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CHARACTERISING NEW ENGLAND (UNITED STATES OF AMERICA) SALT MARSH SEDIMENT HEAVY METAL CONCENTRATION TRENDS VIA PROXIMITY TO ANTHROPOGENIC POLLUTION, SEASONS, AND VEGETATION COVERAGE.

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Salt marsh sediment serves an important ecological service by sequestering carbon but is also a repository for several pollutants including heavy metals. Metal uptake in marshes is affected by numerous environmental characteristics such as sediment pH and redox potential, but anthropogenic activities have also been adding metal loads to these fragile ecosystems. This metal deposition can have negative effects both environmentally and on human health. This study aims to better characterise the concentrations of six metals (arsenic (As), copper (Cu), manganese (Mn), zinc (Zn), lead (Pb), nickel (Ni)) in the sediment of two salt marshes in Massachusetts (United States of America). Metal loadings were compared (1) between anthropogenic loadings (i.e., a rural versus urban site); (2) seasonally; and (3) across native and invasive vegetation types. Heavy metal concentrations were analysed using a Handheld XRF instrument. There was a significant difference (p-value < 0.05) between the urban samples and rural samples, with the urban marsh showing higher rates of metal pollution. There was no significant difference (p-value > 0.05) seasonally among these metals but sediment samples under the invasive plant vegetation (*Phragmites australis*) had significantly higher (p-value < 0.05) metal concentrations compared to those samples under native plant vegetation (*Spartina alterniflora*). This study serves as a foundation for making future predictions in the face of climate change as more people move to urban areas, average atmospheric temperatures increase and precipitation patterns change, and sea level rise changes plant zonation.

Key words: Salt Marsh; Heavy Metals; Seasonality; Vegetation

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Introduction

Salt marsh soil

Salt marshes perform several vital chemical and physical functions: chemical contaminant retention and transformation, organic carbon production and export, groundwater recharge, sediment entrapment, shoreline erosion mitigation, and flood attenuation (Kennish, 2001). They are also vital carbon sinks due to their ability to sequester large quantities of carbon in their biomass and in their sediment (Hiraishi *et al.*, 2014). Coastal wetlands are more effective carbon sinks compared to the majority of terrestrial forests per area (Mcleod *et al.*, 2011; Pan *et al.*, 2011). Between 50% - 90% of all coastal wetland carbon, contingent on vegetation type, is stored in the sediment (as opposed to above ground biomass; Pendleton *et al.*, 2012).

Organic matter is highly concentrated in salt marsh sediments due to both tidal inundation and anoxia (Chmura *et al.*, 2003; Duarte *et al.*, 2005; Donato *et al.*, 2011; Breithaupt *et al.*, 2012; Pellegrini *et al.*, 2015; Chen *et al.*, 2016). Tidal inundation keeps the sediment submerged, preventing microbial action and decelerating decomposition such that marsh sediment carbon remains fairly stable and inert (Howard *et al.*, 2017). The positive

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relationship between soil moisture, which is relatively high in salt marsh sediment due to tides, and total organic carbon (TOC) indicates that the waterlogged condition caused by tidal flooding favours carbon buildup in marsh sediment (Bai *et al.*, 2005; Qu *et al.*, 2019). In addition to high water content (waterlogged soil) and high concentrations of organic carbon, salt marsh sediment is also generally characterised as anoxic. Flooding tidal wetlands (e.g., from tides or storms) results in carried suspended sediment that helps vertical sediment accretion (Schiebel *et al.*, 2020). During extended periods of inundation, oxygen is usually limited, and the marsh sediment column is anoxic (Furukawa *et al.*, 2004). Anoxic soil is also positively correlated with organic matter buildup as oxygen tends to break down organic matter.

Metals in marsh soil

Along with carbon sequestration via marsh sedimentation processes, metals also cycle into marsh soils. Metal sources can be natural as well as anthropogenic and include atmospheric deposition, chemical weathering of rocks and agricultural practices, as well as secondary sources such as the reworking of sediments through the addition of wastes (Demirak *et al.*, 2006; Sayadi and Rezaei 2014). Beneficial metal nutrient elements such as copper (Cu), manganese (Mn), zinc (Zn), nickel (Ni), cobalt (Co), iron (Fe), and molybdenum (Mo) are necessary for regular plant growth as well as development (Loftleidir, 2005). They occur in the soil naturally in limited concentrations and are transported to vegetation via metal transporters (molecules that move metal ions across otherwise impermeable membranes; Krämer *et al.*, 2007), which play a role in metal adsorption and translocation (Krämer et al., 2007; Puig *et al.*, 2007). Grotz and Guerinot (2006) observed the uptake of Zn and Fe in higher concentrations in plants compared to other metals.

The plant availability of micronutrients (i.e., Cu, Mn, Co, Mn) depends on factors such as genetic differences among plant species as well as soil properties (i.e., parent material composition, organic matter content, clay content, soil pH; Loftleidir, 2005). In addition to beneficial metals, salt marsh sediments are also repositories for several pollutants, which includes heavy metals (Bettinetti *et al.*, 2003). Heavy metal uptake is affected by numerous environmental characteristics such as sediment pH and redox potential (Burke *et al.*, 2000). Several studies have determined that higher redox potential (more oxic conditions) as well as lower pH are correlated with higher bioavailability of metals in sediment (De Laune and Smith, 1985; Gambrell, 1994). Heavy and trace metals in sediment can exist in several chemical forms (Rauret, 1997). The largest proportions of metals in unpolluted sediment are usually bound to silicates and primary minerals which form relatively immobile species (Rauret, 1997). However, the metals in polluted sediment are usually more mobile in comparison and bound to other sediments phases (Rauret, 1997). Heavy metals in sediment are commonly a sink but could also become a source under specific conditions, like in heavily contaminated regions (Rauret, 1997).

Some metals in salt marshes can have negative impacts on environmental and/or human health. Six such metals of concern are arsenic (As), Cu, Mn, Zn, lead (Pb), and Ni, all of which are found in both urban and rural areas (note that although more properly referred to as a 'metalloid', As is included in the collective term 'metals' here to keep text concise). As has been added to the environment via domestic and industrial waste discharge over the last few decades (Chen *et al.*, 2000; Feng *et al.*, 2004; Chetelat *et al.*, 2008; Huang *et al.*, 2008; Yao and Zhang, 2009; Zhang *et al.*, 2009). As, in its inorganic forms (i.e., arsenite and arsenate compounds), is fatal to organisms in large amounts (Jaishankar *et al.*, 2014). It is a protoplastic poison that affects the sulphydryl group of cells, which leads to malfunctions of cell respiration, cell enzymes and mitosis (Gordon and Quastel, 1948).

Cu can be spread via geogenic pollution sources (e.g., volcanic activity and rock weathering) and anthropogenic sources such as industry and motor vehicle traffic (De Vivo *et al.*, 1995; Albanese and Cicchella, 2012;

Filippelli *et al.*, 2012). It is a vital micronutrient for both plants and animals but can also cause toxic effects at high concentrations (Guzman-Rangel *et al.*, 2018; Kader *et al.*, 2018).

Mn is added to the environment via various sources of pollution such as burning of coal, release of wastes like fly ash, and effluents from industries and excessive use of chemical-based pesticides in agricultural fields (Drličková *et al.*, 2013) but is also naturally present in the Earth's crust. The numerous sources of Mn can become problematic because at higher concentrations, it is toxic to plants and other organisms with high enough exposure (Mukhopadhyay and Sharma, 1991; Harasim and Filipek, 2015).

Zn is largely utilized in alloys, smelting, pesticides, electroplating and is also frequently linked to mining impacts because of the economic standing of its ores (Gordon *et al.*, 2003; Hudson-Edwards *et al.*, 2011). Zn, like Cu, is an essential micronutrient for both plants and animals but can also lead to toxic effects at high concentrations (Guzman-Rangel *et al.*, 2018; Kader *et al.*, 2018).

Pb is a toxic metal and can be added into natural waters anthropogenically from a mix of industrial wastewaters including paper and pulp, mining, electroplating, lead smelting and metallurgical finishing, and automotive industries (Iqbal and Khera, 2015). It is a highly lethal metal, and due to its widespread use, has led to a large amount of environmental contamination and health problems (i.e., lead poisoning; Jaishankar *et al.*, 2014). The metal can then be taken up by plants, fixed to soil, or enter water bodies, leading to further exposure (Jaishankar *et al.*, 2014).

The main sources of Ni emissions into the environment are combustion of coal and oil for heat or power generation, nickel mining, agriculture steel manufacture, and other miscellaneous sources, such as cement manufacturing (Sreekanth *et al.*, 2013). The many sources of Ni, like Mn, in the environment can also become problematic because at higher concentrations it is toxic to plants and other organisms with high enough exposure (Mukhopadhyay and Sharma, 1991; Harasim and Filipek, 2015).

Urbanization and seasonal trends

Salt marshes in urban areas typically get larger loads of pollution compared to that of rural salt marshes along with greater amounts of heavy metals because of industrial and transportation activities (Burke *et al.*, 2000). Xiao et al. (2013) observed high levels of heavy metal (Cu, Zn, Pb, Ni) pollution in the sediments of a rural river in China, but even higher concentrations were observed in those from an urban river in China. On average, Cu was 25 mg kg-1 higher, Zn was 74 mg kg-1 higher, Pb was 10 mg kg^{-1} higher, and Ni was 48 mg kg^{-1} higher (Cu and Zn was significantly higher ($P < 0.05$), Pb and Ni was not ($P > 0.05$)). This indicates that many aquatic ecosystems face differences between their rural and urban counterparts in terms of pollution loads. Davis *et al.* (2009) studied several metals (As, Cu, Mn, Pb, Ni) in both forested areas (i.e., rural) and urban sites and determined that both broad (e.g., ecoregion) and specific (e.g., soil type and soil physical properties) natural features seemed to be more central determinants of soil metal concentrations compared to land cover and use.

Few studies have considered seasonal trends in New England in terms of heavy metal concentrations in the sediment. However, a study in China (As, Cu, Zn, Pb) found that among three seasons, most soil profiles of three sampling sites exhibited the highest levels in summer, followed by spring, whereas the lowest levels were in the fall (Bai *et al.*, 2014). A study in England, however, found the opposite trend (As, Cu, Mn, Zn, Pb, Ni), with a high in winter and a low in summer specifically due to sewage discharge patterns and possible microbial activity (Wright, 1999). Adversely, another study found that metals (Cu, Zn, Pb, Ni) can vary but are affected by other seasonal factors such as monsoon seasons or dry seasons (Kumar *et al.*, 2012). Additionally, the rate of different industrial activities is an important influence that can alter metal inputs and can differ between specific metals.

Metals interactions with marsh vegetation

Due to the strong interaction between marsh sediment and vegetation, metals move between the two reservoirs and can be altered in the process. Wetland sediment is typically reduced and therefore metals are immobilized as insoluble metal sulfides (Simpson and Good, 1985). These metals, however, do not stay inactive (Lacerda *et al.*, 1997) and marsh vegetation can change the redox of the sediment. Several species of marsh vegetation can move oxygen down to their roots via their aerenchyma tissue and then release said oxygen from the roots, which creates an oxidized sediment environment in the rhizosphere (Giblin *et al.*, 1986) and oxidizes sulfides (Lee *et al.*, 1999). When the rhizosphere becomes oxygenated, it alters the sediment chemistry by creating a concentration gradient that forces metals towards the roots (Lacerda *et al.*, 1997; Sundby *et al.*, 1998). When vegetation receives and relocates metals to the above-ground tissue, it becomes a pathway for the migration of toxic metals from sediments into the food webs of marsh ecosystems and near shore waters (Sanders and Osman, 1985; Kraus *et al.*, 1986; Kraus, 1988). In regions with high concentrations of metals in sediment, plant roots have been observed to take in the metals and then relocate them to above-ground biomass (Burke *et al.*, 2000). Salt marsh plants are positioned in close proximity to the marsh surface and rapidly integrate metals from the sediment (Orson *et al.*, 1992; Windham *et al.*, 2003).

There are three typical New England salt marsh plants. *Spartina alterniflora* (*S. alterniflora*), native to this region, occupies the lower marsh habitat while the invasive *Phragmites australis* (*P. australis*) and native *Spartina patens* (*S. patens*) occupy the marsh flats (Schiebel *et al.*, 2018). In the last 50 years, the presence of this invasive species has risen exponentially (Saltonstall, 2002). *P. australis* is an opportunistic plant that prospers in disturbed areas (Minchinton and Bertness, 2003), and has drastically enlarged its coverage through colonizing expanses of human-altered wetlands as well as salt marsh regions along the east and gulf coasts of the United States (Saltonstall, 2002). Numerous introduced (invasive) species have competitive advantages compared to native species and can therefore colonize in large abundance (Kirk *et al.*, 2011). A main concern is that *P. australis* is tremendously competitive and is replacing native plant species, thus reducing plant community richness and diversity (Medeiros *et al.*, 2013). In New England brackish tidal marshes, the growth of *P. australis* typically results in the reduction of *S. patens* and *S. alterniflora* in areas where they can both grow (Medeiros *et al.*, 2013).

It is known from previous studies that *P. australis* retains a greater fraction of metals in the roots, while *S. alterniflora* transports more into the leaves (Burke *et al.*, 2000; Weis *et al.*, 2002; Windham *et al.*, 2003). The release of metals from the leaf tissues to the surface is a typical adaptation amid plant species for dealing with metal loads (Verkleij and Schat, 1990), but the significance of this differs with the composition of the specific plant species. The differences between *S. alterniflora* and *P. australis* in terms of their interactions with metals are due to the lack of salt glands in *P. australis*. High rates of metal release by vegetation could increase the bioavailability of metals within estuaries, especially in urban industrialized regions where even limited releases may have harmful effects on the food webs (Berk and Colwell, 1981).

An additional important mechanism by which metals from above-ground biomass of vegetation could make its way into the food web is via the ingestion of contaminated detritus by consumers (Burke *et al.*, 2000). The higher levels of specific metals in the leaves of *S. alterniflora* compared to *P. australis* indicates that break down of the former plant could potentially lead to more highly contaminated detritus (Burke *et al.*, 2000). In a marsh system where above-ground biomass of both plant species is alike, it is likely that *S. alterniflora* would release twice as much toxic metals compared to *P. australis* for certain metal species (Burke *et al.*, 2000).

Experimental study

This study was multi-faceted with three main objectives. The first objective was to better characterise the concentrations of six metals (As, Cu, Mn, Zn, Pb, Ni) in the soil of two salt marshes in Massachusetts (United States of America), one urban and one rural, to understand how anthropogenic loadings differ between the two sites. The second objective of this study was to create an annual dataset of metal loadings to analyse and outline any seasonal variations among sediment metal loadings by location. The third objective was to explore how vegetation affects metal availability in salt marshes with a focus on a native (*S. alterniflora*) and invasive (*P. australis*) plant in each study site.

Methods

Urban study site: Neponset River Salt Marsh (NRSM)

The second largest tributary to Boston Harbour (Boston, Massachusetts) is the Neponset River (Gardner *et al.*, 2005). The watershed draining into the Neponset River is made up of 14 cities and towns (Huang and Chen, 2009) but in Boston alone, where the urban study site is located, was comprised of roughly 692,600 residents in 2019 (United States Census Bureau, 2019). Pollution sources to this area include industrial runoff, vehicle exhaust, construction, boating exhaust, and more. The Neponset Estuary is approximately 7 km long and changes in width from about 25 to 250 m at mean lower low water (MLLW; Schiebel *et al.*, 2018). The NRSM (42.277309 N, 71.045837 W) has a total area of 1.1 x 10^6 m^2 and the plant community is composed of three dominant species: *S. alterniflora* which dominates the lower marsh habitat, the invasive reed *P. australis* which dominates the high marsh habitat and *S. patens* which lies in between the two on the marsh platform (Figure 1; Schiebel *et al.*, 2018).

Approximately 29% of the total surface area is below the MLLW mark and is usually covered by water with little to no vegetation (Schiebel *et al.*, 2018). Typical New England salt marsh sediment is made up of peat, with water content ranging from 30 to 60% (Redfield, 1972; Schiebel *et al.*, 2018) and sediment organic carbon values ranging between 0.05 and 0.15 g cm^{-3} (Artigas *et al.*, 2015), as confirmed by observations.

Rural study site: Plum Island Sound Estuary (PISE)

PISE is located in northeast Massachusetts and

Figure 1. Neponset River Salt Marsh (Schiebel *et al.*, 2018)

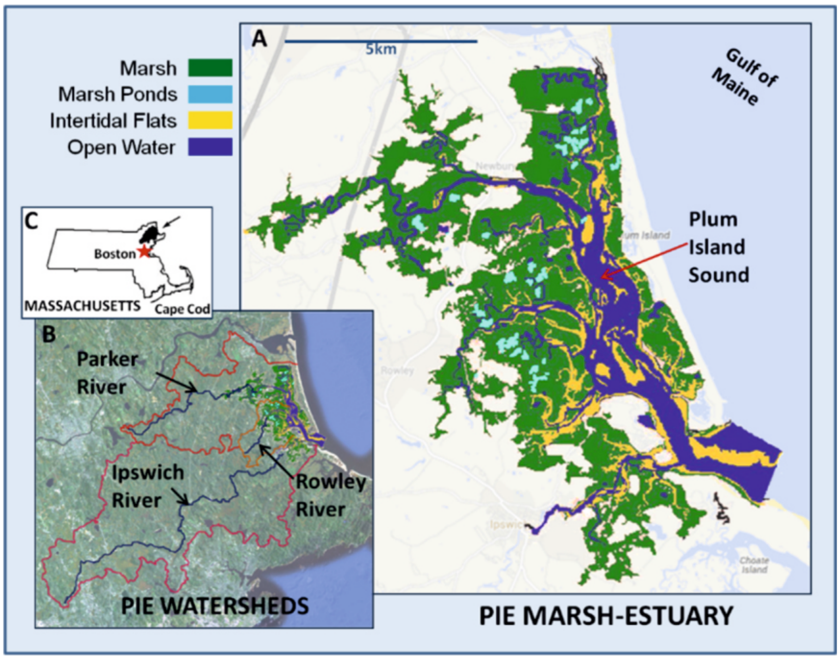

Figure 2. Plum Island Sound Estuary

has been a long-term ecological research site since 1998 (Figure 2).The estuary and its associated watersheds contain 26 towns and is within the Seaboard Lowland section of the New England physiographic province (Fenneman, 1938; PIE, 2020). The town of Rowley, in which the rural study site is located, is made up of approximately 6,473 residents (United States Census Bureau, 2019). It is subjected to less anthropogenic activity compared to NRSM, but includes pollution sources such as shells from hunting, some vehicle exhaust, construction, farm waste, and more. The rivers as well as the estuary itself discharge into the Gulf of Maine. PISE is a coastal plain estuary with immense regions of productive tidal marshes. Mean depth increases along the length of the estuary from roughly 1.4 m at the head of the estuary to approximately 5.7 m deep about 11 km downstream at the head of the sound (Vallino and Hopkinson Jr., 1998; PIE, 2020). Depths then rise through the broad shallow sound to roughly 1.8 m before decreasing to approximately 4.7 m at the mouth of the estuary (Vallino and Hopkinson Jr., 1998; PIE, 2020). Low to high tide ranges from 7.2 - 14.9 km^2 in the water body area (Vallino and Hopkinson Jr., 1998; PIE, 2020). There are broad regions of non-vegetated, intertidal flats seen at low tide. In PISE, where the average spacing of topographic features is substantially less than the tidal excursion and tidal amplitude is of the same order as average depth, tidal shear dispersion is most likely the main mechanism contributing to mixing (Smith, 1977; Geyer and Signell, 1992; PIE, 2020). Vegetation is a conventional characteristic of New England marshes, the foremost species being *S. alterniflora* and *S. patens* in brackish and saline areas as well as *P. australis* in less saline areas, with all three species being observed in PISE.

Seasonal data

Both study sites are in Massachusetts, characterised by four distinct seasons (Table 1; U.S. Climate Data, 2019).

Sample collection and analysis

Sediment samples were collected bi-weekly for a year (June 2019-June 2020) at both marshes (urban and rural) in two locations at each site; one dominated by the invasive *P. australis* and one dominated by the native *S. alterniflora*. Roughly 100 g-discrete grab samples (approximately the top 6 cm of the surface sediment) were collected by hand using a spade and put in Ziplock bags where they were then stored in a freezer until

Season	Average High Temperature (C)	Average Low Temperature (C)	Average Precipitation (cm)
Autumn	16.5	8.5	10.6
Winter	3.6	-3.9	9.0
Spring	13.1	4.7	10.2
Summer	26.1	17.3	10.1

Table 1. Seasonal Massachusetts data temperature and rainfall.

analysis.

In September of 2020, the samples were freeze dried at the Analytical Facilities Laboratory at Brown University in Providence, Rhode Island. Freeze dried samples were homogenized in their bags by hand and then ground using a mortar and pestle. Next, 3-6 representative grams of each sample were transferred into a whirl-pak bag and analysed with an Olympus Handheld XRF instrument (two sixty-second tests). Samples were compared against a NIST 2702 marine sediment standard (commercial product) to obtain heavy metal concentrations (in ppm) for six metals (As, Cu, Mn, Zn, Pb, Ni). Statistical tests (Analysis of Variance and T-test) were completed using R software to determine if there were any significant differences between study sites, seasons, or vegetation coverage.

Results and Discussion

Urbanization trends

All of the metals except for As were higher in concentration in NRSM sediment compared to PISE (Figure 3).

Although As concentrations did not differ between locations, the overall spread of the concentration among seasons never reached higher than 15 ppm, which was the lowest out of all of the metals. Alternatively, Mn concentrations reached approximately 1,000 ppm, the highest out of all of the metal concentrations (Figure 3).

While studies have not widely compared metals in marsh soils in terms of proximity to cities, river studies comparing urban and rural sites have been conducted. Xiao *et al.* (2013) looked at the distribution of heavy metals in sediments from urban and rural rivers of the Pearl River delta located in China. Sediment

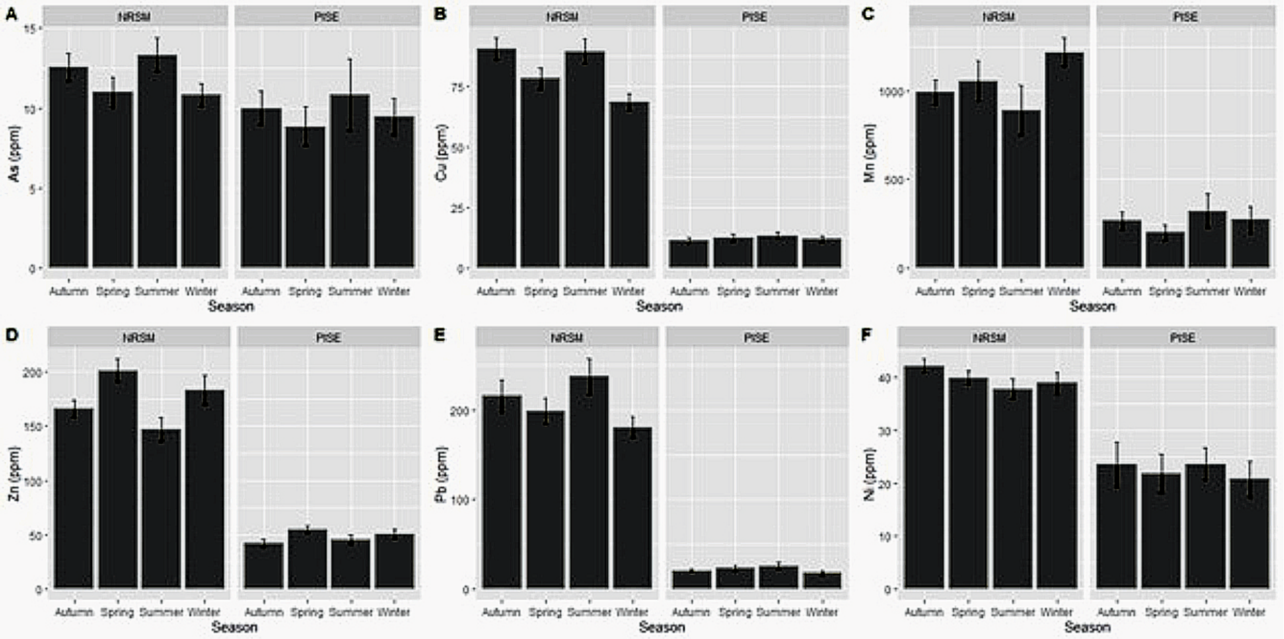

Figure 3: Distribution of heavy metals (A= As, B = Cu, C = Mn, D = Zn, E = Pb, F = Ni) among seasons between the NRSM in Boston, MA and the PISE in Rowley, MA. This data shows the mean of *P. australis* and *S. alterniflora* sites combined. Error bars of indicative of standard deviation.

samples were collected from a 0 - 60 cm depth at low tide throughout the dry season at each sampling site using plastic sampling tools (Xiao *et al.*, 2013). To analyse the total metal content, the samples were digested by an acid mixture and analysed on an inductively coupled plasma atomic emission spectrometer (Xiao *et al.*, 2013). They concluded that the urban river sediments had higher Cu and Zn, compared to the rural river sediments ($P<0.05$). However, there was no significant differences in Pb or Ni concentrations between the urban and rural river sediments ($P>0.05$). Xiao *et al.* (2013) found that Cu and Zn averaged 133 ppm and 327 ppm respectively at the urban site, and 75 ppm and 253 ppm respectively at the rural site. Pb and Ni averaged 96 ppm and 66 ppm respectively at the urban site, and 86 ppm and 53 mg ppm respectively at the rural site. For the current study, Cu and Zn averaged 82 ppm and 174 ppm respectively at the urban site, and 54 ppm and 48 ppm respectively at the rural site. Pb and Ni averaged 209 ppm and 40 ppm respectively at the urban site, and 22 ppm and 25 ppm respectively at the rural site. This current study found similar results to Xiao *et al.* (2013) with significantly more Cu and Zn in the urban marsh compared to the rural marsh. However, contrary to the Xiao *et al.* (2013) study, this study saw a more significant concentration of Pb and Ni in the urban site as well. Different metals may or may not be significantly different between urban and rural areas depending on activity as well as location once inside of the study site. Therefore, it is likely that the different levels of heavy metals between these sites and those of Xiao *et al.* (2013) are due to different levels of anthropogenic activity. Furthermore, since Xiao et al. (2013) observed rivers and this current study observed salt marshes, salinity and tidal impacts could also have accounted for some differences in the current study.

Zhang *et al.* (2017) measured the heavy metal concentrations (Cu, Zn, Pb, Ni) in sediments from an urban, rural, and reclamation-affected river in China. In each sampling site, three sediment columns at a depth of 30 cm were collected and each column were divided into three parts at 10 cm sections, and then those subsamples at the same layer for each sampling site were homogeneously mixed to form a composite sample (Zhang *et al.*, 2017). The samples were air-dried and sieved through a 2-mm nylon sieve. The concentration of heavy metals in the samples were further analysed by an inductively coupled plasma atomic emission spectrometer after the sediment samples were digested in an acid mixture (Zhang *et al.*, 2017). They concluded that urban river sediments, specifically the surface sediment layer (0-10 cm), showed higher metallic pollution levels compared the rural river sediment. They found that Cu and Zn averaged 182 ppm and 487 ppm respectively at the urban site, and 69 ppm and 261 ppm respectively at the rural site. Pb and Ni averaged 151 ppm and 106 ppm respectively at the urban site, and 95 ppm and 46 ppm respectively at the rural site. For the current study, Cu and Zn averaged 82 ppm and 174 ppm respectively at the urban site, and 54 ppm and 48 ppm respectively at the rural site. Pb and Ni averaged 209 ppm and 40 ppm respectively at the urban site, and 22 ppm and 25 ppm respectively at the rural site. This current study saw similar results to Zhang *et al.* (2017), with higher rates of these four metals in the urban study site compared to the rural study site. Zhang *et al.* (2017) noted that the urban river was greatly affected by dusts and aerosol which was a result of human activities (e.g., industrial and energy production, construction, vehicle exhaust and waste disposal) and caused large metallic pollution. Because the NRSM is also subjected to nearby industrial production, construction, and vehicle exhaust, it can be concluded that this was a main contributor to the higher heavy metal concentrations compared to PISE (Figure 3).

Seasonality trends

There were no significant seasonal trends by location or metal ($P > 0.05$; Figure 3, Table 2). As concentrations were the highest in the summer, although not significantly higher compared to the other seasons. The other metals in this study did not follow a discernable seasonal pattern. Roychoudhury (2007) found that trace metal concentrations

Metal	Season	T-value	P-value	T-value	P-value
As	Intercept (Autumn)*	13.0	< 2.0 x10^{-16}	6.9	5.8 x 10^{-09}
	Spring	-1.2	0.2	-0.6	0.6
	Summer	0.6	0.6	0.4	0.7
	Winter	-1.3	0.2	-0.3	0.8
Cu	Intercept (Autumn)	21.0	< 2.0 x10^{-16}	9.9	6.8 x 10^{-12}
	Spring	-1.9	5.9 × 10^{-2}	0.7	0.5
	Summer	-0.2	0.9	1.3	0.2
	Winter	-3.5	1.0×10^{-3}	0.3	0.7
Mn	Intercept (Autumn)	9.3	3.5 x 10^{-13}	4.0	2.0 × 10^{-4}
	Spring	0.4	0.7	-0.7	0.5
	Summer	-0.7	0.5	0.6	0.6
	Winter	1.5	0.2	5.1 × 10^{-2}	1.0
Zn	Intercept (Autumn)	16.0	< 2.0 x10^{-16}	11.0	9.6 x 10^{-16}
	Spring	2.3	2.6 × 10^{-2}	2.3	2.6 × 10^{-2}
	Summer	-1.3	0.2	0.6	0.6
	Winter	1.1	0.3	1.5	0.1
Pb	Intercept (Autumn)	13.0	< 2.0 x10^{-16}	7.2	2.3 x 10^{-09}
	Spring	-0.7	0.5	0.7	0.5
	Summer	0.93	0.36	1.3	0.20
	Winter	-1.5	0.14	-0.62	0.54
Ni	Intercept (Autumn)	25	< 2.0 x10^{-16}	6.8	1.4 x 10^{-08}
	Spring	-0.93	0.36	-0.33	0.74
	Summer	-1.9	6.6 × 10^{-2}	2.5 × 10^{-2}	0.98
	Winter	-1.4	0.18	-0.53	0.60

Table 2. Statistical analysis of metals between locations among seasons. *The intercept, which was autumn for each of the six metals, is indicative of a significant difference from the value of zero. These P-values do not indicate a significant difference between autumn and the other seasons, but that autumn was significantly higher than zero.

(As, Cu, Zn, Pb, Ni) in surface sediment in Georgia (USA) marshes were comparatively lower in summer than winter presumably due to higher wetland plant uptake as well as standing stocks of metals in the summer, but that was not observed here.

Bai *et al.* (2014) characterised the seasonal dynamics of trace elements (As, Cu, Zn, Pb) in tidal salt marsh soils in China over the summer, fall and spring. Sediment samples were collected at three separate sites and total metal concentrations were determined using inductively coupled plasma atomic absorption spectrometry (Bai *et al.*, 2014). Among the three seasons, most sediment profiles of the three sampling sites showed the highest levels of all four metals in the summer, followed by spring, and the lowest in fall (Bai *et al.*, 2014). This seasonal difference indicates the involvement of the flow-sediment regulation in the summer to pollutants from upper reaches deposition and accumulation in the delta as well as higher self-purifying abilities of the salt marshes (Bai *et al.*, 2014). Furthermore, sampling seasons had a leading impact on the spatial distribution patterns and likely ecotoxicity of trace elements (Bai *et al.*, 2014).

Most recently, Nguyen *et al.* (2020) analysed the seasonal and spatial distribution of heavy metals in Saigon River sediment in Vietnam. 96 sediment samples were collected during the rainy and dry season on 13 different sampling sites dispersed over the lower reaches of the river to investigate the concentration of 11 heavy metals. The samples were air-dried and ground to pass through a 2-mm sieve before conducting chemical analyses. The exchangeable concentration of heavy metals (including Mn, Zn, Pb, Ni) were measured utilizing the barium chloride method (Carter and Gregorich, 2008). Three-way analysis of variance revealed that the total exchangeable concentration of these 11 elements were significantly higher in the rainy season than in the dry season as well as significantly higher in the upper part of the river than in the lower part. Given that New England, where the current study sites are located, has roughly the same amount of precipitation in each season (Table 1), this could be a factor as to why no significant differences were found among seasons. Also, Ehlken and Kirchner (2002) noted that higher water contents, lower salinities and bulk densities increase the potential mobility of metals in soil solutions. Therefore, it is reasonable to assume that this current study was influenced by additional factors, such as what Ehlken and Kirchner (2002) stated, which is why no distinct seasonal patterns were detected (Table 1).

Vegetation trends

All of the observed metals (with the exception of Mn and Zn at NRSM only) showed a significant difference in concentration ($P < 0.05$) depending on the dominant vegetation coverage (Figure 4). Each metal had higher concentration under *P. australis* than *S. alterniflora* at both locations with the exception of As (higher under *S. alterniflora* at the urban site). This difference was significant for four of the metals (As, Cu, Pb, Ni) at both locations and significant for the other two metals (Mn, Zn) at the rural site, with Zn almost reaching the accepted value for a significant difference at the urban site (Table 3).

Weis *et al*. (2002) compared *P. australis* and *S. alterniflora* samples in a lab and field experiment to observe how they process trace metals (Cu, Zn, Pb). For the field portion of the experiment, leaves of both plant species were wiped clean of debris and salts with filter paper saturated in distilled water, and then tagged (Weis *et al*., 2002). After 48 hours of dry weather, the same leaves were again wiped with dampened filter papers, identified, bagged in plastic, and analysed for metal content (Burke *et al*., 2000). For the lab portion of the study, plants of both species were removed with intact root masses and sediments from the same site used for the field study (Weis *et al*., 2002). These were potted and grown indoors under fluorescent bulbs. Filter-paper wiped leaves were re-wiped for analysis after one week, then collected for leaf metal analysis (Weis *et al*., 2002). Both the field and lab experiment used

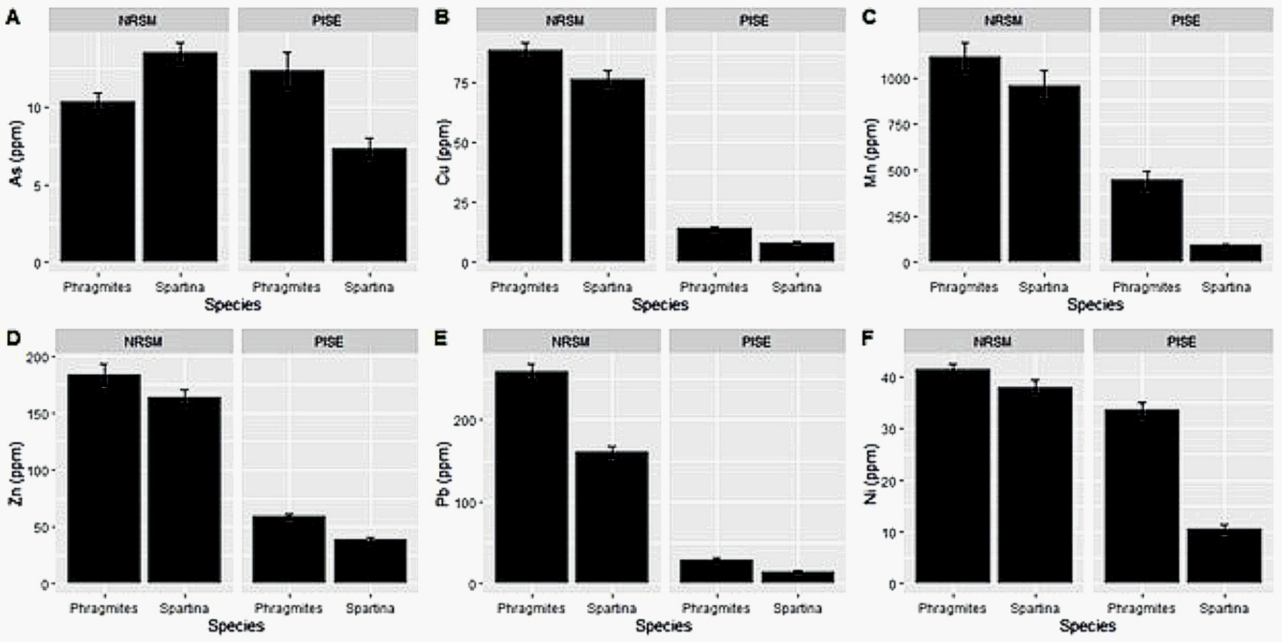

Figure 4: Distribution of heavy metals (A= As, B = Cu, C = Mn, D = Zn, E = Pb, F = Ni) in saltmarsh sediments under either invasive (P. australis) or native (S. alterniflora) vegetation coverage. Error bars are indicative of standard deviation.

Metal	T-value	P-value	T-value	P-value
As	3.7	5.2 × 10^{-4}	-3.9	3.0 × 10^{-4}
Cu	-2.5	1.4 × 10^{-2}	-5.7	1.2 x 10^{-06}
Mn	-1.4	0.2	-7.4	8.4 x 10^{-10}
Zn	-1.7	9.4 × 10^{-2}	-7.2	1.6 x 10^{-09}
Pb	-8.4	8.6 x 10^{-12}	-6.2	6.7 x 10^{-08}
Ni	-2.1	3.6 × 10^{-2}	-14	<2.0 x 10^{-16}

Table 3. Statistical analysis of metals between species and location (seasons pooled) Since there were no distinct seasonal difference for any of the metals, seasonality was pooled when looking at vegetation coverage differences.

atomic absorption spectrophotometry for the heavy metal analysis (Weis *et al.*, 2002). They observed that both plants stored most of their metal burden in their roots, but some was relocated to aboveground tissues. *S. alterniflora* leaves contained roughly 2–3x more Pb than *P. australis* leaves (Weis *et al.*, 2002). Furthermore, *S. alterniflora* leaves have salt glands, so leaf excretion of all metals is typically twice that of *P. australis*, meaning *S. alterniflora* makes more metals available to salt marsh ecosystems than *P. australis* by direct excretion and through dead leaves which will enter the food web as detritus (Weis *et al.*, 2002). However, they did not find a significant difference in Cu and Zn concentrations between plant samples. The same trend for Pb was further supported in the current study, where every studied metal (including Cu and Zn, which was not the same finding in the Weis *et al*. (2002) study) besides As at the urban site had significantly higher concentrations in the sediment beneath *P. australis*. Because *P. australis* holds more metals in its roots compared to *S. alterniflora*, which moves it from the sediment and out of its leaves into the environment, this trend is expected.

Windham *et al*. (2003) conducted a field study over a growing season, where both metal (Cu, Zn, Pb) concentrations and standing stocks (concentration biomass) in the same two plant species were analysed. This study was conducted in northern New Jersey at a contaminated salt marsh where both types of vegetation grew (Windham *et al*., 2003). Both species had high concentrations of all analysed metals in the roots. Cu and Zn concentrations in leaf tissues were significantly greater for *P. australis* in April and October, but not in August, when *S. alterniflora* concentrations were similar for Cu, but greater for both Pb and Zn. Although there were some seasonal discrepancies, the findings of Windham *et al*. (2003) agree with the findings of Weis *et al*. (2002), that *P. australis* holds higher concentrations of heavy metals in the roots/sediment because it cannot excrete it through salt glands like *S. alterniflora*. This was supported in the current study for most of the observed metals (Table 3), however, seasonality (Table 2) did not play an influential factor like in the Windham *et al*. (2003) study.

Future considerations

Currently 55% of the world's population lives in urban regions, a proportion that is predicted to rise to 68% by 2050 and Northern America specifically has the most urbanised areas, with 82% of people residing in urban locations (RWUP, 2018). Additionally, 81% of the inhabitants of Latin America and the Caribbean are in urban areas, as well as 74% of Europe, and 68% of Oceania (RWUP, 2018). Projections indicate that by 2050, urbanisation combined with overall population increase will lead to approximately 2.5 billion more people living in urban regions (RWUP, 2018). This drastic increase of urbanisation will most likely increase metal loading in sediment through higher anthropogenic industrial activities, which could lead to higher risk of exposure via an increase of metals released into the water column, which could cause health concerns including various metal poisonings.

Evidence has continued to grow in support of human-induced climate change altering precipitation and the hydrological cycle as a whole, but especially the extremes (i.e., droughts and floods; Trenberth, 2011). The discrepancy between increased moisture from the Clausius-Clapeyron equation (used to estimate the vapour pressure at a certain temperature) and a smaller change in the quantity of total precipitation confirms that there will be a shift in the nature of precipitation events to more powerful and less frequent rains (Trenberth, 1998; Trenberth *et al.*, 2003). Nguyen *et al.* (2020) concluded that rainy versus dry seasons affect the concentrations of metal loading, with rainy seasons having higher concentrations. Additionally, as the global temperature increases due to climate change, glaciers will melt which will cause the seal level to rise as well as salinity levels to decline, which in turn will increase the potential mobility of metals in soil solutions (Ehlken and Kirchner, 2002). As these factors change around the world, it will alter seasonal patterns of heavy metals. For example, stronger rains will create larger runoff and carry more metals into waterbodies where it can move up the food chain. Additionally, more extreme rain events coupled with a lower frequency has the potential to create even stronger seasonal divisions than what is currently being seen.

As climate change worsens due to an increase of carbon dioxide emissions, water bodies will become more acidic due to carbonic acid being formed when carbon dioxide reacts with water. Many studies have concluded that higher redox potential and lower pH are linked with an increase in bioavailability of sediment-bound metals (De Laune and Smith, 1985; Gambrell,1994). Therefore, as the Earth continues to warm from greenhouse gas emissions, largely including carbon dioxide, metals will become more prominent and available in the soil, leading to a larger plant uptake of said metals. Not only does *S. alterniflora* interact with the water more because it lies in the low marsh habitat, but as climate change worsens, pH will continue to decrease and sea level will continue to rise, and plant zonation will be altered, meaning *S. alterniflora* will most likely dominate the area due to their higher salt tolerance. Therefore, the metals will move up through the vegetation more (as seen in the data of this current study via *P. australis* holding significantly more metal in its roots and therefore not releasing it), unloading more metals through salt gland excretion into the water column, and potentially cause higher rates of toxic metals in organisms as well as other unforeseen events.

Conclusion

Heavy metals in marsh sediment are concerning because these metals do not stay inactive and marsh vegetation can change the redox of the sediment, allowing the metals to become mobile. When vegetation receives and relocates metals to the above-ground tissue, it becomes a pathway for the migration of toxic metals from sediments into the food webs of marsh ecosystems and near shore waters. Salt marsh plants, in particular, are positioned in close proximity to the marsh surface and rapidly integrate metals from the sediment.

This study analysed six metals (As, Cu, Mn, Zn, Pb, Ni) across urban versus rural marsh sites, seasons, and vegetation types. Urban salt marsh samples had significantly higher ($P < 0.05$) concentrations of all metals with the exception of As which was not different between locations. No significant difference ($P > 0.05$) was seen among seasons between either location presumably due to the lack of a defined wet and dry season as well as other factors such as water content, salinity levels and/or overall bulk density. Invasive *P. australis* sediment samples had significantly higher ($P < 0.05$) metal concentrations compared to native *S. alterniflora* samples (with the exception of As in the urban site) due to their lack of salt glands to excrete it through its leaves.

As more regions shift from rural to urban spaces and as climate change continues to worsen, one could expect to see urban dominated areas with higher loads of metal pollution, an increase in heavy metal uptake and translocation of metals higher up the food chain, and a shift in seasonal patterns depending on if precipitation lightens or worsens in a certain region. This drastic increase of urbanisation will most likely increase metal loading in sediment through higher anthropogenic industrial activities. As *S. alterniflora* starts to dominate, a higher rate of metals will be released into the water column and lead to an increased risk of exposure. Furthermore, stronger rains will create larger runoff and will also carry more metals into waterbodies.

Limitations to this study include its duration. It is recommended that for future work, multiple years of data are acquired to determine an even more accurate trend. This would allow for potentially more consistency as well as a way to compare both short-term and long-term observations. Furthermore, it is recommended that a larger range of metals are analysed, as numerous metals have the potential to effect humans and ecosystems.

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