phragmites Australis* grown in the greenhouse and soil metal rank
Table 7 – Factor analysis for biomass production of *Phragmites australis* in the laboratory greenhouse study
The Phragmites sampled from LSP show some trends that can help to explain some of the behavior seen in the greenhouse. The *Phragmites* growing at the least contaminated sites had more energy allocated towards stem development and reproduction. The *Phragmites* growing at contaminated sites had more energy allotted towards root and rhizome development, a sign of stress. Site 25 had the largest rhizomial and leaf percentage of all the sites. This supports the theory that it may have had an advantage when transplanted to the greenhouse.

The Phragmites growing within the chamber anchors in LSP displayed the negative relationship between soil metal concentration and primary production. Site 1 had a much higher growth rate than the other sites. Site 43 showed similar initially strong growth before it was damaged. The three contaminated sites showed low growth rates and poor plant development. The data suggests that soil metal contamination was a likely cause of the difference in primary production.

Analysis of the *Phragmites* grown in the greenhouse shows a difference in growth rate and final biomass between the five sites. There was a weak trend of decreased growth at the sites with higher soil metal concentrations. The exceptions to this trend are Site 43 and Site 25. Site 43 had poor soil quality and below optimum nutrients levels that may have led to decrease in growth. Site 25 may have been so stressed in the field that it placed more energy into its roots that gave it an advantage when grown in optimal conditions. Sites 1, 7/8, and 16 best display the negative relationship between soil metals and primary production. There seems to have been a stronger relationship between soil nutrients and biomass production that between metal contamination and biomass.
Discussion

*Phragmites australis* is an aggressive invasive species that is replacing native wetland plants across the wetlands of the United States. It is important to understand the how *Phragmites australis* will respond to metal contamination as it moves in to contaminated wetlands, which are plentiful on the east coast of the United States. Management strategies should take into account the impacts that the contamination may have on the invasive species they are trying to control as well as the native species that ought to replace them.

The primary production of *Phragmites australis* was decreased at sites containing high levels of soil metal contamination in the field study. This could have important implications for the restoration of urban brownfields. *Phragmites australis* does not provide the level of ecological benefits as native wetland grasses do. Where possible it is important to decrease the invasive spread of *Phragmites australis* and replace them with native species. If *Phragmites australis* is shown to be stressed under metal contaminations then the door may be open for native species to propagate in its place.

Liberty State Park contains several wetland areas that have become dominated by monoculture stands of *Phragmites australis*. Some of these sites contain high levels of soil metal contamination, while other areas have lower or background levels of contamination. In order for managers to get the most out of these natural areas it is important for the native species to regain control. The invasive nature *Phragmites australis* has allowed it to take advantage of these disturbed sites and out compete the native species. Its high tolerances to varying hydrologic and soil conditions have led to its large distribution throughout the park. It does not seem feasible to remove all of the *Phragmites australis* and replace it with native species.
The conclusion of the field study that the biomass production of *Phragmites australis* was negatively impacted by the soil metal contamination in Liberty State Park may be fundamentally beneficial for this area. The *Phragmites australis* overtook the park during a time of early succession. Now that it has been left alone for close to fifty years later successional native plant species are starting to thrive in the area (Gallagher et al 2011). If the metal contamination is negatively impacting the *Phragmites australis* it may just decrease the vigor of the plants enough for the native species to take their place. At the upland sites this is already becoming evident by the poor growth and stressful conditions of the *Phragmites australis*. Over a longer period of time the *Phragmites australis* may just be confined to the uncontaminated wetland areas of the park, and these too may be taken back by the native species.

**Conclusion**

Invasive species are a major problem for a world that is becoming smaller every year. Areas that were once heavy developed and are now being converted back to natural areas. These early sessional areas are especially vulnerable to re-colonization by invasive species instead of native species. Areas such as Liberty State Park that are also contaminated must account for the benefits as well as the problems caused by the spread of invasive species. The ecosystem functions of *Phragmites australis* although less than those of the native species are still preferable over an abandoned lot, or a commercially developed area.

*Phragmites australis* may have initially occupied Liberty State Park, but over time it seems that its grip is weakening. Although there may be an influence by the impacts of soil metal contamination on the health and distribution of *Phragmites australis*, time seems to be the controlling factor in the struggle over Liberty State Park between invasive and native species.
Chapter 4 – The Impacts of Soil Heavy Metal Contamination on Methane Flux

This methane flux study will assess the emission or sequestration of methane from Liberty State Park. The impacts of soil metal contamination, site hydrology, soil characteristics on methane flux will be examined. The same five study sites used in the plant study, with varying levels of soil heavy metal contamination and hydrology will be used to assess methane flux at Liberty State Park. The objective was to assess the impacts of soil heavy metal contamination on the natural operations of wetland and upland sites, emitting or absorbing methane. A field and a laboratory study were developed for this investigation.

Liberty State Park Field Methane Flux Study

Methods and Materials

Gas sampling chamber design was modeled on the Chamber-based Trace Gas Flux Measurement Protocol Developed by the Trace Gas Protocol Development Committee (Baker at al. 2003). The chamber consisted of 2 parts, a permanent anchor driven in to the soil, and a portable cap. Chamber anchors consisted of a 5 gallon bucket whose bottom was removed to allow for insertion into the soil (Figure 19). Buckets have a height of 35.8cm, a top diameter of 29.5cm, and a bottom diameter of 25.5 cm. Three PVC end caps were screwed into the inside of the top lip of the anchor to support the chamber cap. A total of 15 chamber anchors were produced for LSP.

Chamber caps were constructed from PVC pipes, 5 gallon buckets, and plastic sheeting. Four chamber caps were utilized in this study. To construct the chamber caps the tops of 5 gallon buckets were removed creating a ring. Four rings were used for each chamber. Three PVC pipes were screwed length wise inside the rings to create the frame of the chamber. At the bottom of
the chamber cap the ring was attached 15 cm from the end of the PVC pipes. This created three supports that fit into the PVC end-caps along the rims of the chamber anchors to hold up the chamber cap. The fourth ring was positioned at the top of the chamber cap to create the lid. This frame was then wrapped with plastic sheeting on the sides and top, and heat sealed to ensure an air tight chamber. Extra plastic sheeting was positioned at the bottom the chamber cap to cover the anchor. A vent tube was then added on the top of each chamber to create a natural flow between soil and atmosphere, and prevent a build-up of gas. When chamber caps are attached to the anchor a bungee cord or tape was wrapped around the extra plastic and the anchor to create an air tight seal. Two battery powered fans are screwed to the PVC pipes supports inside the chambers to circulate the air. A septum was installed in the side of the chamber cap near the top for gas sampling.

Chamber anchors were installed in LSP in July of 2011. Areas within each selected site where _Phragmites australis_ was growing in monoculture were selected. A small trench was excavated by hand shovel around a group of monoculture _Phragmites australis_. Care was taken to disturb as little of the surrounding plants and soil as possible. Anchor rings were buried at least 20 cm below the surface. Three anchors were deployed to each of the five study sites. The three anchors at each site were placed close together, separated by 2 or 3 meters. The chamber anchors will remained in place during the duration of the study to minimize soil disturbance and root damage (Baker at al. 2003).
Figure 19: Chamber Anchors installed in Liberty State Park
Methane flux field sampling was performed approximately every other week beginning on April 1, 2012. Sampling was commenced at approximately 10:00 am at every sampling event. Batteries were then attached to the chamber fans, and fans were checked to make sure they were running. Care was taken to disturb the area surrounding the chambers as little as possible. Chamber caps were placed over the *Phragmites australis* growing within the anchor and then attached to the anchors utilizing the PVC end-caps (Figure 20). The plastic extending from the bottom of the chamber cap was wrapped around the anchor and secured with bungee cord or duct tape.

Sampling was done using a gas-tight BD 30 ml syringe with a luer-lock tip and BD 20 gauge precision glide needles. Gas samples were taken through the chamber septas using the airtight syringes. Samples were stored in 20 ml glass vials. Sampling vials were prepared one or two days before every sampling trip. The vials are sterilized before each round of sampling using an autoclave. Rubber stoppers were then inserted into the vials. The vials were then sealed with an aluminum ring using a capper. Vials were then vacuumed to -90 kpa using a Nalgene Mityvac hand pump. Vials were then labeled using masking tape and permanent marker. Each vial was labeled for a specific site and sample number. A countdown timer was used to control the timing of samples.

Before each sample was taken the syringes were first flushed. This was done by inserting the syringe in to the chamber, drawing a full 30 ml of air, removing the syringe from the chamber and releasing the syringe in to the open air. After flushing a 25 ml sample was taken from the chamber and injected in to its designated vial. Samples were taken from each of the three chambers simultaneously by three people. After sampling, vials were refrigerated until the samples were measured using a gas chromatograph.
During sampling the soil temperature was taken using a soil thermometer probe at a depth of 20cm. The air temperature was taken using a separate thermometer during sampling. Water table levels for each site were then measured. A pit near the chamber locations was dug by hand shovel down to 1m. This was allowed time to fill with water and the depth to the water level were measured. If the site was saturated and had surface water its depth was measured. Water depths were recorded as positive or negative, related to the ground level.
Figure 20: Gas Chamber deployed in Liberty State Park
Gas analysis methods

Methane concentrations will be analyzed from both the fields study and the laboratory study using gas chromatography. A Hewlett-Packard 5890 Series II Gas Chromatograph located at Montclair State University will be used to examine the gas samples (Figure 20). The GC uses flame ionization detector to ionize the injected gas and induce a current. Oven temperature was set to 35 °C and detector temperature was set to 200 °C. The current was measured and fed to an integrator which produces a curve for methane at a retention time from 1.15-1.25 min. Samples will be compared to a standard curve to determine methane concentrations from which flux will be determined.
Figure 21: Hewlett-Packard 5890 Series II Gas Chromatograph
Laboratory Greenhouse Methane Flux Study- Materials and Methods

A laboratory study was conducted to parallel the field study and was designed to perform this testing over the winter months while examining heavy metal contaminations influence on methane fluxes in a controlled environment. Sites 1, 43, 7/8, 16, and 25 are used in the laboratory study as in the field study. The five-gallon buckets containing the soil and *Phragmites australis* removed from Liberty State Park and propagated inside of the water filled pools which were used in the laboratory plant study were used for the laboratory methane flux study. Four replicated from each site were employed for this experiment. Buckets were saturated with water to -14 cm from soil level throughout the entire study.

Methane sampling began after the *Phragmites australis* was then trimmed down to the soil level and allowed to regrow. This will allow the study of gas levels throughout the complete growth cycle of plants. Gas chamber caps will be placed on the buckets and samples will be drawn as in the field study. Once this laboratory study was completed the soil and plants were returned to their respective sites at Liberty State Park.

Greenhouse sampling was conducted approximately every week (Figure 22). Sampling commenced at 10:00 am at every sampling event. Methane sampling vials were prepared using the same method as with field sampling. Batteries were connected to the chamber fans and fans were tested. Gas chamber caps were then placed over the *Phragmites australis* and attached to the buckets. The plastic extending from the bottom of the chamber cap was wrapped around the anchor and secured with bungee cord or duct tape.

Pools containing soil and *Phragmites australis* from a single site were sampled one at a time. Syringes were flushed using the same method as in LSP. Samples were then taken from the
gas chamber and injected into glass vials using the same method as in LSP. The timer was set
for five minutes and gas sampling was begun at “Position A”. The sample was then injected into
the correct vial. The rest of the chambers in that pool were then sampled one at a time in order
from “Position B” to “Position D” in that same five minute period. When the timer sounds and
five minutes are up the chamber at “Position A” was sampled again and then the rest are sampled
in order. After thirty minutes are up with seven samples taken from each position in one pool the
chambers are moved to the next pool for the sampling of another site and the process was
repeated.
Figure 22- Gas chambers deployed for methane flux sampling in the laboratory greenhouse study
Liberty State Park Field Methane Flux Study

Results

Methane Flux readings were taken over a 211 day period at Liberty State Park beginning on April 1, 2012 (Figure 23). The tests occurred over the growing season of Liberty State Park, and during the time that the soil will be warm enough for microbial activity. The time series provides an overview comparing the five sites. The sites show varying trends culminating with all sites showing a relatively neutral flux on the final study day. The sites may have showed low and neutral methane flux rates at the end of the study due to decreased soil and air temperatures.

The less contaminated wetland sites, 1 and 43, show a similar trend of a generally positive methane flux though the study period. They then increase to a peak at day 79, and then decrease towards the end of the study. This could be possibly due to a combination of warmer temperatures with the wet soil conditions of mid-June (Singh et al. 2000). Site 7/8 a contaminated wetland site had a methane flux that jumps from slightly positive to slightly negative through the study. Site 16 a contaminated upland site had a mix of neutral and positive and negative methane flux over the study period. Site 25 a heavily contaminated upland site shows a negative flux through the entire study period. ANOVA was used to determine whether the methane flux results were significantly different between the five study sites. The results showed a large variation between the study sites with an ANOVA p-value of 0.0023.

Site 1 was a wetland site with ambient levels of TSML. The average flux show large levels of variability over the study period. The initial high flux rate was accompanied by a significant amount of uncertainty as shown by its large standard deviation. The flux rate then decreased to a local low at day 29 before increasing to a local high flux at day 79. Average flux
then decreases over the last study dates to the sites lowest methane flux on the last day of the study period. Site 43 a wetland site with a low TSML shows a relatively stable level of positive methane flux through the study period, with a couple exceptions. Study day 15 and 79 show increased flux levels with day 79 being the highest overall. The last two study days each show a negative average flux. Day 149 was the lowest while day 211 was just slightly negative.

Site 7/8 was a wetland site with TSML greater than average soil levels. The average methane flux for Site 7/8 hovers jumps from slightly positive to slightly negative for the first four study dates. On day 61 shows the largest negative flux followed by site 7/8's largest positive methane flux on the next study period. The flux was then negative on day 111 followed by the second largest positive flux on day 149. The last day of the study shows the smallest positive flux. Site 16 was an upland site with TSML greater than ambient soil levels. The methane flux on the first study day was the greater of two instances of negative flux at site 16. The methane flux was slightly negative flux on day 29, and then two positive fluxes on days 41 and 61. Then the three largest positive methane fluxes occur consecutively at days 79, 111, and 149, with the flux at day 111 being the greatest. The methane flux then drops back down on the last study day. Site 25 was an upland forested site with a TSML much greater then ambient soil levels. The average methane flux for site 25 was negative on every study day. It varies from near neutral on day 29 and 211 to more significantly negative flux levels on days 0, 15, 44, 61, 111, and 149. The greatest negative flux occurs on study day 111 with a large standard deviation.

The average methane flux rate over the entire study period was calculated with one standard error (Figure 24). Site 1 a wetland site with ambient levels of TSML had the largest average methane flux of 0.783 ± 0.657 mg ch4-c/m2/hr. Site 43 which was also a wetland site with ambient levels of TSML had the second largest average methane flux of over 0.723± 0.791
mg ch4-c/m2/hr. These two sites are the only with positive methane flux significantly above neutral levels. The three sites with high soil metal contaminations have low or negative flux. Site 7/8 a wetland site with TSML above ambient levels had a low average methane flux just over 0.126 ± 0.536 mg ch4-c/m2/hr. Site 16 an upland site with TSML above ambient levels had an average methane flux of 0.199 ± 0.528 mg ch4-c/m2/hr, slightly above that of site 7/8. Site 25 a forested upland site with the highest TSML was the only site with an average negative methane flux. The flux sum was significantly negative at -0.326 ± 0.256 mg ch4-c/m2/hr. The sites with lower TSML have a higher methane flux sum, while the sites with higher TSML have a lower and negative flux. The wetland sites had higher positive flux averages while the upland sites had lower and negative flux averages.

Liberty State Park Methane Flux and Soil Metal Load

Liberty State Park methane flux showed a negative relationship with site soil metal load. (Figure 25). The graph of methane flux average and Soil Metal Rank had a negatively sloping linear regression line with a low R². The trend shows that at the sites with a higher soil metal load methane flux was lower or negative. Sites 1 and 43 had a low Soil Metal Rank corresponding to high methane flux average. Sites 16 and 7/8 had a high Soil Metal Ranks corresponding to low methane flux average. Site 25 had the highest Soil Metal Rank and a negative methane flux average.

There was a negative trend between the methane flux average of each site and soil As load. The graph displaying the relationship had a negative linear regression line with low R². There was a cluster of sites with low soil As and high flux rates, then a group of with higher
levels of soil As and lower positive, and some negative methane flux rates. The site that had high levels of soil As had negative flux rates. The overall trend appears to be that as soil As load increases the methane flux sums were decreasing.

There was a negative trend between soil Cu load and the methane flux rates of each site. The linear regression line was negatively sloping with a low $R^2$. Sites with low levels of soil Cu are bunched in the upper left hand corner of the graph with high positive methane flux rates. There was then a site with higher soil Cu levels that had a decreased positive flux rate and some negative flux rates. The site with much greater level of soil Cu then the other sites had negative flux rates, adding to the overall negative trend.

Methane flux also displayed a negative trend with soil Pb load. The linear regression line of flux average and soil Pb concentration was negatively sloping with an insignificant $R^2$. The sites with the lowest levels of soil Pb had the highest positive methane flux rates. Site 7/8 showed nearly double this level of soil Pb with a low methane flux average. A site with the second highest levels of soil Pb showed lower positive and negative flux rates. The site with the highest levels of soil Pb had negative methane flux rates.

Soil Cr load and the methane flux rate of each site had a negative relationship as well, although less defined than some of the other metals species. The regression line was negatively sloping with a low $R^2$. The site with the lowest levels of soil Cr had the highest positive methane flux rates. This was followed by another site with high positive methane flux rates and low levels of soil Cr. The next site shows a comparatively mid-range level of soil Cr with a negative methane flux average. The last two sites with high levels of soil Cr have lower positive and some negative methane flux rates.
Methane flux rate displayed a negative trend in relation to soil Zn concentrations. This trend was weaker than the correlation displayed between methane flux and soil As, Cu, and Pb. The linear regression line of methane flux rate and soil Zn was negatively sloping with a low $R^2$. There was a cluster of three sites with low levels of soil Zn that have mostly higher positive methane flux rates, with just a few negative rates. The next group of points shows a site with high soil Zn levels and negative methane flux rates. The last site with the highest levels of soil Zn had lower positive methane flux rates and the most negative flux rate.

The results display a meaningful connection between soil metal contamination and methane flux. Metal concentrations maybe negatively affecting methanogenic microbial soil communities. The chemistry of the soil and redox potential could have also been altered by the soil metal contaminations impacting the ability of methanogenic microbes to reduce $CO_2$ to $CH_3$. Altered soil chemistry could also affect methane rising through the soil column and prevent it from entering the atmosphere.

**Liberty State Park Methane Flux Rates and Water Table Level**

The relationship between water table levels and their equivalent methane flux at each of the five study sites was investigated (Figure 26). A positive trend was discovered between water table and methane flux rates. Higher methane flux rates occurred at wetland sites with higher water table levels. Lower positive and negative methane flux rates were recorded at upland sites and at wetland sites that were drying out. The highest recorded flux occurs at a water table level of 0cm. For all water table levels at ground level and above the methane flux was positive. There was a cluster of higher methane flux data points between -10cm, and +10 cm. At water table
levels between -40cm and -85cm five out of seven methane flux data point are positive with a high of 2.0 mg ch4-c/m2/hr. Methane flux was negative only when water table was below ground level. At the MDL limit of -100 methane flux varies from -1 to 0.6 mg ch4-c/m2/hr. The linear regression line was positive with a moderate $R^2$.

The data shows that the drier upland sites are releasing less methane into the atmosphere or absorbing methane into the soil from the atmosphere. This difference could be a product of the microbial communities that should be present in upland vs. wetland ecosystems. Upland soil is home to methanotrophs that provides a net intake of methane from the atmosphere into the soil. Wetland soil is predominated by methanogens that produce methane as a metabolic byproduct. It appears that the methane flux at LSP was strongly influence by soil hydrologic conditions which support dissimilar microbial communities.

**Liberty State Park Field Study Methane Flux Factor Analysis**

A factor analysis statistical test was applied to the principle factors to determine the significance of the factors involved in determining the methane flux rates at each of the study sites (Table 8). The program Systat 12 was used for this analysis and all data was standardized prior to the test. Varimax rotation was applied to the factor analysis to better assess the correlation between factors.

The factors analyzed along with the average methane flux for each site were; the soil concentrations for each site of the individual heavy metals studied, the soil metal load, the soil pH, the soil percentage organic matter, the average water table level of each site, and the final biomass of *Phragmites Australis* at each site. Four factors were calculated which together
described 100% of data set variance. Factor 1 had the highest percent of factor loading, explained 40.9% of the variance. Factor 1 contained the methane flux averages and the factors most closely related to it. These factors could be said to have had the greatest influence on the methane flux rates calculated at LSP.

Three heavy metals were included with methane flux in Factor 1. These metals, Cu, As, and Pb had the highest factor loadings within Factor 1. These metals showed a negative relationship with methane flux as was previously observed. As concentrations of soil Cu, As, and Pb increased by site, methane flux decreased. These three metals thus seemed to be more highly correlated with methane flux than Zn and Cr were. The high concentrations of soil Cu, As, and Pb, may have been inhibiting the production of methane by methanogens at the more contaminated sites, therefore causing the negative relationship between these metal species and methane flux rates. Zn and Cr occur in smaller concentrations and may have had less of an effect on the soil microbes. Soil Metal Rank was also included in Factor 1 and shows a negative relationship to methane flux. The Soil Metal Rank includes all five metal species involved in this study and as such had weaker factor loading then the three significant individual metal species.

Water table level also had high factor loading with in Factor 1 and corresponds positively with methane flux. Water table level was an important factor in the oxidation of soil and thus the microbial structure of that soil. This positive relationship within Factor 1 strengthens further the notion that within LSP the upland sites have varying methane flux rates and direction from the wetland sites. The positive relationship corresponds with the trend previously observed from Figure 16. The wetland sites, home to methanogenic soil microbes, were emitting methane from the soil into the atmosphere, corresponding to higher positive methane flux rate. The upland sites, home to methanotrophic soil microbes, had lower positive, neutral, or negative flux rates.
Factor 2, which accounted for 20.9% of the variance, reflects the distributions of soil Pb, Zn, and Cr, with the water table of the study sites. These metals had a negative relationship with water table height. Factor 3 describes 16.5% of the variance the relationship between soil percent organic and the biomass production of Phragmites australis. Neither of these factors involved methane flux.

Factor 4 which accounts for 21.6% of the variance involves methane flux, soil metal rank, and soil pH. Soil metal rank had a negative relationship with methane flux as was shown in Factor 1. Soil pH also had a negative correlation to methane flux. The soil at the study sites had pH's ranging from 5.41 to 6.42. Site with higher (more neutral) pH had lower positive and negative methane flux rates.
Figure 23- Liberty State Park Field Study Methane Flux Rates for each Study Site over the 211 day study period from 1/4/2012 - 10/24/2012 a. Site 1 Methane Flux Rates, b. Site 43 Methane Flux Rates, c. Site 7/8 Methane Flux Rates, d. Site 16 Methane Flux Rates, e. Site 25 Methane Flux Rates.
Figure 24 – Average LSP methane flux rate for each study site over the entire 211 day study period with 1 standard error.
c. y = -0.0004x + 0.5638
R² = 0.2151

Cu µg/g

flx mg ch4-c/m2/hr

0 500 1000 1500 2000 2500

-d. y = -0.0001x + 0.6494
R² = 0.2436

Pb µg/g

flx mg ch4-c/m2/hr

0 1000 2000 3000 4000 5000 6000 7000 8000
Figure 25- Soil Metal Load and Methane Flux Rates. 

a. LSP study site Soil Metal Rank and methane flux rates 
b. LSP study site soil As load and methane flux rates 
c. LSP study site soil Cu load and methane flux rate 
d. LSP study site soil Pb load and methane flux rates 
e. LSP study site soil Cr load and methane flux rate 
f. LSP study site soil Zn load and methane flux rate
Figure 26- Methane flux rates from all study sites over the entire 211 day study period with their corresponding water table level.

y = 0.0078x + 0.7173
R² = 0.2341
### Rotated Loading Matrix (VARIMAX, Gamma = 1.000000)

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### Percent of Total Variance Explained

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Table 8- Factor analysis of LSP Methane Flux
Laboratory Greenhouse Field Methane Flux Study

Results

The methane flux greenhouse study was done in a controlled environment to eliminate the impacts of external factors such as water table level, climate, and surrounding vegetation on the soil atmospheric methane flux rate. The only factor that differed between study sites was the environmental conditions where the soil and Phragmites was originally harvested from.

Methane flux readings were taken over a 165 day period beginning on March 23, 2012 (Figure 27). The methane flux at each site showed some variations on the short term, but over the course of the entire study period some trends became apparent. The original wetland study sites 1, 43, and 7/8 had mostly strong positive methane flux rates, while the original upland sites 16 and 25 had lower positive and negative methane flux rates. Sites 1, 43, and 7/8 show largely increasing methane production rates throughout the study period. Site 16 shows initial increases followed by lower and negative production rates. Site 25 shows the mostly negative and very low positive methane flux rates.

The soil used at Site 1 in this greenhouse study was removed from Site 1 at LSP, a wetland site with ambient levels of TSML. The methane flux rate at Site 1 was negative for the first three study dates. The flux rate then becomes positive and increases with a local peak at day 36. The flux rate then decreased until it becomes negative on day 63. The greatest positive rate of methane flux then occurred on day 86, the next study day. Flux rates then decrease on the last two study dates.

The soil used at Site 43 in this greenhouse study was removed from Site 43 at LSP, a wetland site with ambient levels of TSML. Methane flux rates at Site 43 in the greenhouse study
had a lot of variation through the study period. The lowest positive flux occurs on the first day of sampling, with the greatest positive flux rate occurring on day 86. There are three other dates with relatively high methane flux; day 28, 42, and 116. There at two dates with negative flux rates; day 7, and day 57.

Site 7/8 had the most positive methane flux rates of all the study sites in the greenhouse experiment. The soil used at Site 7/8 in this greenhouse study was removed from Site 7/8 at LSP, a wetland site with levels of TSML above ambient soil levels. The two highest rates of methane flux occur on days 28 and 42, and both have high levels of uncertainty. The only negative flux rate occurred on the first day of sampling. The next three sampling date have comparatively smaller positive methane fluxes that during the rest of the study period. From study date 50 until the end of the study the methane flux rates were higher than those in the beginning of the study.

The soil used at Site 16 in this greenhouse study was removed from Site 16 at LSP, an upland site with levels of TSML above ambient soil levels. Site 16 showed a mix of positive and negative methane flux rates. There were five sampling dates with a negative flux rate and 8 dates with a positive flux rate. Four out of the five dates with negative flux occur during the second half of the study dates.

The soil used at Site 25 in this greenhouse study was removed from Site 25 at LSP, an upland site with levels of TSML above ambient soil levels. The methane flux rates for Site 25 were all negative with the exception so the second and fourth study dates. The two exceptions have low positive flux rates. The negative methane flux rates increase to its peak on sampling
date 57, before decreasing to the end of the study. Dates 36, 50, and 57 all show high levels of variability.

The average methane flux rate, calculated for the entire study period with one standard error, was highly variable between the five study sites (Figure 28). All of the methane flux averages had a high level of error. Sites 1 and 43 with soil taken from wetland sites with low soil metal contamination had similar methane flux averages of 0.40 ± 0.53 and .36 ± 0.46 mg ch4-c/m2/hr respectively. Site 7/8 the only wetland site with high metal contamination had the highest methane flux average of 0.73 ± 0.57 mg ch4-c/m2/hr. Site 16 an upland contaminated site had the lowest positive flux average with 0.18 ± 0.46 mg ch4-c/m2/hr. Site 25 had a methane flux average of -0.44 ± 0.42 mg ch4-c/m2/hr. Site 25, with its soil taken from an upland site with the most metal contamination, was the only site with a negative methane flux average. The three sites with their soil removed from wetland areas had higher positive flux while the sites with their soil removed from upland sites had low and negative flux.

**Laboratory Greenhouse Methane Flux and Soil Metal Load**

The relationship between methane flux and soil metal concentration was analyzed using the methane flux and the TSML data (Figure 29). There was a negative relationship when you look at the methane flux average for each study site compared to the Soil Metal Rank of that study site. The graph had a negatively sloping linear regression line with a low R². Sites 1 and 43 have the lowest Soil Metal Ranks and have mostly strong positive methane flux rates. Site 7/8 with a high Soil Metal Rank had the highest positive methane flux rates in the laboratory greenhouse study. Site 16 had a high Soil Metal Rank with lower positive and negative methane flux rates. Site 25 had the highest Soil Metal Rank with very low positive and mostly negative...
methane flux rates. The sites with soil removed from wetland areas with low contaminations have high positive flux averages. The sites with soil removed from upland contaminated sites have low or negative methane flux averages. Site 7/8 was different than any other site; it was the only wetland site with high levels of soil metal contamination. It had the highest positive methane flux rates of any study site in the laboratory greenhouse study.

There was a negative trend between the methane flux rates of each site and soil As load. The linear regression line was negative with a low R². Sites 1, 43, and 16 had similarly low levels of soil As with methane flux rates varying from negative to positive. Site 7/8 had a higher concentration of soil As, and the highest positive methane flux rates, going against the negative trend. Site 25 had a negative flux with the highest levels of soil As. This trend appears to have been driven by Site 25 having the highest soil As concentrations and negative methane flux rates.

The methane flux rates of each site showed a negative trend with soil Cu load. The linear regression line was negatively sloping with a low R². Sites 1 had the lowest concentration of soil Cu and the second highest methane positive flux rates. Site 16 had a slightly higher concentration of soil Cu with the lowest positive and some negative methane flux rates. Site 43 had a higher concentration of soil Cu with a mostly positive methane flux rates. Site 7/8 with almost double the concentration of soil Cu than site 43 had the highest positive methane flux rates. Site 25 had the highest concentration of soil Cu which was an order of magnitude greater than the other sites. Site 25 had mostly negative methane flux rates throughout the study. This trend again appears to be driving by the high concentrations of soil Cu and negative methane flux rates of Site 25.
Soil Pb load showed the strongest negative trend with the greenhouse laboratory study methane flux rates of any individual metal. The linear regression line was negatively sloping with a low $R^2$. Sites 1 and 43 had the lowest concentration of soil Pb with the second and third positive methane flux rates respectively. Site 7/8 had almost double the concentration of soil Pb with the highest positive methane flux rates. Sites 16 had a high concentration of soil Pb, an order of magnitude greater than the first three sites and had the lowest positive and some negative methane flux rates. Site 25 had a soil Pb concentration almost double that of Site 16 and was the only site with mostly negative methane flux rates. Site 7/8 was again an exception to the negative trend having with its high positive flux and increased levels of soil Pb. Sites 16 and 25 had such high soil Pb levels and low and negative flux rates and appear to be the driving force in this negative trend.

There was no significant relationship between soil Cr load and the methane flux average of each site. There was a horizontal linear trend line with an insignificant $R^2$. Site 43 had the lowest levels of Cr and mostly positive methane flux rates. Site 1 had higher positive methane flux rates, and Site 25 had negative methane flux rates, while having similar concentrations of soil Cr. Site 7/8 had a higher concentration of soil Cr with the highest positive methane flux rates. Site 16 had the highest concentration of soil Cr with the lowest positive and some negative methane flux rates.

There was a negative relationship between soil Zn load and the methane flux rates of each site. The linear regression line was negatively sloping with a low $R^2$. Site 43 had the lowest levels of soil Zn with mostly positive methane flux rates. Sites 1 had the second lowest concentrations of soil Zn with the second highest positive methane flux rates. Site 7/8 had a soil Zn concentration slightly higher that Site 1 and had the highest positive methane flux rates. Site
25 had the second highest concentrations of soil Zn, an order of magnitude greater than the concentrations at sites 1 and 7/8. Site 25 was the only site with a negative methane flux average. Site 16 had the highest concentrations of soil Zn; almost double that of Site 25. Site 16 had the lowest positive methane flux average. The three sites with soil removed from wetland areas had the three lowest soil Zn concentrations and the three highest positive methane flux averages. The two sites whose soil was removed from upland areas had the highest soil Zn concentrations and the lowest positive and a negative methane flux average.

**Laboratory Greenhouse Study Methane Flux Factor Analysis**

A Factor analysis was computed on the components of the laboratory greenhouse methane flux study in order to better understand the correlation between the study sites and their methane flux rates (Table 9). Along with the average methane flux rates for each site, the factors included in this analysis were, individual soil metal concentrations, the soil metal rank, soil percent organic, and soil pH. Three factors were produced that together explain 94.6 percent of the total variance in the data set.

Factor 1 explains 44.4 percent of the total variance. Factor 1 contains methane flux, the soil concentrations of Cu, As, and Pb of each study site, and the soil metal rank. There was a strong negative relationship between methane flux and the soil metal concentrations of Cu, As, and Pb. These metals showed the strongest negative trend when plotted against methane flux. Study sites with high soil concentrations of these three metals showed decreased positive
methane flux and negative methane flux rates. The relationship was stronger between methane flux and these three metals than it was with Zn and Cr.

Methane flux showed a negative relationship with soil metal rank. This was consistent with the previous analysis of soil metal rank and greenhouse study methane flux averages, which exhibited decreasing positive methane flux rates and negative methane flux rates at sites with higher soil metal rank. The relationship between soil metal rank and methane flux was the weakest significant correlation due to the inclusion of all five metal species within the soil metal rank.

Factor 2 explained 27.0 percent of the variance. It described the distribution of soil metal load, Zn, and Cr as having some relationship to soil percent organic matter. The soil metal concentrations were positively correlated with soil percent organic. Soil organic percentage did not have a significant correlation with methane flux in this factor analysis. Factor 3 described 23.2 percent of the variance. Soil metal load was positively correlated with the soil pH and again with soil percent organic. This group seems to be related to the distributions of soil metals being similar to that of soil pH and soil percent organic. In this factor analysis soil pH was not significantly correlated with methane flux.
Figure 27- Laboratory Greenhouse Study Methane Flux Rates for Each Study Site over the 165 day study period from 3/23/2012 - 9/13/2012 a. Site 1 Methane Flux Rates, b. Site 43 Methane Flux Rates, c. Site 7/8 Methane Flux Rates, d. Site 16 Methane Flux Rates, e. Site 25 Methane Flux Rates.
Figure 28 – Average Laboratory Greenhouse methane flux rate for each study site over the entire 165 day study period with 1 standard error.
**c.**

\[ y = -0.0004x + 0.5059 \]

\[ R^2 = 0.2678 \]

**d.**

\[ y = -0.0001x + 0.5987 \]

\[ R^2 = 0.3196 \]
Rotated Loading Matrix (VARIMAX, Gamma = 1.000000)

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Percent of Total Variance Explained

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Table 9- Factor analysis of Laboratory Greenhouse Methane Flux
The results of the greenhouse and the LSP methane flux study are noticeably similar. Both studies showed higher positive methane flux rates at the wetland sites with less soil metal contamination. In both studies the upland sites with increased levels of soil metal contamination had lower positive flux and negative flux. The only major difference between the two studies was the results of site 7/8. This wetland contaminated site had a low positive methane flux rates in the field study and high positive methane flux rates in the greenhouse study.

In the greenhouse the external conditions were controlled, isolating the soil properties impacts on methane flux rates. The sites were all saturated with water leading to anaerobic conditions. This created conditions suitable for the production of methane by methanogenic microbes. The sites however had both positive and negative methane flux rates similar to those in the field. Sites 1 and 43 both had significant positive methane flux rates in the greenhouse and in the field. Site 16 had low positive methane and negative methane flux rates under saturated conditions in the greenhouse experiment and in its native upland habitat in the field. Site 25 had a negative flux in its upland field location and in the greenhouse study where the soil was saturated.

Site 7/8 had the highest rates of positive methane flux in the greenhouse, but barely positive methane flux in the field. One possible explanation for this behavior was related to the high soil metal load at site 7/8. In the field the high concentrations of soil metals may have caused the methanogenic microbes to become stressed. When the water levels decreased during the summer at site 7/8 it was too much for them to handle and they died off or ceased functioning more easily the non-contaminated wetland sites. In the greenhouse the site remained saturated and the microbes endured, producing larger amount of methane. These microbes may have been
more hearty than those of the non-contaminated sites because they have had to survive more stressful conditions.

Site 25 behaved as expected for an upland site in the field, absorbing methane from the atmosphere into the soil with a negative flux rate. Site 25 also had a strong negative flux rate under saturated conditions in the greenhouse. It was possible that the high metal concentrations at Site 25 had a negative impact on the methanogens causing the methanotrophs to dominate. It also may have been the case that the methanogenic microbes did not have sufficient time to develop in the newly saturated soil. If the greenhouse study was conducted for a longer time period the flux at Site 25 may have become positive.

In the LSP field study the site hydrology as well as the soil metal concentrations appear to be the two major factors to have influenced methane flux. A combination of a high water table and low soil metal concentrations may have caused sites 1 and 43 to produce higher positive methane flux rates. Site 7/8 was under similar hydrologic conditions, but had a lower flux rate. It may have been the heavy metal contaminations that led to this lower flux rate, as heavy metal contamination had been shown to decrease soil microbial biomass, or impair biological functions.

Site 16 was an upland site with high levels of soil metal contamination. Site 16's hydrology along with its high levels of soil metal contamination could account for its low positive and negative methane flux rates. In the greenhouse Site 16 actually emitted slightly less methane on average from its soil despite being under anaerobic conditions. This was the opposite of what would be expected to happen under anaerobic conditions. This anomaly may have been due to the soil metal contamination having a greater negative effect on methanogenic soil
microbes than on metabotropic microbes. In more time there may more positive methane flux rates may have developed.

It was clear that the site hydrology was a major cause of the difference between the methane flux rates of five study sites. The two upland sites had low and negative methane flux rates in the field study as was usually the case in aerobic soil. Site 25 the most upland site acted as a methane sink in the field as predicted. When these sites were saturated they still produced low and negative methane flux rates, a testament to the dominance of their soil methanotrophic microbial populations. The three wetland sites acted as methane sources in both studies with mostly positive rates of methane flux. The anaerobic conditions of these sites were suited to the emission of methane by methanogenic microbes.

A negative trend between soil metal contaminations and methane flux was shown in both studies. It was less clear whether this trend was a product of the metal contaminations influence on the microbial populations or whether it was driven by the hydrologic conditions of the study sites. In the field study the negative trend was stronger than in the greenhouse study. Site 7/8, the only wetland site with high levels of soil metal contamination, was major reason for this difference. In the field study it had significantly less methane production than the other wetland sites. It seemed that something was negatively effecting the methane production of the methanogenic microbes. The soil heavy metal contamination was the only other significantly correlated site characteristic with methane flux, and may be the reason for the decrease in methane production. In the greenhouse study where water levels were kept constant site 7/8 had the highest positive methane flux rates. This goes against the trend that the soil metal contaminations was decreasing the output of methane from the soil. Future studies could address
this problem by studying the methane flux rates of heavy metal contaminated sites that more similar site hydrology and that are preferably all wetland sites.
Discussion - The Impacts of Soil Heavy Metal Contamination on Methane Flux

Liberty State Park has undergone a great deal of change throughout the last several centuries. It was altered to fulfill the transportation needs of The New York City metropolitan area without much regard for the environmental impacts of a major rail head. Now abandoned for almost 50 years, the inner study area of Liberty State Park had time to redevelop into an area that can provide important ecosystem services. This methane flux study was designed to assess whether the natural processes of methane sequestration and emission were affected by these alterations.

The sequestration of methane gas within the soil by methanotrophic microbes is an important step in the global carbon cycle. Worldwide anthropogenic sources of methane into the atmosphere have been increasing due to global industrialization (USEPA 2012). This had made the natural processes of methane sequestration ever more important. Upland forested areas with aerobic soil conditions provide this significant function through the effort of methanotrophic microbes (Le Mer et al. 2001). In Liberty State Park many of these upland areas have been contaminated by heavy metals. These metals have been shown to decrease the biomass and reduce the biological functions of microbial life (Giller et al. 1998). If forested areas lose their natural ability to sequester methane gas their value as a natural area is decreased. This must be accounted for in any cost benefit analysis that evaluates the economic and ecological value of a piece of contaminated forest or wetland.

This study has shown that despite the high level of soil contamination the two upland sites which were studied are still preforming the valuable function of methane sequestration. Site 16 which had a higher water table level of the two upland sites had mostly neutral or negative
methane flux rates in both the field and greenhouse study despite being heavily contaminated. Site 25, the most upland and heavily forested site, provided the greatest amount of methane sequestration in both the field and greenhouse study even though it was the most heavily contaminated site. This site produced negative methane flux rates on a consistent basis for the entirety of both studies. It can then be concluded that based on this study, soil heavy metal contamination was not impairing the methane sequestration of the upland sites at Liberty State Park.

This analysis can be applied to the land management practice at Liberty State Park and similar upland forested brownfield areas. It shows that despite being contaminated with heavy metals, the soil was still serving an important purpose. This function, along with the other ecosystem functions of upland forests, must be accounted for when determining what to do with these polluted sites. The concerns of global climate change and the increasing concentration of methane in the atmosphere will serve to increase the importance of keeping forested upland areas in their natural state, even if they have been contaminated in the past.

Wetland areas also serve many significant ecological functions and provide important ecosystem services (USEPA 2012). In the New York City metropolitan area, many wetlands have been filled for commercial or residential use. The effect of soil heavy metal contamination on the wetland sites within Liberty State Park was less clear than at the upland sites. The three wetland sites all had positive methane flux rates in both the field and greenhouse study. Site 7/8, the only contaminated wetland site, had a lower methane flux rate than the other wetland sites in the field study. Site 7/8 had a higher methane flux rate than the other wetland sites in the greenhouse study when water table level was kept constant.
Due to this difference it was hard to conclude whether soil metal contamination had an inhibitory, positive, or insignificant effect on the methanogenic populations. There may have been other factors such as; the transplantation, differences between tap water and natural water, or the effect of a controlled climate which could have impacted the results of the greenhouse study. Further study will be needed on contaminated wetland in order to make any decision as to the effect of metal contamination on methane flux rates.

What is clear is that the negative impact of methane emissions from wetland environments is a small price to pay for their many benefits and services. If heavy metal contamination will increase the amount of methane released from a wetland environment then this is just another reason to protect our wetlands. If heavy metal contamination was found to be negatively effecting methanogenic soil microbes and decreasing their output of methane it does not mean that the contaminations of wetland areas is justified. For if methanogenic microbes are being negatively affected it is reasonable to presume that other beneficial soil microbes are also being harmed, effecting other important wetland function.
Conclusion

The increasing amount of global industrialization is placing a strain on the abilities of ecosystems to provide the natural services essential for biodiversity and human wellbeing. The processes of methane emission and sequestrations are just some of the many natural functions that may be impacted by soil heavy metal contamination. Calculating methane flux from contaminated wetland and upland area is an important factor in determining whether these environments are still functioning as expected, and thus what their benefits are of remaining in a natural state. This relationship should be explored further as more of the world become increasingly industrialized leading to the pollution of natural areas.

This study showed that changes in soil metal concentrations maybe affect the amount of methane moving from the soil into the atmosphere in the wetland areas of Liberty State Park. It also exhibited that the upland areas are still functioning as methane sinks despite being the most heavily contaminated areas within the park. Further development of the natural study area within the center of Liberty State Park should take in to account all of the ecosystem functions provided by this area before determining whether to develop, remediate, or leave this area in its natural state.
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