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Corrosion Mechanisms and Products of Common Bird Shot Types in North Carolina Environments

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Abstract

Studies of lead shot corrosion in shooting ranges to ascertain impacts on the environment and to better understand the process of lead corrosion have been well documented in the scientific literature. However, these studies have not evaluated other types of shot nor described corrosion behavior in environments other than well aerated soils. This study compared corroded lead, steel, copper-coated lead, tungsten steel, and bismuth varieties of shot in different sedimentary and aquatic environments in North Carolina. Sets of individual plastic vials containing all five types of shot were placed in the following environments: marine beach, marine dune/soil, barrier island lagoonal mud, brackish water, running (stream) freshwater above and below sediment surface, still (pond) freshwater above and below sediment surface, and forest soil and surface. After approximately 4.5 years exposure, samples were collected and analyzed with scanning electron microscopy, energy dispersive spectrometry, and powder X-ray diffraction (XRD). Sample that were placed below the sediment surface were the most severely corroded while samples that were at or above the water table were least corroded. Analyses reveal the production of lead oxides, hydroxides, chlorides, carbonates, sulfides, and sulfates in lead and copper-coated lead shot. Steel and tungsten steel had a layer of iron oxides/hydroxides. Bismuth shot had very little corrosion in many environments.

1. Introduction

The heightened awareness of lead poisoning has led to increased concern on the introduction and movement of lead through the environment. Lead shot and bullets constitute the single greatest introduction of lead into the environment today, contributing more than 50,000 metric tons every year[1]. A study of the Blacksburg Shooting Range determined that the average rate of lead accumulation was about 1.4 tons per year[2]. Lead shot made up more than 95% of recovered metal from the majority of sampling sites at this public shooting range while alternative shot types containing no lead whatsoever were recovered in trivially small amounts. The study indicated that, at the range, concentrations of 100g of lead per square meter can be found at as far as 300m from the shooting box and that more than 80% of lead shot falls beyond the cleared field in which stationary targets are place. This distribution is mostly accounted for by the use of moving targets[2]. High concentrations of lead metals in the top section of a berm at a shooting range indicates that large portions of shot and bullet fragments enter the environment through ricochet or poor targeting[3]. Though periodic cleaning of shooting ranges remove the larger fragments of debris, most of the shot is not recovered and removed [2]. The Blacksburg site also revealed that most of the lead fragments remain in the A horizon of soil, thus making them susceptible to erosion by wind or water. Increasing soil pH and decreasing tillage are both practices ranges may use to reduce the risk on lead movement on the range site[4]. While best management practices can minimize the risk of lead dispersal in the environment, a continuous health threat results from the large quantities of lead shot being left in the environment.

Extensive studies on shooting ranges have been undertaken to elucidate the behavior of lead once it enters the environment. The corrosion or passivation behavior of the geochemical environment has a profound influence on the mobility of lead. The study of the Blacksburg Shooting Range determined that, in upland range environments, passivation coats consist of cerrussite, hydrocerrussite, and massicot [1]. Swedish studies suggest that roughly 10% of lead pellets will decompose once the shot has come into contact with the soil[5]. Studies have consistently found the formation of cerrussite and hydrocerrussite ($PbCO_3$ and $Pb_3(CO_3)_2(OH)_2$, respectively) on lead shot [1,4,5,6]. Hydrocerrussite found on shot from the Blacksburg Shooting Range remains stable in conditions of high pH and Eh. The formation of this layer will seal the remaining metal lead away from oxygen and hydrogen but requires the formation of a massicot (PbO) layer to stabilize any soluble lead left [4]. The formation of layers is the result of the interaction of the metal and the soil. This weathering process of lead shot and bullets increases the pH of the soil as the interactions occur. Though all lead shot weathers, the movement of corrosion product depends on the soil characteristics and lead loading [6]. The primary byproduct of lead shot corrosion appears to be the lead carbonates.

Lead shot and bullets, despite the potential for environmental harm, continue to be the favored ammunition for hunters and gun enthusiasts. Several states have seen increasing tension between hunters, legislators, and environmentalists over the issue of whether or not lead shot and bullets should be allowable for sport hunting. The growing concern over lead poisoning in wildlife and natural environments has led to regulations limiting or banning lead ammunition when hunting in 35 states[7]. Before these bans, lead poisoning led to the annual loss of 2-3% of waterfowl[8]. Non-toxic ammunition is commonly offered as friendlier substitutes to lead shot but also comes with differing issues. Steel shot is harder than lead, leading to increased chances of crippling rather than killing targets, and it can increase the chance of introducing chromium to the environment [8]. Many hunters also argue that steel shot, though being the most popular of the alternative ammunition choices, behaves poorly in comparison to lead, spreading over a narrower area and covering less distance [7]. Tungsten steel enables hunters to avoid the chromium loading while still maintaining non-toxic ammunition. Bismuth shot must be mixed with a small amount of tin or the ammunition would be too brittle to be useful, thus increasing the overall cost of the ammunition. A pure copper shot reacts similarly to lead shot on impact and has little ill-effect on birds and mammals, though can be highly toxic to aquatic biota [8].

This study compared corroded lead, steel, copper-coated lead, tungsten steel, and bismuth varieties of shot in different sedimentary and aquatic environments in North Carolina. The majority of lead ammunition studies have occurred in shooting ranges, with little examination on alternative types of shot. Examining lead, copper coated lead, steel, tungsten steel, and bismuth shot in a variety of environments with varying levels of water, oxygen, and nutrients will provide greater understanding of corrosion mechanisms. This study aims to further the understanding of lead ammunition corrosion and its potential interactions with freshwater and saline environments. To examine corrosion mechanisms of ammunition types beyond the popular lead shot, as many bans limit the use of lead ammunition in sport hunting, this study proposes to also examine the corrosion byproducts of copper coated lead, bismuth, steel, and tungsten steel shot.

2. Methods

2.1 Sampling Environments

Five plastic vials, of which one vial would be removed each year, containing 2 sets of lead, copper-coated lead, bismuth, steel, and tungsten steel shot were placed in the environmental location by securing the vials either on top of the sediment surface, burying them beneath the surface, or suspending them within the water column. The vials provided exposure to the environment via holes in the cylinder and the shot types were separated and padded with polyester wool (aquarium filter floss). A vial from each locality was removed after approximately 0.5, 1.5, 2.5, 3.5, and 4.5 years. Sampling occurred in ten locations in both saline and freshwater conditions in the Asheville and Emerald Isle regions of North Carolina (Table 1). The freshwater environments included three sites with two locations at each site, one buried within the sediment below the site and one set suspended on top of the sediment of the site. The Bent Creek site exhibited a small mountainous freshwater creek. The Turner Pond site was characterized by a standing freshwater pond. At Miller Yard sampling sets were placed within the top layer of soil and had no permanent water features. The saline environments had four sites with one location at each site. In Emerald Isle Marsh the sample set was submerged in the brackish marsh water beneath *Juncus* grass. At Pelley Beach the sample set was buried in the sand at least 20 meters from the ocean, preventing contact with ocean water.

At Craig's Yard the sample set was buried in the second dune back from the ocean. At Anderson Dock the sample set was suspended free hanging in the intracoastal waterway.

Table 1: Environmental Characteristics of Sample Locations.

Sample Location	**Water Type**	**Sediment Type**	**Oxygen Levels**
Bent Creek sediment	Running freshwater	Suspended in creek	Oxidizing
Bent Creek buried	Running freshwater	Stream sediment	Oxidizing and Reducing
Turner Pond sediment	Still freshwater	Suspended in pond	Oxidizing
Turner Pond buried	Still freshwater	Organic pond soil	Oxidizing
Miller Yard sediment	Rain infiltration	Sediment surface	Oxidizing
Miller Yard buried	Rain infiltration	Forest soil	Oxidizing and Reducing
Emerald Isle Marsh	Seepage	Organic marsh soil	Oxidizing and Reducing
Pelley Beach	Water table	Sand	Oxidizing
Craig's Yard	Rain infiltration	Sand	Oxidizing
Anderson Dock	Brackish water	Suspended in sound	Oxidizing and Reducing

2.2 Sample Preparation

After collection, samples were prepared for analysis. To cast an epoxy plug, one shot of each type of metal from each environmental location was placed in the bottom of a plastic plug mold with sample label. An epoxy resin and hardener mixture with a ratio of five parts resin to one part hardener was poured into the mold. The mold was then placed under vacuum to remove all air bubbles and allowed to harden overnight. Each plug was ground and polished using a succession of grit sizes, starting at a 35μm fixed diamond grit surface and over five five-minute intervals moved to a 0.3μm nylon surface with 0.3μm alumina grit. The remaining sampling sets were either scraped for powder X-ray diffraction analysis or left intact for imaging.

2.3 Analysis

Optical microscopy was initially used to identify key properties of each polished cross section and photography of the cross sections established a detailed record of the initial features. A scanning electron microscope with an energy dispersive spectrometer (SEM/EDS; FEI Quanta 400 SEM with an Oxford Inca 450 EDS) was employed to determine chemical compositions within a variety of points on each shot type in each cross section. Several thin sections were mapped to establish and identify different phases within highly corroded shot samples. Whole samples were also imaged and analyzed using point analysis with the SEM. Several samples were scraped and analyzed using powder X-ray diffraction (XRD; Philips PW3040) to establish key minerals, and this data set was cross referenced with the point identification under the SEM/EDS to identify minerals and mineral phases on each shot type from each environment.

3. Results and Discussion

3.1 Environmental and Metal Trends

The amount of corrosion left on the shot at each environment varied from location to location. Evaluation of corrosion was based on amount of corrosion by-products found through analysis and the visual degradation of samples. High levels of corrosion were found on shot placed at Emerald Isle marsh, Turner Pond buried, and Anderson Dock, which were typically oxidizing environments containing a large portion of organic matter and plenty of water. The interaction of these richer environments with the metals resulted in a number of carbonates, lead and iron oxides, and sulfates (Table 2). However, fairly low levels of corrosion were found on shot at Pelley Beach, Craig's Yard, and Bent Creek sediment, environments characterized by sandy soils, little organic material, and little water exposure. These environments were far less corrosive and left little evidence of interactions with the metals over the 4-5 year exposure period. Alternatively, Miller's Yard buried, Miller's Yard sediment, and Bent

Creek buried displayed intermediate corrosion and were environments that contained moderate levels of moisture and organic matter. The most common corrosion products in these environments were the lead carbonates and sulfates.

Just as the differing environments resulted in varied levels of corrosion, different types of metals had various levels of corrosion. The most highly corroded ammunition was consistently the steel shot, with iron oxides being common corrosion products. The presence of these corrosion products indicates that the environments were fairly rich in free oxygen. Lead ammunition corroded less than the steel but about equally to that of copper-coated lead shot. The copper coating had often corroded away from the underlying lead, however, leaving it a difficult task to ascertain the level of corrosion of the copper-coated shot. Cerussite and hydrocerussite were the primary corrosion products of lead in all the environments. Sulfates, sulfides, and chlorides were also identified in the wet saline environments of Emerald Isle Marsh and Anderson Dock. A copper sulfide, covellite, was identified at Turner Pond. The tungsten steel ammunition was more resistant to corrosion mechanisms than the steel and lead ammunitions. The two corrosion products of the tungsten steel shot were Scheelite, in Anderson Dock, and Stolzite, at Emerald Isle Marsh. The bismuth shot was the least corroded and showed little mineral formation. Oxidized byproducts were more common among all the types of shot than reduced byproducts.

Table 2: Mineral Corrosion Products Identified in Shot Samples.

Mineral Name	Chemical Composition	Presence in Sampling Locations
Cerussite	$PbCO_3$	Emerald Isle Marsh, Anderson Dock, Bent Creek sediment, Turner Pond sediment & buried
Hydrocerussite	$Pb_3(CO_3)_2(OH)_2$	Anderson Dock, Turner Pond sediment & buried
Plattnerite	PbO_2	Emerald Isle Marsh, Turner Pond sediment & buried
Cotunnite	$PbCl_2$	Emerald Isle Marsh, Anderson Dock
Laurionite	Pb(OH)Cl	Anderson Dock
Anglesite	$PbSO_4$	Emerald Isle Marsh, Anderson Dock, Bent Creek sediment
Galena	PbS	Emerald Isle Marsh
Scheelite	$CaWO_4$	Anderson Dock, Turner Pond buried
Stolzite	$PbWO_4$	Emerald Isle Marsh
Akaganeite	βFeO(OH,Cl)	Anderson Dock
Lepidocrocite	γFeO(OH)	Emerald Isle Marsh
Goethite	αFeO(OH)	Turner Pond sediment, Miller Yard sediment
Covellite	CuS	Emerald Isle Marsh

3.2 Anderson Dock

The Anderson Dock site was consistently a highly corrosive environment. XRD identified cotunnite, laurionite, hydrocerussite, anglesite, scheelite, and akaganeite (Figure 1). Imaging and chemical analyses with the SEM/EDS identified cerussite and hydrocerussite crystals on the lead shot surface (Figure 2). The ratio of oxygen to lead in the lead shot was roughly 2:1. Also, XRD clearly identified cotunnite, laurionite, and anglesite minerals, though EDS detected little to no chlorine or sulfur at points on the lead shot during analysis. That cerussite and anglesite were detected in analysis suggests, when plotted on an Eh-pH diagram, that the environment at Anderson dock falls along a boundary line, with a pH range from 4 to 6 and an Eh range from -0.2 to 0.2 (Figure 3). The presence of chlorides such as cotunnite was exclusive to the wet, salty environments like Anderson dock, suggesting higher levels of the chloride in the saline waters, as opposed to freshwaters. The presence of lead chlorides at Anderson Dock supports the identification of akaganeite by XRD as a corrosion product of steel shot, though little to no chlorine was detected by EDS. Though the steel shot primarily corroded to iron oxides, the tungsten steel had new chemical features added to its corrosion chemistry. Analysis of the tungsten steel shot revealed a 1:1 ratio of calcium to tungsten, which implies the presence of scheelite that was verified by XRD. While the lead, steel, and tungsten steel shot contained a variety of corrosion products, the copper-coated and bismuth shot had much less to examine. The copper coating on the copper-coated lead shot was completely absent, but little corrosion occurred on the underlying lead metal. There was a 2:1 oxygen to lead ratio indicated by the chemical analyses through EDS indicates the potential for plattnerite. Very little corrosion occurred on the bismuth shot.

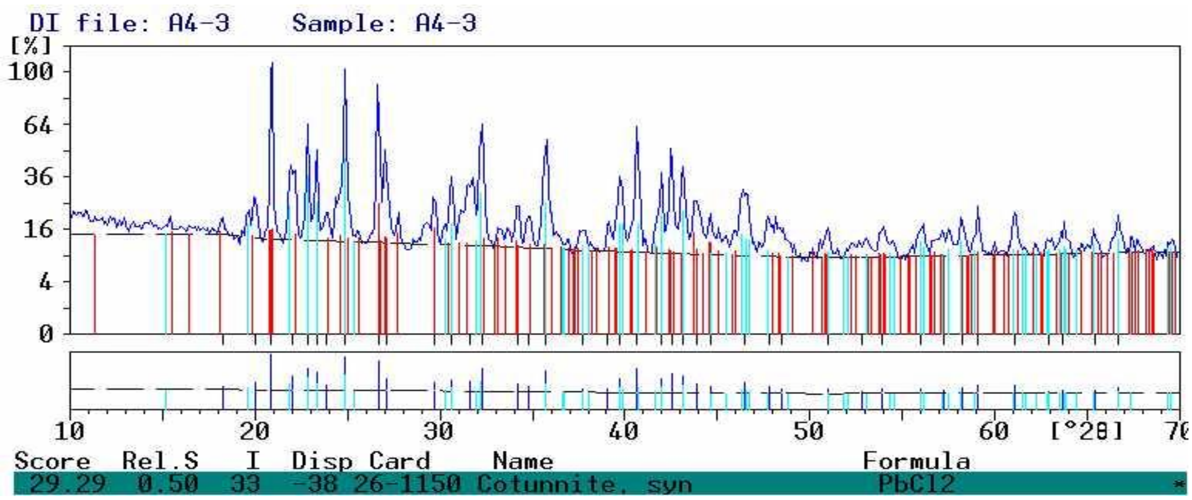

Figure 1: The XRD scan identifying cotunnite as a corrosion product of the lead shot at Anderson Dock.

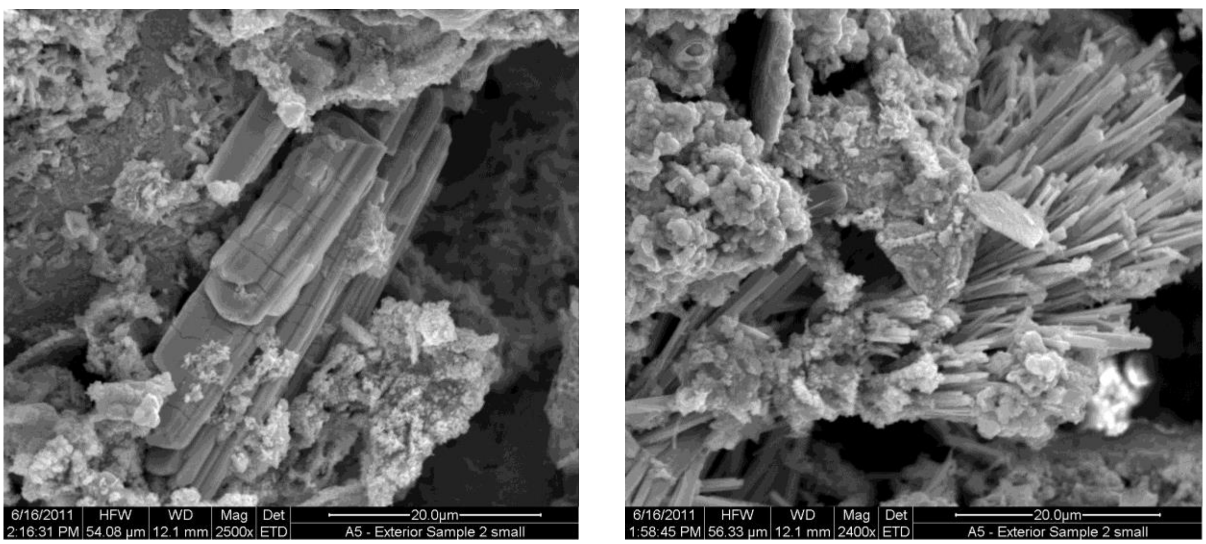

Figure 2: The cerussite crystals, on the left, and hydrocerussite crystals, on the right, were both identified on the exterior of the lead shot from Anderson Dock.

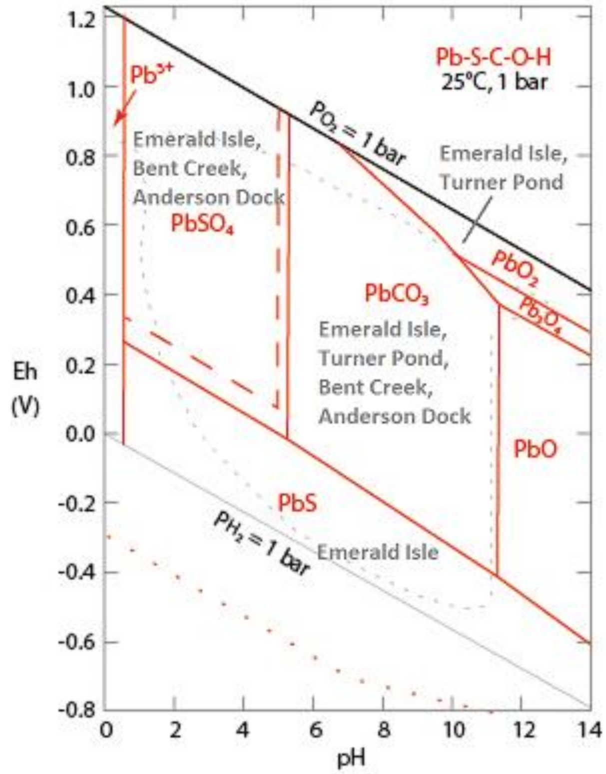

Figure 3: An Eh-pH diagram for lead phases[9].

3.3 Emerald Isle Marsh

Emerald Isle Marsh was one of the more corrosive environments and had a lot of new material, from its saline and organic compositions, contributing to the corrosion of metals. The tungsten steel shot was lost from the last sample set at this location. The finding of stolzite on an early tungsten steel sample suggests some interaction between the lead and tungsten shot during the study period (Figure 4). XRD identified cotunnite, plattnerite, cerussite, anglesite, galena, stolzite, covellite, and possibly valleriite ($4(Fe,Cu)S{\cdot}3(Mg,Al)(OH)_2$) present on the shot placed in the Emerald Isle marsh. The wet, saline environment may have higher amounts of chloride than other types of environments and a number of minerals that form in reduced conditions were identified (Figures 3 and 5). Cotunnite was also identified by XRD, announcing the presence of chlorides and XRD revealed the presence of covellite, a copper sulfide, on the copper coated lead shot, though very little sulfur was detected on the copper-coated lead with the EDS (Figure 6). Another sulfide identified by XRD was galena, a lead sulfide. The 1:1 ratio of sulfur to lead on the lead shot detected by EDS indicates that galena and/or anglesite are likely to be present. Though many minerals that form in reduced conditions had been detected, there was an oxygen to lead ratio of about 5:1 detected by EDS on the lead shot, which indicates a much more oxidized environment. The EDS suggested that the steel shot was composed primarily of oxidized iron, and lepidocrocite was identified by XRD. The presence of lead oxides, carbonates and sulfates, such as plattnerite, cerussite and anglesite, also indicate an oxidized environment. A 2:1 ratio of oxygen to bismuth on the bismuth shot suggested that the bismuth corroded in an oxidized environment. The vast number of minerals that form in oxidized environments and a similarly large number of minerals that form in reduced environments suggests that Emerald Isle Marsh not only has an abundance of chemical variety, but that the Eh conditions varied over a large range.

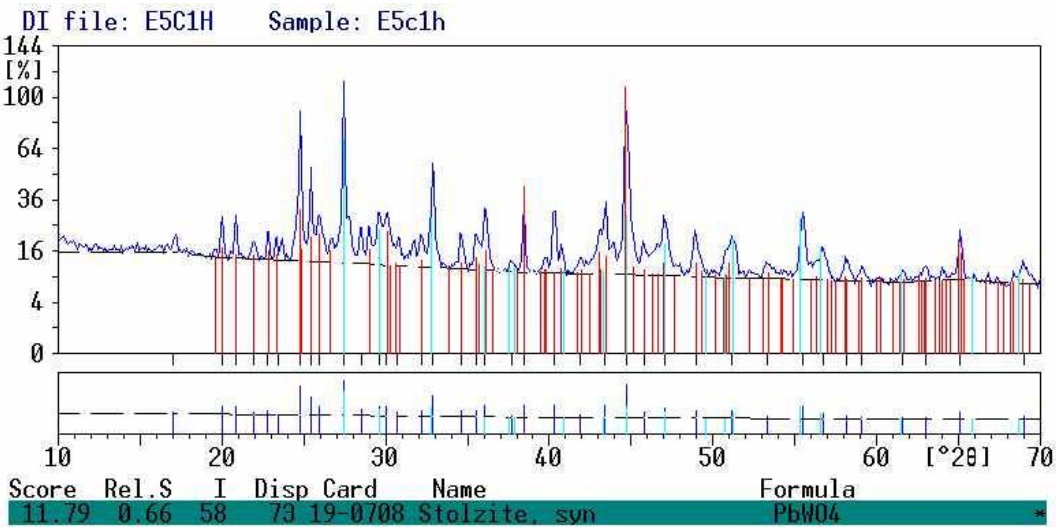

Figure 4: An XRD scan showing the presence of the mineral stolzite on the tungsten steel shot at Emerald Isle Marsh.

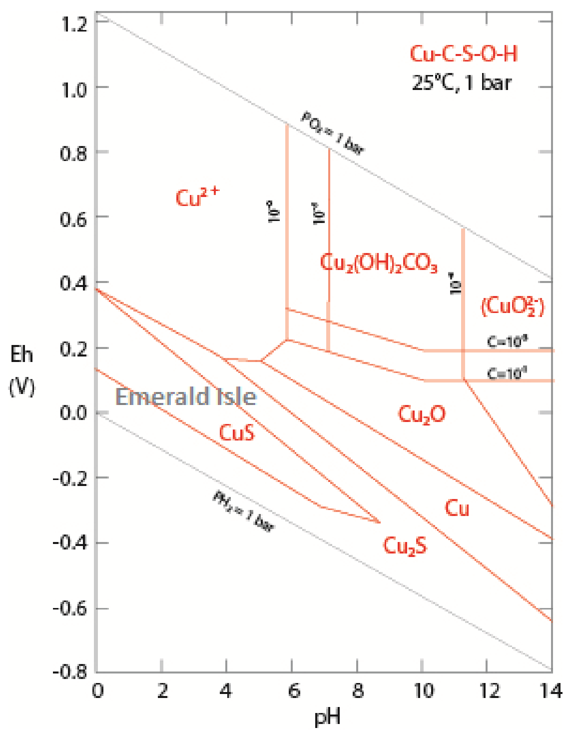

Figure 5: An Eh-pH diagram of copper phases [9].

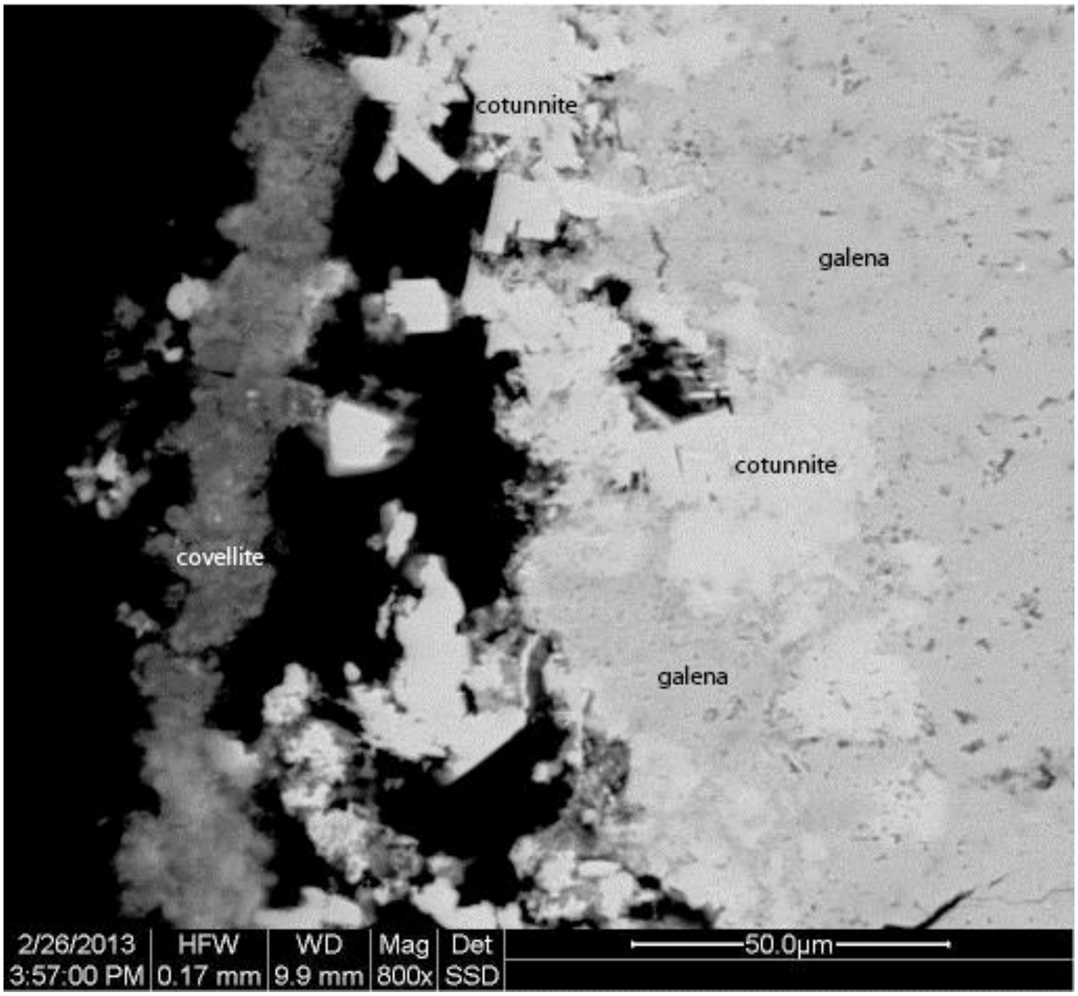

Figure 6: Phases of corrosion on a polished cross-section of the copper-coated lead shot from Emerald Isle Marsh showing minerals at the edge (left) to the interior of the shot (right), identified as covellite, cotunnite, galena, and lead.

3.4 Turner Pond

Turner Pond had a comparatively high amount of corrosion on the buried sample set while only a moderate amount of corrosion on the sample set placed on top of the sediment surface within this freshwater pond. The steel shot from the buried sample set was lost during the exposure period. XRD of the buried shot identified plattnerite, cerussite, and hydrocerussite. The oxidizing environment allows for large amounts of oxygen molecules to interact with the shot and results in the formation of lead oxides and carbonates. By plotting the corrosion byproducts on an Eh-pH diagram, it is revealed that the Turner Pond environment appeared to have a pH above 6 and an Eh above 0.5 to allow the formation of plattnerite and cerussite (Figure 3). Point analysis with EDS indicated the presence of sulfur on the lead shot. This detection of sulfur and the availability of oxygen in this environment suggest that there is the potential for the formation of anglesite. Not only was the presence of sulfur indicated, but the SEM/EDS revealed the presence of calcium in the environment by identifying scheelite crystals on the buried tungsten steel shot (Figure 7). Another more unusual finding from EDS was that it indicated a larger than average amount of antimony in the bismuth shot at Turner Pond when compared to the mean amount of antimony in other shot samples from other environments. Since antimony is a component of the shot that prevents the ammunition from becoming too brittle [8], it is possible that this is simply a sample that happened to have a higher mixture of antimony added to it. The oxygen to bismuth ratio was approximately 1:1. Though the metals buried under the sediment surface had several different corrosion products found by XRD, the sample set on top of the surface had relatively little identification. The XRD identified lepidocrocite and potentially limonite (Figure 8), suggesting that the surface area was an environment that encourages rusting.

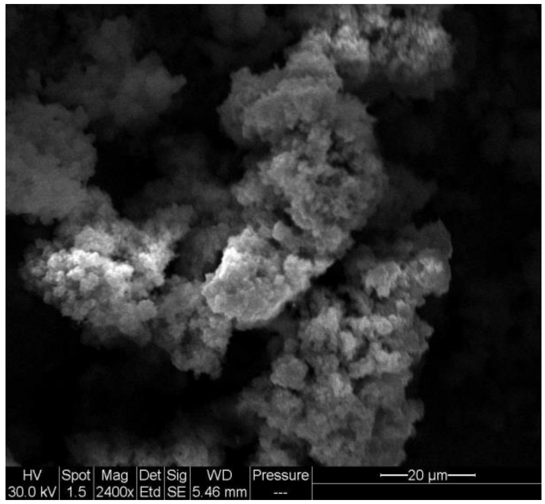

Figure 7: The tungsten steel shot contained scheelite crystals on its surface when buried beneath the sediment surface at Turner Pond.

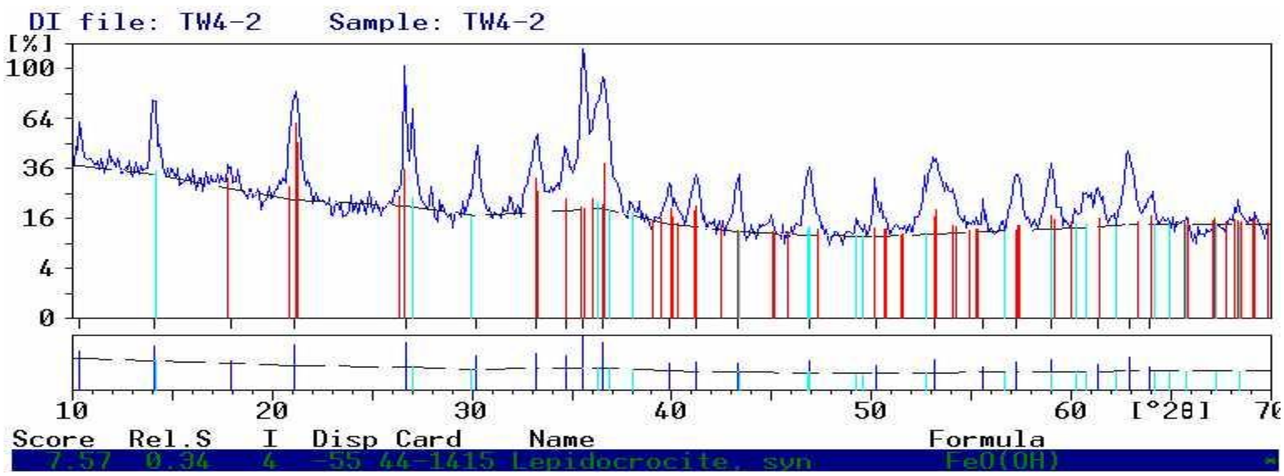

Figure 8: The XRD scan identifying lepidocrocite as a corrosion product of the steel shot at the sediment surface of Turner Pond.

3.5 Other Findings

Though the other environments had little corrosion products to contribute to the study, there were a few more notable observations. EDS analyses of the Miller Yard samples, both buried and on the sediment surface, revealed the presence of zinc on the steel shot. Other analyses did not reveal any other findings of zinc, though the element was consistently present through chemical analysis. XRD of the sample set on the sediment surface at Miller Yard identified cerussite and hydrocerussite on the lead shot, which was supported by EDS analyses (Figure 9). These carbonates suggest an oxidizing environment, which is supported by the imaging of the goethite crystals on the steel shot. XRD of the samples on the sediment surface at Bent Creek reveal the presence of cerussite and anglesite, indicating the presence of sulfur in that oxidizing environment.

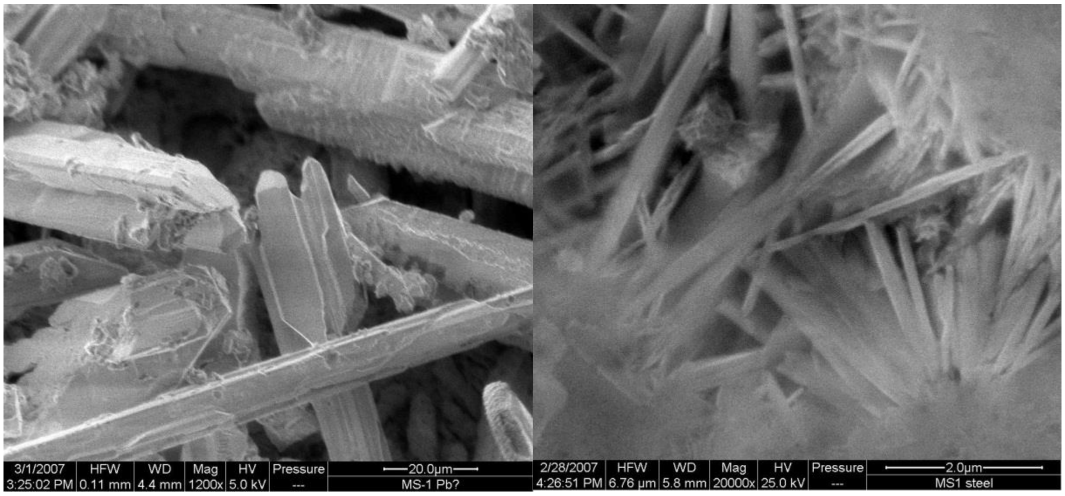

Figure 9: Imaging through SEM/EDS revealed that, at the sediment surface of Miller Yard, the lead shot formed cerussite crystals and the steel shot formed goethite crystals.

4. Conclusion

Through the examination of these five ammunition types, the corrosion products of various freshwater and saline environments of North Carolina have been further examined. The formation of cerussite and hydrocerussite as the primary corrosion product in lead shot was supported further by the results of this study. The environments that were fairly oxidized, contained large amounts of organic matter, and experienced water flow were the environments that left the most corroded ammunition while environments that were well drained and had little accumulation of organic matter were the least corroded. Steel shot corroded most quickly while bismuth shot corroded hardly at all. Sulfates, sulfides, chlorides, oxides and hydroxides were all present throughout the environments. The saline waters of the Emerald Isle Marsh and Anderson Dock contained the chlorides, suggesting that these environments held more free chloride than other North Carolinian environments. The noble reputation of bismuth was confirmed in this study, suggesting it would release very few products into the environment via corrosion compared to lead, albeit at a much higher purchase price than lead shot. Lead and copper-coated lead often were among the most highly corroded ammunition types, though the copper coating often provided some insulation to the lead beneath. However, several environments, particularly environments exposed to water, penetrated through the copper to the lead. Some issues with the security of sample sets at several location resulted from the hegemony of wildlife, with losses most likely resulting from theft by raccoons. Understanding the corrosion mechanism and by-products of common metal types better enables regulators and environment agencies to protect and preserve the environment.

5. Acknowledgements

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6. References

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