# The Effects of Salinity, Inundation Length, and Vegetation on Lead and Copper in Salt Water Tidal Marshes and Estuaries: A Review

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# Abstract

Heavy metals pose a direct threat to the biological diversity of wetlands. Heavy metal contamination, such as copper and lead, reduces the growth of vegetative stands, decreases the vegetation population density, and causes health issues for organisms that can be passed up the food chain. Although most of the noted wetlands affected by heavy metals receive metals in the form of mine tailings or other industrial activity, there are a small few that receive metals inputs from rifle projectiles. One such location is the impact range found on the northwest side of Parris Island, South Carolina. The Marine Corps Recruit Depot uses the adjacent salt water tidal marsh and estuary as an impact range for their marksmanship training. Salinity, inundation period, and vegetation have all been shown to affect the activities of lead and copper in wetlands, but this knowledge was gained by investigating other parts and situations across the globe. The goal here is to review current literature to determine the various ways that salinity, inundation length, and vegetation will affect lead and copper in saline wetlands. Moreover, discussion will be presented as to how the information gathered can be used to predict how an altered metal composition of projectiles may affect lead and copper in our study area. The implications of this paper may be used to greater assess the environmental impact of using a lead free projectile and also to determine a possible strategy for remediation.

# Contents

# 1 Introduction

Salt water tidal marshes and adjacent estuaries serve as valuable buffers between the world's oceans and the developed land masses. These wetlands serve as a biologically diverse environment with unique sets of physiochemical properties (Wieski et.al., 2009, Zedler et.al., 2001, Palomo et.al., 2013, Lillebo et.al., 2010). Wetlands often serve as sources and sinks for nutrients (Fisher & Reddy, 2001), organic contaminants (Hwang et.al., 2005) and heavy metals (Du Laing et.al., 2009). Wetland soils and sediments have been shown to sequester and release heavy metals with changing pore water composition, salinity, pH, bioturbations, and inundation cycle (Speelmans et.al., 2010, Atkinson et.al., 2007). The overall consistency of the world's oceans taken at individual locations can be considered to be fairly constant overtime, but decreases in pH and increased carbon dioxide composition have been witnessed with rising sea levels (Cao et.al., 2007). Locations around the globe can have differing levels of salinity but variations in salinity at one point should not rapidly fluctuate without the influence of tides or freshwater introduction into the system, but do fluctuate during the annual cycle for the previously mentioned reasons (Reverdin et.al., 2007). Tidal oscillations can be predicted with accuracy and it would not be expected that the water chemistry of tidal cycles would vary significantly.

Heavy metals pose a threat to flora and fauna within estuaries. Heavy metals have been shown to affect the sediment chemistry (Hwang, et.al., 2011), the vegetation population density and variety (Deng et.al., 2004, Reboreda & Caçador, 2007), and the health of invertebrates and vertebrates (Speelmans et.al., 2007). Vertebrate and invertebrate health can effect higher organisms as metals are biomagnified within the food chain by being passed to water fowl or directly to humans (Pascoe et.al., 1996). The accumulation of metals within the soils and sediments can cause the decreased growth and reproduction of plants and cause the spread of metals accumulated in plant matter that is released in senesce and redeposited into the wetland as detrital material (Duarte et.al., 2010). Tides have already been shown to effect the sediment chemistry and the possible spread of metal contaminated soils (Personna et.al., 2015).

Heavy metals can enter a wetland system by various means; through mining activities, direct and indirect runoff, erosion of soil parent material, or as the projectiles from shooting ranges. An accurate count of shooting ranges utilizing tidal marshes as impact areas in unknown. More over little research has been identified to accurately detail the fate of depositional metal from shooting range projectiles in salt water wetland environments, although research has been conducted in freshwater systems (Perroy et.al., 2014). Much is known about the fate of lead projectiles in terrestrial systems (Fayiga et.al., 2011, Hardison Jr. et.al., 2004), but the unique oxidation and reduction environments present in estuaries and the tidal exchange of fluids represent a dynamic of metal fate that will not be analogous to terrestrial systems.

The United States military has been using a standard North Atlantic Treaty Organization (NATO) approved projectile for their service weapons. These projectiles are comprised of a steel penetrator, a lead core, and a copper jacket (Woods, 2010). In a move to create a more environmentally friendly round, i.e. the removal of the lead, two alternated were tested (Department of Defense, 2010). The first projectile tested replaced the lead core with a tungsten-composite core. This projectile was found ineffective not because the composition but because of the ballistics tests. The second round being tested and being partially adopted has replaced the lead core with a copper core, such that the projectile now consists of a steel penetrator, copper core, and copper jacket (Woods, 2010). Figure 1 contains specifications for the M855 NATO round and the M855A1 enhanced performance round. The US army has instituted the use of this projectile in their M4A2 service rifle but the US Marine Corps has not followed suit because it has retained the M16A4 as its service rifle. The decision not to switch is based on the weapons fatigue that was experienced in the early phases of testing with the “green round” (Sanborn, 2015).

| Characteristic | M855 | M855A1 EPR |
|---|---|---|
| Cartridge Length | 2.248 in | No Change |
| Bullet Weight and Length | 62gr | No Change |
| Tip ID | Green | Bronze from Corrosion Protection |
| Slug | Lead | Copper |
| Cup/Jacket | Copper | No Change |
| Penetrator | Steel | Steel Arrow Head |

*Figure 1: Produced by Woods (2010). Altered to show characteristics of the M855 and the M855A1 enhanced performance round*

Marine Corps Recruit Depot, Parris Island, South Carolina utilizes a salt water tidal marsh and estuary as the impact area for its rifle ranges. Parris Island has been the training depot since 1915, and although no records indicate the length of time that the marsh has been used as an impact area it can be reasonably assumed that deposition of projectiles has been ongoing for generations. Currently the fate of lead and copper is well known in salt water tolerant macrophytes that inhabit estuaries and the process that cause their mobility and stabilization (Duarte et.al., 2010, Reboreda & Caçador, 2007, Windham, et.al., 2003). Much of this research however, has focused on mining tailings or treatment wetlands. Research has been conducted to determine the fate and transport of lead in freshwater impact areas but not salt water environments (Perroy et.al., 2007).

The purpose of this paper is to review current literature as to how inundation length, salinity and vegetation affect the mobility or stabilization of lead and copper in a salt water tidal marsh and estuary; to discuss the use of phytoremediation and phytostabilization to limit the transport of lead and copper within the tidal marsh and provide a suggestive means of remediation the study area; and present brief rhetoric on how the new lead free projectiles may affect the stability of copper and lead in the tidal marsh.

## 2 Study Area

The study area is located northwest and adjacent to Parris Island, SC. Parris Island is comprised of barrier island sand, silt and clay which overlies an unconfined surficial aquifer that is not used for drinking water. Below the surficial aquifer is the Hawthorn formation which separates the unconfined aquifer from the Floridan aquifer. The study area is comprised mostly of salt water tidal marsh but does contain a small portion of upland area from Horse Island and sections of Ribbon Creek and Archer Creek. Northwest to northeast of the study area is more tidal marsh lands. From the northeast to southeast is Parris Island, and from southeast to northwest is the Broad River. Our study area will remain focused in what is the greatest probability of impact area in the tidal marsh. The impact area was determined by following the lateral limits of the range out into the marsh to the maximum range of the M16A4 service rifle (approximately 3,300 meters). Coordinates for this area are as follows: 32.3587°N 80.7367°W; 32.3608°N 80.7342°W; 32.3364°N 80.7130°W; 32.3423°N 32.3423°W. The total area outlined is approximately two square kilometers. No previous research has been identified to quantify the salinity gradient within the Broad River, Ribbon Creek or Archer Creek. Moreover, no certified tidal instrumentation has been located in the area. The study area is shown in figure 2.

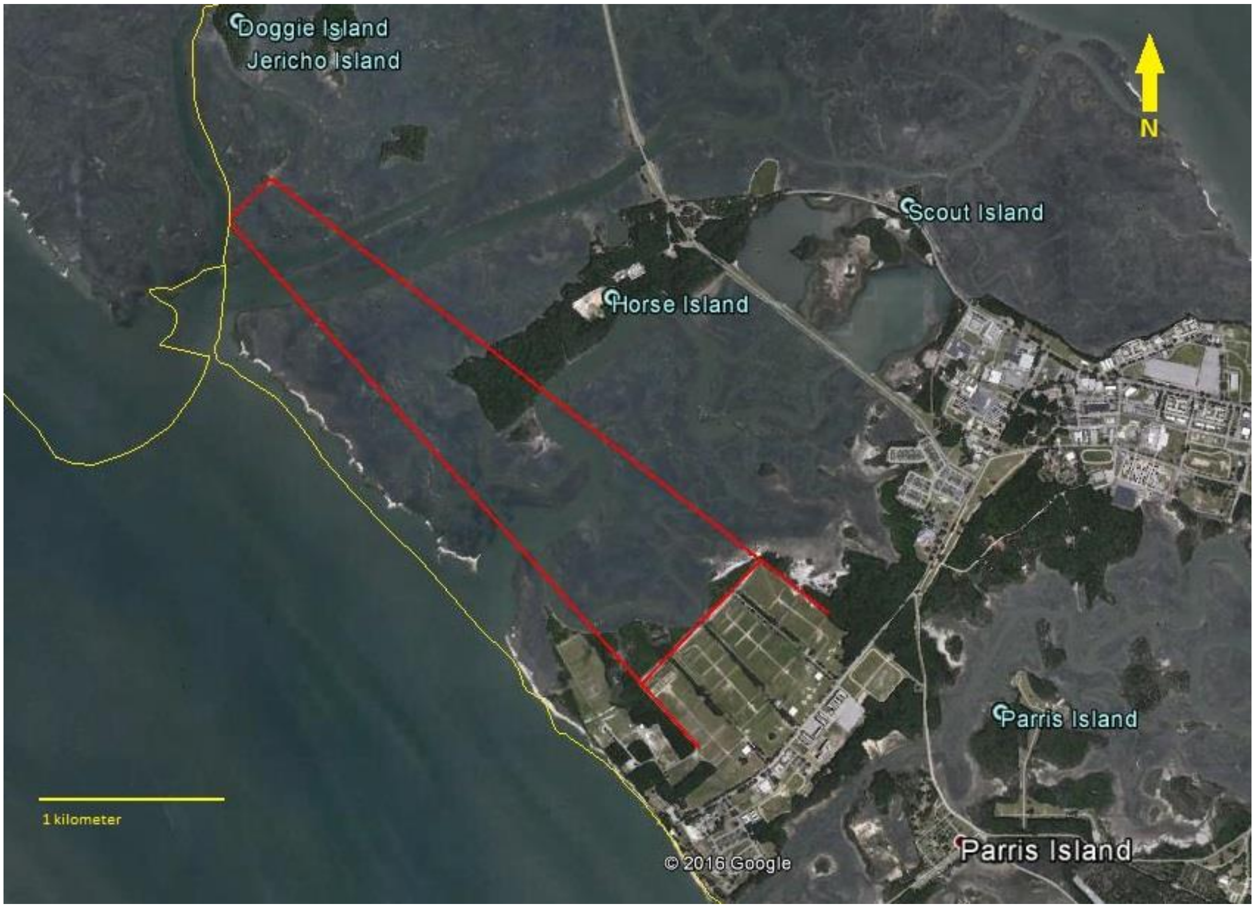


*Figure 2: Created using Google Earth. Map shows the study area outlined by the solid red line*

# 3 Literature Review

No literature was found to contain specific information regarding the variety or density of vegetation growing in the study area. However, the effects of salinity, inundation length, and vegetation population have been studied in other areas of the world, and the understanding of these effects can be analogously applied to our current study area.

## 3.1 Inundation: Redox Properties

Soil characteristics should not be expected to be uniform throughout the study area, and thus the interactions with the tidally introduced ions would not be expected to be identical throughout the study area. The area of greatest projectile impact would be suspected to contain the greatest density of projectiles which should correlate with the highest levels of metal concentrations (Hui, 2011). Hui (2011) further determined that the levels of lead in the upland sites was greater than those at the tidal locations. The differing soil characteristics between the tidal and upland sites typically include: soil pH, organic matter content, soil constituents, and vegetative populations.

The tidal cycles in the estuary allow for an exchange of soluble materials, dissolved ions, and gases (most importantly oxygen). In a well-mixed situation the exchange of gases and ions will be continuous and the overall properties and conditions in the soils and pore water should over time reach an equilibrium either with the concentrations in the water or in the background concentrations of the soil. The equilibrium may take a significant amount of time to reach due to the complexity of conditions within a wetland (Personna et.al., 2015). Personna et.al. (20015) sought to describe how the concentrations of metals changed temporally in a residential area compared to a wetland area after Hurricane Sandy created storm surges on the New Jersey coast; results of the differences are shown in figure 3.

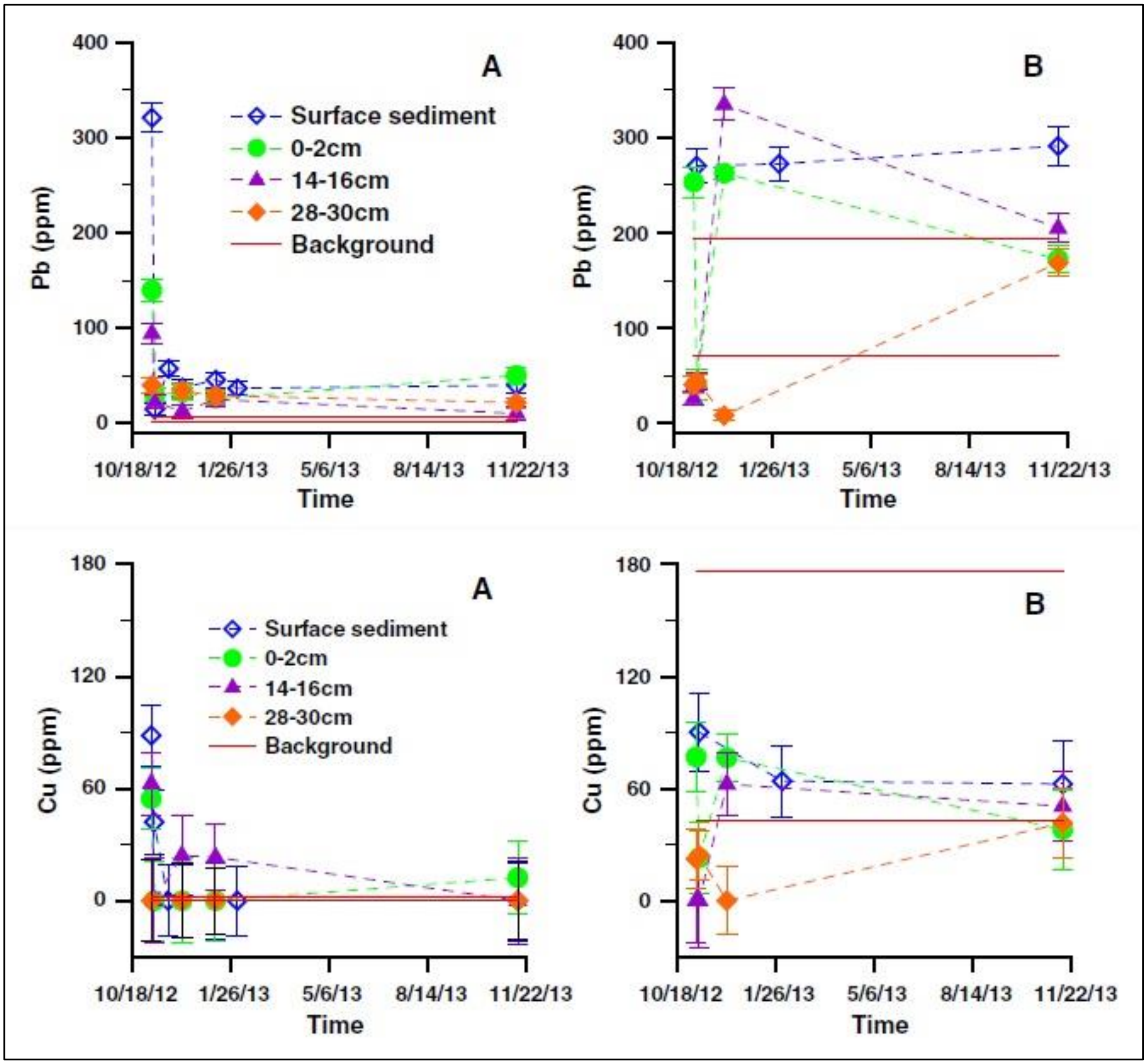


*Figure 3: Produced by Personna et.al. (2015). Altered to show the change in concentration of lead and copper overtime. Solid red line represent the range of background concentration in the areas. A) residential area, B) wetland area*

While investigating copper and zinc in wetlands, Speelmans et.al. (2010) found that oxidation of the media would cause a rapid increase in availability of metals, but that flooded conditions would minimize the metals availability. Organisms living in these prolonged flooding conditions will therefore have less uptake of these metals (Speelmans et.al., 2007). The dissolved oxygen that is able to diffuse through the water column to the sediments will work to form a crust on the outer portions of the lead and copper thereby limiting the dissolution of these metals (Perroy et.al., 2014). To illustrate this Atkinson et.al. (2007)

showed that under a medium range dissolved oxygen level and low dissolved oxygen level there was a net release of lead into the overlying water after a simulated sediment disturbance. The levels in lead after the disturbance remained higher during the remainder of the experiment than the levels prior to the disturbance.

Beyond the extent of dissolved oxygen, under reducing conditions, the rate of organic matter decomposition is low and the release of organic acids into the water column will decrease the pH of the system creating acidic conditions within the wetland. The acidic conditions are likely to cause the formation of lead carbonates and are likely to cause weathering of the lead projectile thereby increasing the ability of the lead to spread and the increased concentration of the lead in the sediment (Perroy et.al., 2014, Zheng et.al., 2011). Perroy et.al. (2014) speculated the increased concentrations of lead not directly above or below a shot pellet was due to mixing within the soil by organisms or the exchange of gases. Organic matter shares a commonality with clay materials in their abilities to adsorb metals into their structures. Metals can be incorporated into the clay structure and thereby greatly reduce the mobility of the metal in the system. Clayey materials in metal contaminated wetlands can thus serve as an immobilizing matrix for the metals much like organic matter (Du Laing et.al., 2009).

Reduction and oxidation reaction taking place within the soil and water column greatly influence the mobility and stability of metals. As oxygen is removed from the system alternate sources of electron acceptors are utilized in metabolic processes. The sequestration of lead and copper have been shown to be influenced by the reduction and oxidation of iron, manganese, and sulfur (Du Laing et.al., 2009, Atkinson et.al., 2007, Speelmans et.al., 2007, Romano et.al., 2016). Under oxidizing conditions iron and manganese exist as in soluble solids bound to negatively charged particles. In the process of iron and manganese oxidation lead and copper can be adsorbed onto a mineral structure and subsequently locked in the mineral by more iron or manganese settling around it. The reduction of these iron and manganese minerals would thus release the lead or copper back into the system. Sulfur can assume various states in the oxidized and reduced forms; typically oxidized sulfur is in the form of sulfate and reduced sulfur is in the form of sulfides. Sulfate is regularly introduced into the wetland via tide water, but sulfides may also persist in the parent material of the soil. The reduction of sulfate to sulfide causes the co-precipitation of metals from the pore water. Spencer et.al. (2003) noted that while investigating diagenesis in salt marsh sediment in the United Kingdom that generally less than 25% of copper and lead was associated with the sulfide and organic fraction of the sediment. Although sulfides can sequester lead and copper out of the water column the sulfides and organic matter are not solely accountable for the immobilization of these metals.

## 3.2 Salinity

The spread of salinity throughout the study area is unknown. As mentioned previously the study area consists of open water creeks, upland area, a tidal marsh, and estuary. The upland area would only experience higher than normal salinity levels due to storm surges or direct sea breeze off the Atlantic Ocean. The creeks are tidally influenced with the major source of fresh water input being from precipitation so it is reasonable to assume that there may be a gradient of salinity in the creeks with the greater concentration at the mouth of the creek. The salt marsh and the estuary are not expected to have a homogenous concentration of salts within them. Moore et.al. (2011) mapped the salinity gradient within the Great Bay Estuary and found that the salinity concentrations of the wetland were due to the ease of water drainage; specifically that the tidal marsh has channelized drainage allowing for a greater amount of salt to exit the wetland during low tide whereas the estuary did not have well defined channelized flow and this increased the salt concentrations in the wetland. It is speculated that the lack of channelized flow led to an increased amount of time the tidal water spent in the estuary allowing for a greater amount of evaporation from the tidal waters thereby increasing its salinity composition.

The primary anions found in seawater are sulfate and chloride ions. Sulfur in the tidal marsh and estuary will undergo oxidation and reduction depending on the oxidation and reduction potential of the soils and sediments. The highly mobile sulfate can potentially be exchanged and flushed from the wetland system in during low tide moments or high precipitation moments. During periods of inundation, regardless of the salinity, the sulfide within the system is not expected to undergo oxidization unless there is available oxygen in the vicinity; the lack of sulfide oxidation implies that the lead and copper bound in sulfide minerals will remain immobile. Du Laing et.al. (2008B) explains that copper mobility is not affected by salinity and postulated that this is due to the low stability of copper chloride complexes and the low solubility product of copper sulfide. Copper insolubility due to salinity was also noted by Speelmans et.al. (2007), the study identified that salinity and the interaction of salinity and time had no significant effect of the concentrations of substrate with p-values>0.2.

To determine the effect of salinity on lead and copper in the salt water tidal marsh multiple levels of salt concentration will need to be consider as well as the type of ions present in the solution. Investigations have been conducted with salinities ranging from 0 psu up to 35 psu depending on the location of the study and the research groups objectives. The effects of the salinity on copper and lead were not always predictable. Atkinson et.al. (2007) noted how rapid the less saline pore water would equilibrate with the more saline sediments, but found that there was no difference in the rate of metal release between the 15psu and 25psu setups in their experiment. The authors noted that unforeseen rates of evaporation were seen in one of the experiments resulting in a saline level of 45psu but this also had no effect on the release of copper or lead. The buffering capacity of the sediment is probably due to small less tightly held ions being released into the pore water, such as sodium or calcium as opposed to lead or copper.

## 3.3 Vegetation

Changes in water column salinity have also shown to have an effect on the overlying vegetation species and population density. No catalog of plant species in the study area was found during the research phase of this paper. Therefore a broad range of wetland macrophytes and halophytes will be discussed in the following section with either a specific study being discussed or particular macrophytes depending on the amount of relevant information available. Vegetation is of interest because of its ability to translocate and sequester metals and the ability of plants to alter soil conditions in the rhizosphere which will either mobilize or mineralize metals.

### 3.3.1 Twelve Wetland Plants

The ability to translocate metals from roots to shoots to leaves has been documented (Duarte et.al., 2010). The accumulation of metals in twelve wetland plant species was studied by Deng et.al. (2004) and found that the majority of metals accumulated by wetland plants was stored in the roots; this was especially important for lead which showed the lowest amount of translocation from root to shoot. The authors did note that the ability to translocate metals was varied between the species studied. Furthermore, the fraction of total lead and copper found in the soil and sediments was positively correlated with the amount of lead and copper found in the plant biomass, which implies that the concentration of metals did not reach a toxic level in the plants as to inhibit growth. The study's results showed that extraction of lead is best accomplished by *Equisetum ramosisti* and the extraction of copper is best achieved by *Eleocharis valleculosa*.

### 3.3.2 *Spartina maritima* versus *Halimione portulacoides*

Three projects were identified that focused their attention on the processes by which *Spartina maritima* and *Halimione portulacoides* influence the concentration of lead and copper in salt marsh sediments, the speciation of lead and copper in the sediments, and how these metals are cycled in the system in the Tagus estuary in Portugal. Vegetated arears of the Tagus estuary were shown to have a greater amount and variability of metals in the salt marsh sediments, and the greatest concentration of these metals was found at the five to fifteen centimeter depth (Caçador et.al., 1996). The authors postulated that the alterations in the composition of the rhizosphere led to the increased sequestration of metals in the root zone which is approximately five to fifteen centimeter depth. The low metal concentration of the nonvegetated sediments is in accordance with the observations witnessed by Hui (2002); that the areas with the greatest frequency of tidal water exchange contained the least amount of organic matter and therefore had a reduced ability to hold metals in the sediments. More specifically, it was uncovered that higher concentrations of copper and lead were found in vegetated areas dominated by *S. maritima* than in arears dominated by *H. portulacoides* (Reboreda & Caçador, 2007A). Reboreda & Caçador (2007A) conducted a study to determine the levels of lead and copper in a method of sequential extraction. The results showed that lead was highly associated with the organic fraction and that this organic fraction of lead was higher the areas of *S. maritima* than in the areas of *H. portulacoides*. The exact mechanism of the metal fractionation was not uncovered but the authors hypothesized that either the differences in metal fraction was due to the overall location of the plants in the salt marsh (topological differences affecting inundation time and gaseous exchange in water and sediments) or the root exudates being released within the rhizosphere (enzymatic composition and function may be different for the two species). The roots of these plants were shown to have statistically significant different levels of copper accumulation but were shown to have statistically insignificant different levels of lead accumulation (Duarte et.al., 2010). Duarte et.al. (2010) concluded that the decomposition rate of *S. maritima* was capable of maintaining mobility of lead and copper in the system and that due to this mobility and exchange that *S. maritima* would be best suited for phytostabilization projects. The amounts of lead and copper found in the roots, stems, and leaves as well as the amounts of lead and copper lost be these parts of the plants due to senescence are shown in the figure 4.

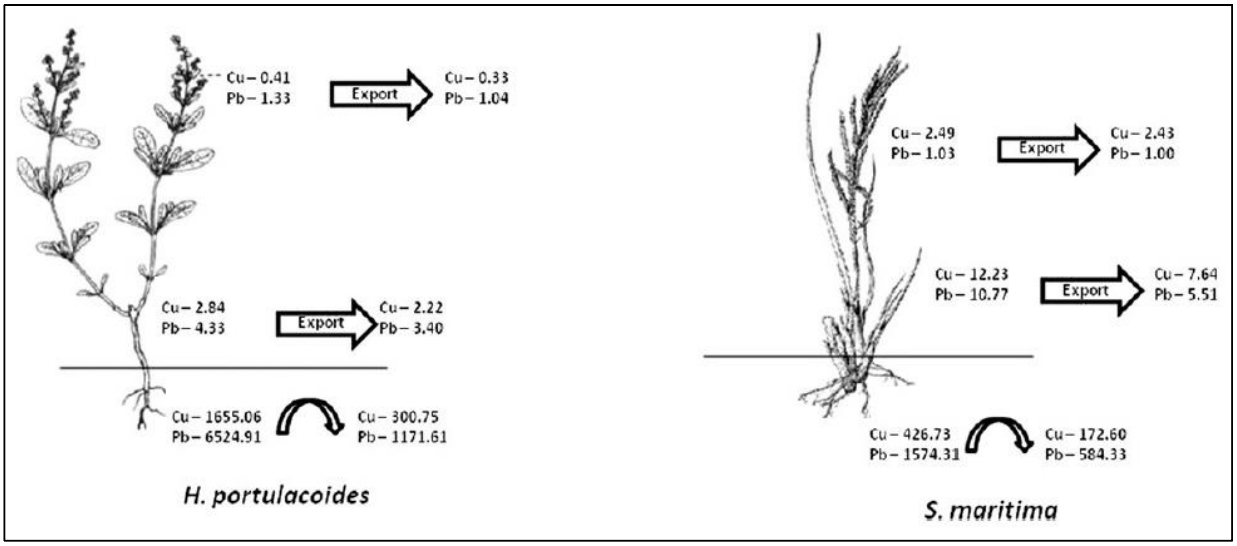


*Figure 4: Produced by Duarte et.al. (2010). Altered to show the accumulation of lead and copper in roots, stems, and leaves of the living plants and the accumulation of metals in the plant litter of H. portulacoides and S. Maritima.*

### 3.3.3 *Spartina alterniflora* versus *Phragmites australis*

*Spartina alterniflora* and *Phragmites australis* have both been described as invasive species depending on the habitat they are in and their ability to alter that habitat (McCormick et.al., 2010, Taylor et.al., 2004). Laboratory analysis of these plants has shown that *P. australis* was more adapt to high levels of lead than was *S. alterniflora* and that a greater amount of lead was found in the above ground tissue of *S. alterniflora* than in *P. australis* (Windham et.al., 2001); furthermore, the difference in lead proportions in the plant body were determined to be that 75% percent of the lead in *P. australis* was in the roots and 75% of the lead in *S. alterniflora* was in the rhizomes, leaves, and stems. The translocation of lead from the sediment to the aboveground biomass suggests that there is a greater opportunity to spread lead via senescence of plant matter from *S. alterniflora* than *P. australis*. Conversely in a field experiment by Windham et.al. (2003) it was calculated that the concentration of metals in root structures of both species was 4 to 1000 times greater than the leaves, stems, and rhizomes; the concentrations of these plant parts are displayed in figure 5. Burke et.al. (2000) found that the concentration of copper in the leaf tissue of both plants was greater than the concentration of lead in the leaf tissue and according to Windham et.al. (2003) the level of copper was greater *P. australis*. The greater amount of copper should not be of surprise because copper is a micronutrient for plants. Burke et.al. (2000) were working to determine which plant species released more heavy metals via leaf excretion. They determined that there was no significant difference in the amount of metals released between species but in general the release of metals from *S. alterniflora* was twice that of *P. australis*, this conclusion was also reached by Weis et.al. (2002). Weis et.al. (2002) quantified the release of lead and copper from leaves during the growing season of *S. alterniflora* to be 116g and 125g, respectively, and further stated that the release of lead and copper was greater in the field environment than in the laboratory.

| Metal | Species | Month | Leaf | Stem | Root | Rhizome |
|---|---|---|---|---|---|---|
| Cu | *P. australis* | April | 10.70 (1.56)* | 19.2 (4.51)* | 55.1 (30.4) | 8.60 (4.35) |
| | | June | 7.30 (0.24) | 4.60 (0.43) | 99.0 (14.74) | 8.73 (1.95) |
| | | August | 3.73 (0.54) | 1.60 (0.45) | 120.7 (39.82) | 7.33 (1.15) |
| | | October | 7.41 (0.41)* | 3.40 (2.26) | 184.6 (28.61) | 12.64 (3.40) |
| | *S. alterniflora* | April | 6.45 (0.81) | 7.10 (1.22) | 146.6 (55.34) | 52.80 (15.99)* |
| | | June | 4.76 (0.99) | 3.60 (0.35) | 118.0 (13.00) | 12.55 (4.85) |
| | | August | 4.75 (0.61) | 2.5 (0.44) | 100.8 (27.04) | 18.27 (7.39) |
| | | October | 3.66 (0.27) | 0.9 (0.23) | 212.3 (43.43) | 6.29 (1.13) |
| Pb | *P. australis* | April | 1.07 (0.29) | 3.2 (2.06) | 91.1 (36.75) | 7.60 (5.33) |
| | | June | 2.98 (0.44) | 2.4 (0.32)* | 122.3 (20.54) | 6.25 (1.99) |
| | | August | 0.09 (0.07) | 0.9 (0.43) | 137 (38.43) | 8.43 (1.97) |
| | | October | 0.32 (0.05) | 0.6 (0.41) | 142 (31.49) | 8.10 (2.55) |
| | *S. alterniflora* | April | 1.53 (0.23) | 1.9 (0.45) | 104 (29.67) | 45.73 (26.29) |
| | | June | 3.09 (0.28) | 1.06 (0.29) | 92 (6.80) | 1.93 (0.56) |
| | | August | 0.72 (0.29)* | 0.7 (0.43) | 84.5 (37.8) | 27.05 (8.28)* |

*Figure 5: Produced by Windham et.al. (2003). Altered to show the lead and copper concentrations in mg/kg for the leaf, stem, root, and rhizome for the species P. australis and S. alterniflora. Mean concentrations are given with the standard error in parentheses. * indicates a significantly higher concentration for that given species.*

# 4 Remediation

## 4.1 Phytostabilization

Phytostabilization is utilized as a technique to reduce the mobility of metals within wetland systems (Cambrolle et.al., 2008). The goal of phytostabilization is achieved by means of rhizosphere oxidation, translocation, or formation of organometallic complexes. Discussion here will focus on two specific species: *Spartina maritima* and *Halimione portulacoides*. Reboreda & Caçador (2007B) sought to determine which plant, *S. maritima* or *H. portulacoides*, was better suited for stabilization of copper, cadmium, and lead. The authors found that the larger proportion of metals was stored in the root portion of the plants and that there was significant difference between the amounts of metals in the roots between plant species. The figures that were generated show 99% of copper and 87% of the lead in the plant was in the root structure. This metal fractionation was true even given that the root zone of *S. maritima* was found to be in reduced conditions and *H. portulacoides* was in an oxidized condition. No discussion is made of the reason for the difference in oxidation reduction potential in the root zone but it can be speculated that the difference is due to either gaseous exchange with the atmosphere or the topology of the area. The reducing conditions found in the root system of *S. maritima* are better suited for the formation of sulfides in the zone which are capable of immobilizing lead and copper. Reboreda and Caçador (2007B) concluded that *S. maritima* would be a better choice for phytostabilization than *H. portulacoides*.

## 4.2 Phytoremediation

Phytoremediation is the act of using plants to metabolize metals in their biomass and then remove that particular part of the plant from the wetland or to remove the entire plant. Depending on the species of plant, the metals may be accumulated in the roots, stems, or leaves. The process of phytoremediation is a more active process which requires the removal of plant material rather than that of phytostabilization which merely requires maintaining a homeostasis for the plants to continue recycling metals in place or immobilizing metals in the root zone. The growth and subsequent senescence of plant material is highly regulated by the available nutrients as well as the level of contamination. The rate of decomposition was seen to increase when a lower carbon to nitrogen ratio was present (Du Laing et.al., 2008A). Willow (*Salix ssp.*) litter was observed to decompose faster than stems of *P. australis* due to the lower carbon to nitrogen ratio in the leaves as opposed to the stems, which implies a faster release of organo-bound metals from the leaves. Copper concentrations were also noted to decrease more rapidly than cadmium concentrations; no rate of copper concentration decrease was reported but it could can suggested that the rapid decrease was due to copper being a micronutrient in plants. The vegetation present may not be suitable to release the metals from the sediments and soils so the process of liming the area may be used as a means of increasing the concentration of soluble copper and lead available to the plants (Gonzalez-Alcarz et.al., 2013).

## 4.3 Site Proposal

Again, no catalog was located that contain information regarding the species of plants that are present in the study area, so only a general proposal about remediation can be made. The following list describes measures that can be taken to aid in the remediation or stabilization of the study area

1) Attempt to maintain water levels within the salt marsh. This may require the movement of earthen material into the wetland or the creation of channelized flow out of the estuary to be accomplished. The stable conditions in the wetland will decrease the regularity of the system moving from reducing conditions to oxidizing conditions and vice versa. It discussed previously that reduced conditions can limit the mobility of lead copper by binding them in sulfide minerals, that in oxidized conditions lead and copper may form precipitate and settle out of the water column, or remain soluble and be removed with the tides.
2) Diversity in vegetation population. Although properties of metal accumulation and distribution of several macrophytes species have already been discussed, no determination can be made as to which plant species would be best our area of interest. Species have been identified to grow across gradients of salinity, inundation length, and metal contamination so any one species would not fit all locations in the study area. Most importantly with plant species though, is to let the natural scheme dictate the vegetation because the act of replacing plants or harvesting plants will inadvertently release metals into the wetland (Burke et.al., 2000).

3) To aid in maintaining the conditions within the salt water tidal marsh it will be necessary to limit or end the deposition of metals. This can be achieved by constructing an impact berm on the island to absorb the projectiles. Best management practices for shooting ranges are well established and these BMPs should facilitate the almost complete reduction of lead and copper entering the tidal marsh and estuary.

# 5 Discussion of Lead Free Projectiles

Most of the literature reviewed for this paper discussed how treatment wetlands were being used to remove heavy metals from mine tailings or other industrial effluent, or the mobility and stability of heavy metals within natural (non-treatment) wetlands. Literature has yet to be uncovered that investigated what would happen if the compositional proportion of the metals entering the wetland were to be altered permanently. It can be assumed that one of three situations will evolve in the wetland. First, that the lead is bound in sulfide complexes and thus the lack of lead entering the system and the increased of copper deposition should not cause the lead to become free from the sulfides; it is plausible that lead that is not tightly bound to sulfides could be released into the water column due to equilibration of the soil/sediment properties and the water column. Second, that the lead is being recycled via phytostabilization throughout the wetland, and the lack of continued lead deposition should not hinder this process. Third, that the lead is regularly undergoing reduction and oxidation reactions which is causing the cyclical solubility of lead in the pore water and water column. In this case the lead over a long time period would be washed from the wetland via the tidal cycle or due to freshwater inputs. The long term end point would then be the background concentration of the sediment or soil parent material. Over a long time scale it may be possible that the flora in the area would diversify to include new species or approach uniformity of just one species dominating the area.

# 6 Conclusion

Wetlands possess dynamic characteristics, these characteristics are only amplified when one looks at the dynamics of tidally influenced wetlands. Periodic inundation and influx of salinity cause a cyclical and almost predictable behavior of lead and copper in salt water wetlands. The behavior is linked not only to the salinity but how the underlying soil ad sediment reacts to the saline conditions and how the underlying material equilibrates with the water column. Particular types of vegetation have been revealed to be prefect for the phytostabilization of lead or copper and others have been revealed to act as the perfect phytoremediation tool by translocating metals out of the sediment into the aboveground biomass of the plant. In particular the processes of phytoremediation and phytostabilization were discussed as tools to reduce the mobility of lead and copper within the study area. More importantly though, it was determined that the best course of action is to alter the current natural settings as little as possible to maintain a balanced system.

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