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Elemental Contamination of an Ancient Copper Mine in Killarney National Park, Killarney, Ireland

A senior thesis written by

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in partial fulfillment of the graduation requirements for the major in geology

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ABSTRACT

Ross Island Copper Mine, located in Killarney National Park, Killarney, Ireland, is known for archeological artifacts of copper from the Bronze Age. Copper production surged in the late 1700s and into the mid-1800s. The mine included both open pits (e.g. Blue Hole) and underground excavations (e.g. Western Mine). Copper veins were found in the Mississippian-aged limestone bedrock along with chalcopyrite and tennantite ore. In 1912, tourism had become the main source of income in the area, and the mines and the land surrounding them were remediated and became a part of the national park. Mine shafts were filled in, waste piles were moved or disposed of, and trees were planted. Little remediation has been done since the original work in 1912. The purpose of this study is to investigate the levels of contamination in the soil and water in and around mine sites. Twelve water samples and four soil samples were taken from Blue Hole, Western Mine, Lough Leane (the nearby lake), and River Laune, located several miles downstream from the national park. The water samples were dried on micro-carry filter papers and analyzed in an XRF spectrometer for S and Cu. Soil samples, mostly of a sand or silt texture, were dried and pressed into pellets for XRF analyses of S, Pb, Cu, and Zn. Water samples had low concentrations of both Cu and S (<4 and 23 ppm, respectively). Much higher concentrations of S and heavy metals were observed in soil samples, with maximum concentrations of S >134,000 ppm, Zn >63,000 ppm, Pb >62,000 ppm, and Cu >17,000 ppm. These high levels may be of concern, although leaching of these metals is unlikely to adversely affect local aquifers or wells because of dilution in nearby Lough Leane. There is no immediate threat to humans from contaminated soil, though the health of some plant species could be compromised, especially with high levels of Pb and Zn.

INTRODUCTION

The purpose of this study is to examine the levels of sulfur (S) and heavy metals, specifically zinc (Zn), lead (Pb), and copper (Cu), in the soil and water at an ancient copper mine within Killarney National Park, Killarney, Ireland. The town of Killarney is located in County Kerry near the southwest coast of the country. The national park has 3 main lakes that ultimately flow northwest towards the Atlantic Ocean-Lough Leane (pronounced “Lock Lean”), Muckross Lake, and Upper Lake. Lough Leane is the largest of the 3 lakes and is located closest to the various sample sites.

12 water samples and 4 soil samples were taken over 11 days from 6 different sites with weather varying from sunshine to light rain to several hours of downpour. Samples were taken with weather in mind because it is possible that rain could have an effect on the results, either by diluting possible contaminants or causing an increase in S levels due to acid rain.

The importance of this research lies in the fact that few studies have been conducted in this area. Despite the mine being located in Ireland’s largest national park, very little scientific research on the quality of the water and soil has been done. This study aims to give a snapshot of the current state of the soil and water at the specific sample sites. Each element was chosen because of the close elemental relationships with copper mining.

BACKGROUND

Ross Island, a peninsula located within the boundaries of Killarney National Park in Killarney, Ireland, has been home to several thousand years of mining activity. Tools found around the area in the late 1700s indicate that mining began here in the Bronze Age (3500 BC). Mining continued again in the late 1700s and the Ross Island Copper Mine was established. The original site location is known as the “Blue Hole” site and was a large open pit mine. When production grew in the early 1800s, a second site was opened. The Western Mine was a typical underground shaft mine located slightly west of the Blue Hole site. Between 1804 and 1829, more than 5,000 pounds of copper were sent to smelters in England (Ross Island). In the late 1800s, production at the mine began to slow due to increasing production costs and a growing tourism industry in the area. The mines were finally closed, but an attempt was made in 1911 to reopen the mines. Because tourism was now the main source of income for the area, the mines were permanently closed in 1912. Mine buildings were demolished, shafts were filled in, and various trees and plants were planted in an attempt to remediate the mine sites (Ross Island).

Ross Island has a Devonian-aged, copper-rich limestone matrix (Ross Island). Chalcopyrite ($CuFeS_2$) and tennantite ($Cu_{12}As_4S_{13}$) ores are present in vein-type structures. The peninsula of Ross Island is located on 2 different geologic thrusts- Head of Ross Thrust and Ross Island Thrust (Nex et al., 2003). The carbonate lithology of the region, along with a ductile nature, suggests that a ductile-thrust model is the most applicable model for the area (Nex et al., 2003). Figure 1 is a geologic map of Ross Island and the various lithologies, thrusts, and other structural information. Ross Island consists of Ballysteen Formation limestone overlying the Rockfield Formation limestone (Nex et al., 2003). Mineralization of copper extended only to a maximum depth of 13-16 meters (approx. 42-52 feet) (Ross Island).

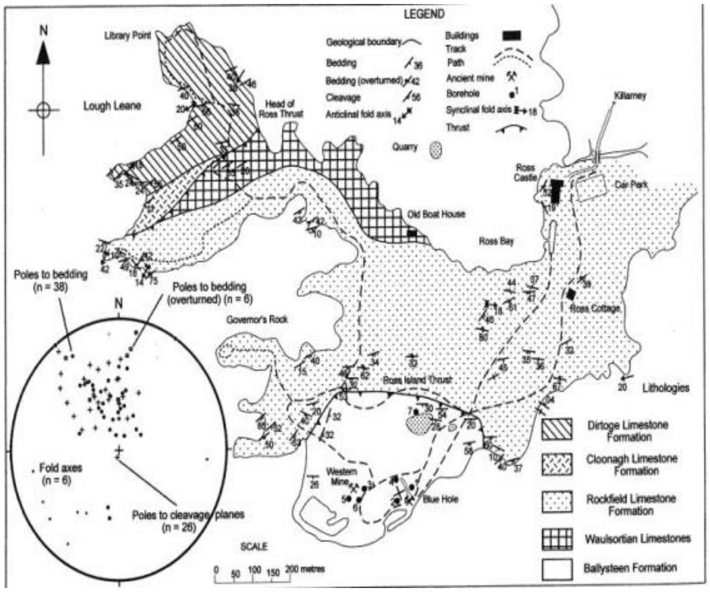


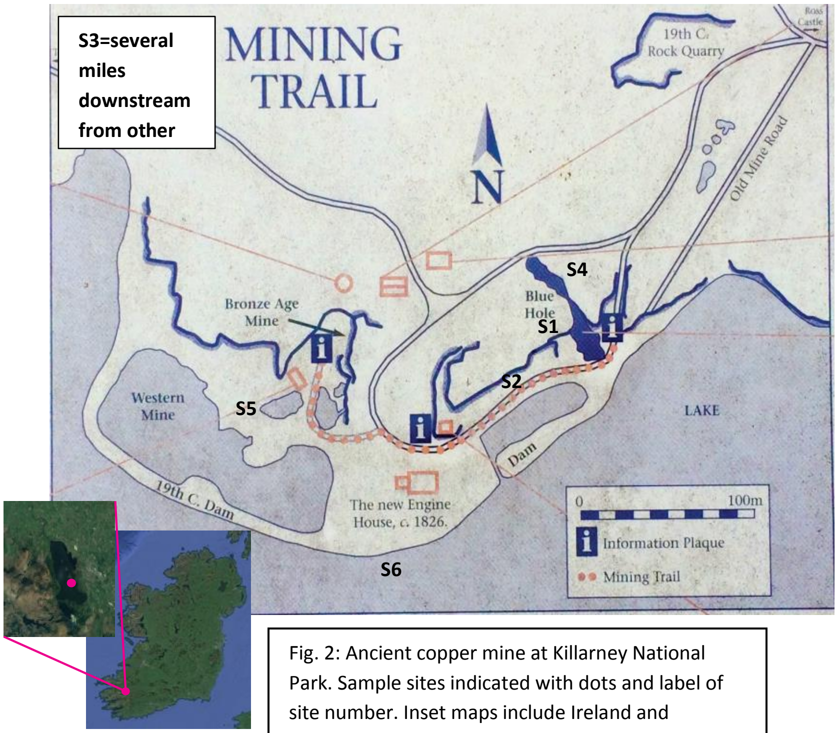
Fig. 1: Geologic map of Ross Island peninsula. The lithologies and thrusts can be seen as well as structural variations throughout. Taken from Nex et al., 2003

The implications of heavy metal contamination in soil have been studied extensively. High heavy metal levels in soil have been known to lead to soil acidification, which can, in turn, lead to a diminishing in the health of plants (Sowinski et al., 2016; Shi et al., 2015; Verdejo et al., 2015; Motuzova et al., 2014; Rutkowska et al., 2015). Heavy metal content depends on different variables, including the type of parent material, soil texture, pedologic factors, and anthropogenic forces (Sowinski et al., 2016). Cu, Pb, and Zn all have significant effects of the health and productivity of soil. Cu is a necessary micronutrient, but after a certain threshold, becomes highly toxic (Verdejo et al., 2015). The total content of Cu in soil can be used as the main predictor of plant growth (Verdejo et al., 2015). Zn also has the ability to negatively affect soil. Zn is toxic to microorganisms and can have adverse effects of soil fertility (Rutkowska et al., 2015). All 3 heavy metals (Cu, Pb, and Zn) can be affected by decreasing levels in pH. As the pH of the soil lowers, mobilization of metal cations increases (Sowinski et al., 2016). This means that heavy metals in the soil have the ability to affect the soil's pH while the pH of the soil can affect the mobility of heavy metal ions.

Phytoremediation, the use of plants as bioremediators, has proved to be the most effective form of remediation in terms of heavy metal contamination (Shi et al., 2015). Lab studies have shown that Cu levels in soil can be dramatically remediated by phytoremediation (Sowinski et al., 2016). Phytoremediation has been used in northeastern China, the Avoca mines in eastern Ireland, and Chile to much success (N. F. Gray, 1996; Verdejo et al., 2015; Shi et al., 2015).

SITE DESCRIPTION

For this study, samples were taken from 6 different sites. The study was around Blue Hole but samples were also taken near the entrance to Western Mine as well as downstream from the national park. Figure 2 shows the location of each sample site. Table 1 lists each sample site, along with the date of collection, site name, designated abbreviation, GPS location, elevation, and what water and soil samples were collected.



S3=several miles downstream from other

Fig. 2: Ancient copper mine at Killarney National Park. Sample sites indicated with dots and label of site number. Inset maps include Ireland and Killarney National Park. Ross Island map photo taken by C. Chouinard (2016). Ireland and Killarney National Park images from Google Earth (2017).

Table 1: Lists of site number date of collection, site name, abbreviated site name, GPS coordinates, elevation, and water and soil samples taken from each site.

Site #:	Date:	Site Name:	Label:	GPS Location:	Elevation (ft. above sea level):	Water Samples:	Soil Samples:
1	3/21/2016	Blue Hole (main)	S1	+52.0353, -009.5368	70	1, 2, 9	3
2	3/21/2016	Blue Hole (SE)	S2	+052.0352, -009.5370	70	4, 6	5
3	3/31/2016	River Laune	S3	+052.0711, -009.5883	160	11, 13	10, 12
4	4/1/2016	Blue Hole (NW)	S4	+052.0352 -009.5368	70	14	-
5	4/1/2016	Western Mine	S5	+052.0710, -009.5883	75	15, 16	-
6	3/24/2016	Lough Leane	S6	+052.0353, -009.5362	60	7, 8	-

S1 is the original Blue Hole site. The water was a deep turquoise blue with deciduous trees and shrubs and a thick understory. The depth of the water is unknown, but appeared to be deep. The remaining half of the site was surrounded by an asphalt walking trail. Sand and gravel led from the walking path to the exact sample site.

S2 is another portion of Blue Hole, located slightly southeast of the original pit mine. The sample site was directly across the walking trail from S1 and was significantly smaller. The water at S2 was several feet deep at the maximum. Half of the perimeter of the reservoir was the walking path and the other half consisted of some deciduous vegetation and a thin tree line that bordered Lough Leane.

S3 was a sample site located approximately 5 miles downstream from the mine sites. River Laune flows through the 3 Lakes of Killarney (Lough Leane, Muckross, and Upper Lake) and northwest towards Dingle Bay. Ultimately, River Laune flows 25 miles, eventually converging with the Atlantic Ocean. The sample site was about 50 feet from large rapids and the water moved at a fast pace. A road bridge crossed over the ricer and a small dam was built beneath the bridge; this appeared to be the source of the rapids. Water samples were taken directly from the river, about 4 inches out from the shoreline, and soil was taken from the shore of the river as well as approximately 15 feet inland from the shoreline.

S4 was the northwest portion of Blue Hole. The site was located on a small hill but the waterline of the pit itself was about 10 feet below the tree line. Dense trees and shrubs encircled the entire area. The water was murky and polluted with natural debris such as leaves, twigs, larger fallen branches, and plants. There was also some exposed bedrock on the northern side of the pit.

S5 samples were taken near the entrance of Western Mine. The shafts of Western Mine were in-filled in the early 1900s during the remediation of the land, but fences still remain around the historic shaft entrance. The site was densely forested with deciduous trees, extensive ground cover, and a thick understory.

S6 was taken from Lough Leane, the largest of the 3 lakes in the national park. Mountains followed 2 sides, while a rocky shoreline surrounded another side, and the lake continued around a small curve, where it opened into the largest portion of the lake. Samples were taken from the rocky shoreline because that was closest to the other sample site. This site was used as a control site as a way to understand high or low levels of Cu and S in water samples taken from other sites as well as try to understand how contaminants may be moving between water sources.

FIELD PROCEDURES (WATER):

Water samples were collected at various depths, ranging from the surface to 6 inches deep, with individual plastic vials. The plastic vial was submerged straight down into the water then brought straight back up. A few millimeters of water were poured out before putting the cap on the vial and sealing it tightly. Samples were given several hours to a day for suspended sediment to settle out before the water was transferred to micro-carry filter paper. Once the suspended sediment had settled, a pipette was used to transfer 10 mL of the water from the plastic vials to micro-carry filter paper. A sterile pipette tip was used for each transfer in an attempt to limit the amount of cross contamination. Once the water was on the filter paper, samples were left out to dry for 2 days before being put into small, individual zip lock bags. All vials, micro-carry filter paper, and zip lock bags were labeled with the date of collection and given a sample number.

Weather when collecting samples at S1 and S2 was overcast with minimal winds and it had not rained for at least 2 days. Samples at S3 were collected 10 days after the collection of samples at S1 and S2. The day of collection was sunny with few clouds, though 3 days of rain occurred leading up to the collection. S4 and S5 were collected during a heavy downpour that had been ongoing for several hours.

FIELD PROCEDURES (SOIL):

A metal garden trowel was used to dig to depths ranging from the surface to 6 inches deep. Once samples were collected, the soil was put into individual zip lock bags and sealed tightly. All samples were dated with the day of collection and given a sample number. Most samples consisted of a sand or silt texture.

Samples 3 and 5 were taken from the surface whereas samples 10 and 12 were dug to a depth of 6 inches with the top 2 inches of soil removed before placing the samples in zip lock bags.

LAB PROCEDURES (WATER):

Water samples were taken from their individual bags and placed on plastic holders before being analyzed in an XRF spectrometer. Each sample was run 3 separate times.

LAB PROCEDURES (SOIL):

Before beginning the process of creating pellets for the XRF spectrometer, an application for the analysis of S needed to be made. The application was made using computer software linked to the XRF spectrometer and was used as the guidelines for the machine. Due to unrealistic results and skewed data, several different applications were created until a reliable application was made. XRF standards were used to test the accuracy of each application.

Once the application was created, soils were placed in aluminum tins and dried in a small oven at 50ºC for several days. As samples dried, each was put through a 50/50 splitter with the intention of avoiding any potential bias. Samples were then put in a porcelain crucible inside a mixer mill. Ethanol was added to the soil sample to give a mud-like consistency and avoid dust from forming in the mixer mill. For samples with a course-grained texture, large pieces were placed in a pedestal grinder and crushed using a mallet before being put in the mixer mill. Samples were dried a second time in an oven, again at 50ºC for several days. Once samples were dry, each was crushed and weighed. 8.5g of each sample and 1.5g of paraffin binder were needed for the XRF to correctly analyze the samples. Exact measurements were important for the XRF spectrometer. The crushed sample and paraffin binder were mixed thoroughly and prepped for the hydraulic press. A 16-ton hydraulic press was used to compress the samples into thin pellets. 2 tons of pressure was applied for 30 seconds followed by 14 tons of pressure for 2 minutes. Pressure was released slowly to avoid causing cracks and fractures from forming in the pellets. Once all the samples had been pressed into pellets, they were placed in an XRF spectrometer and run continuously for 16 hours. Applications and standards used included S_in_soil, TraceSr-Pb, and TraceS-Rb. S_in_soil was the application created using the computer software and measured only S. TraceSr-Pb and TraceS-Rb were standards. TraceSr-Pb measured Pb while TraceS-Rb measured Cu and Zn.

Due to unrealistic data results after the first run for samples 3 and 5, 2 new sets of pellets were made. A 2nd pellet was made from the remains of the sample after it had been run through the 50/50 splitter. A 3rd pellet was created by starting the process over again. Creating pellets from the existing sample allowed for the results to be compared the previous runs through the XRF spectrometer while entirely new pellets were made to test for any inconsistencies in the soil. This process was also done to help minimize the amount of error in the results. Samples 10 and 12 did not have enough soil remaining in the 50/50 splitter to make a 2nd pellet. Table 2 shows the labeling system used for each sample.

Table 2: Table of a visual representation of how each soil sample was labeled.

3.1.1- Original Sample	5.1.1- Original Sample	10.1- Original Sample	12.1- Original Sample
3.1.2- From existing 50/50 splitter sample	5.1.2- From existing 50/50 splitter sample	10.2- Entirely new pellet	12.2- Entirely new pellet
3.2- Entirely new pellet	5.2- Entirely new pellet	-----------------------------	-----------------------------

A test pellet of pure silica was made to test for any contamination from the equipment. This sample was made following the same process as the other pellets. Results of running the silica test through the XRF spectrometer exhibited no evidence of cross contamination.

RESULTS

Water samples were found to have low concentrations of both Cu and S (<4 and 23ppm respectively). Much higher concentrations of all measured elements were observed with maximum concentrations of S of >134,000ppm, Zn of >63,000ppm, Pb of >62,000ppm, and Cu of >17,000ppm. S1 and S2 had the highest levels of all elements tested while S3 had significantly lower levels of all contaminants. S6 had contaminants levels consistent with the other samples collected. Table 3 shows the measured levels of each water sample. Table 4 shows the analyzed values of S, Cu, Pb, and Zn. Figure 3 is the water values analyzed by the XRF spectrometer and compared by sample number and figure 4 is the analyzed soil values, also compared by sample number.

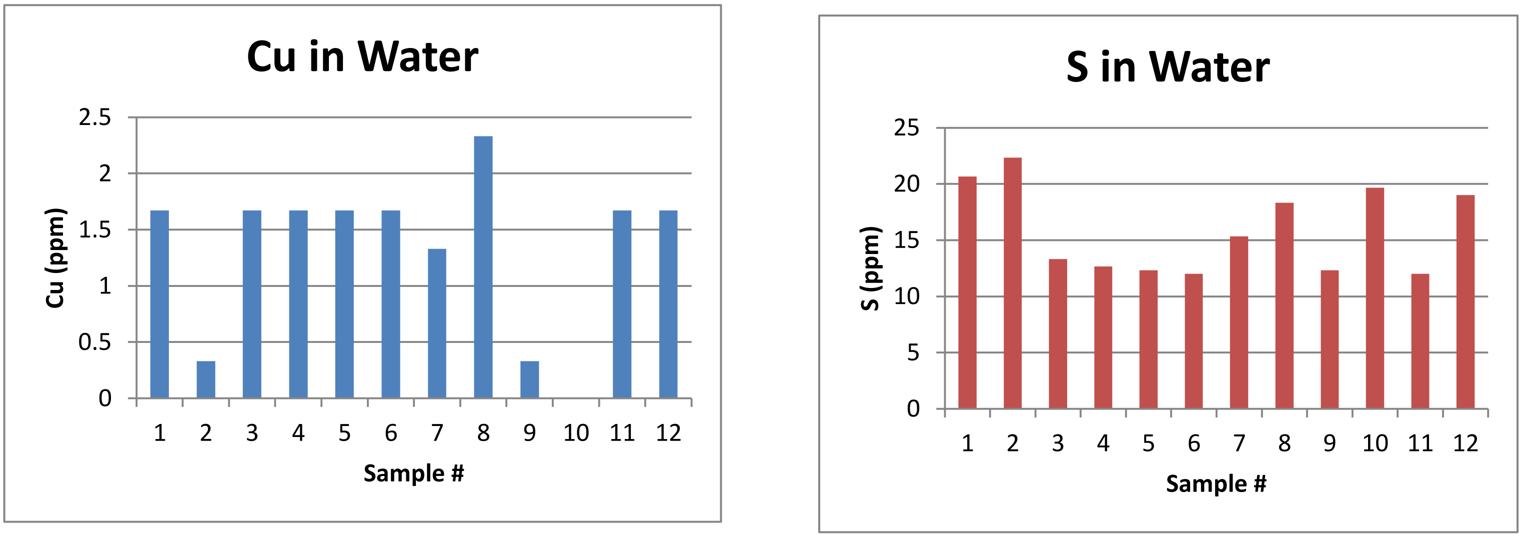


Fig. 3: Side by side comparison of measured Cu and S levels in water samples.

Table 3: Cu and S values of analyzed water samples. Also shown is calculated averages of each sample as well as standard deviation.

Sample #	Cu (ppm)	S (ppm)	Avg. Cu	Avg. S	Std. Dev. Cu	Std. Dev. S
1	2	20	-	-	-	-
1	2	21	1.67	20.67	0.58	0.58
1	1	21	-	-	-	-
2	1	23	-	-	-	-
2	-1	22	0.33	22.33	1.15	0.58
2	1	22	-	-	-	-
4	2	14	-	-	-	-
4	1	13	1.67	13.33	0.58	0.58
4	2	13	-	-	-	-
6	2	12	-	-	-	-
6	3	13	1.67	12.67	1.53	0.58
6	0	13	-	-	-	-
7	3	12	-	-	-	-
7	0	12	1.67	12.33	1.53	0.58
7	2	13	-	-	-	-
8	2	12	-	-	-	-
8	1	12	1.67	12	0.58	0
8	2	12	-	-	-	-
9	0	16	-	-	-	-
9	2	15	1.33	15.33	1.15	0.58
9	2	15	-	-	-	-
11	2	19	-	-	-	-
11	2	19	2.33	18.33	0.58	1.15
11	3	17	-	-	-	-
13	1	13	-	-	-	-
13	-1	12	0.33	12.33	1.15	0.58
13	1	12	-	-	-	-
14	0	20	-	-	-	-
14	0	20	0	19.67	0	0.58
14	0	19	-	-	-	-
15	1	12	-	-	-	-
15	2	13	1.67	12	0.58	1
15	2	11	-	-	-	-
16	1	19	-	-	-	-
16	2	19	1.67	19	0.58	0
16	2	19	-	-	-	-

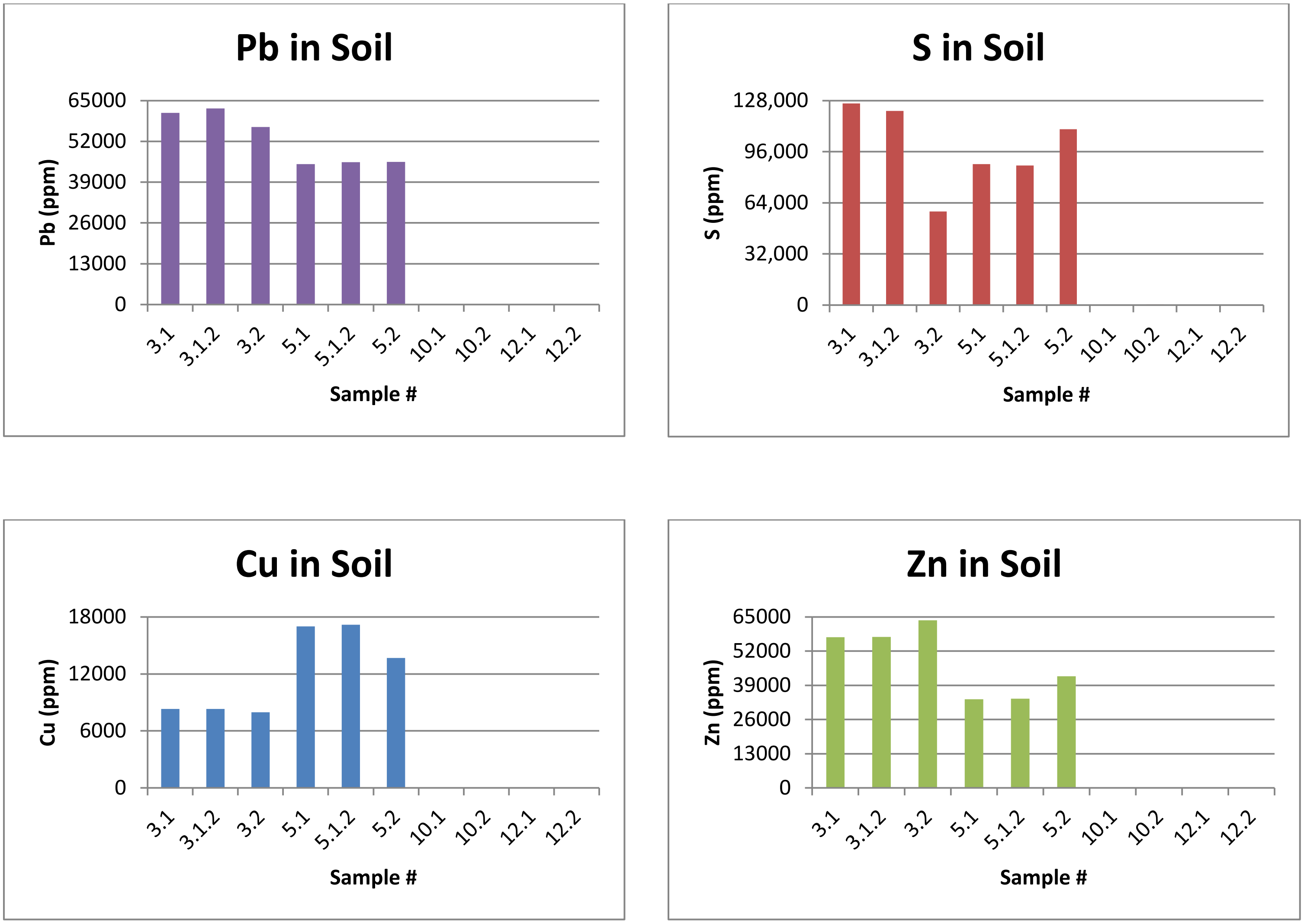


Fig. 4: Side by side comparisons of XRF spectrometer analyzed values of Pb, S, Cu, and Zn for each soil sample site.

Table 4: XRF spectrometer analyzed soil sample results. Values shown in parts per million (ppm) and mass percent (mass %).

Sample #	S (ppm)	S (mass %)	Pb (ppm)	Pb (mass %)	Cu (ppm)	Cu (mass %)	Zn (ppm)	Zn (mass %)
3.1	126,215	12.6215	61,115	6.1115	8,314	0.8214	57,294	5.7294
3.1.2	121,520	12.152	62,458	6.2458	8,300	0.83	57,354	5.7354
3.2	58,583	5.8583	56,609	5.6609	7,965	0.7965	63,722	6.3722
5.1	88,152	8.8152	44,741	4.4741	16,985	1.6985	33,730	3.373
5.1.2	87,363	8.7363	45,402	4.5402	17,184	1.7184	33,938	3.3938
5.2	110,127	11.0127	45,477	4.5477	13,666	1.3666	42,414	4.2414
10.1	373	0.0373	47	0.0047	6	0.0006	69	0.0069
10.2	480	0.048	53	0.0053	10	0.001	74	0.0074
12.1	143	0.0143	114	0.0114	-13	-0.0013	90	0.009
12.2	198	0.0198	120	0.012	15	0.0015	107	0.0107

DISCUSSION

The results of the XRF spectrometer analysis for soil samples supported the hypothesis that samples taken from Blue Hole would have the highest levels of S and heavy metals tested. Samples 10 and 12, taken from River Laune, showed significantly lower values of all tested elements. Cu and S levels in water were very low. These levels were expected because of the ability of Cu and S to dilute in water and be easily transported. It was hypothesized that Cu and S levels would be lower in Lough Leane compared to samples taken at Western Mine and Blue Hole. The analysis negated this hypothesis, showing consistent levels for every sample taken. S had slightly elevated levels when compared to Cu levels in water, but this could be the cause of acid rain, weathering of S- and Cu-rich rocks, or runoff from nearby farms. In regards to the analysis of the water samples, there is little concern for the health and safety of human, animal, and plant life. Levels were not significant enough to cause serious damage to ecosystems and none of these sample sites serve as a drinking water aquafer.

It can be assumed that all elements were found in high amounts in soil because of the inability to dilute as well as the heavy metals' inability to be re-uptaken by plants. These elevated levels are most likely residual of the mining activity that once occurred at these sites and pose a significant concern for the health of plants and animals within the national park. All tested heavy metals lower acidity of the soil, leading to a decline in plant life. As the pH of the soil decreases, mobility of heavy metal ions increases, thus leading to the possibility of more acidic water (Sowinski et al., 2016).

It is always possible for errors to occur when collecting samples as well as conducting lab work. Mis-calibration of the XRF spectrometer proved to be a serious issue while less significant errors could stem from cross contamination of equipment, an inaccurate S XRF application, and poor sample collection techniques.

CONCLUSION

The copper mines at Killarney National Park have existed for several thousands of years. The significant mining activity that occurred came to an end in the late 1800s, and were permanently ceased in 1912.

Irelands' National Parks and Wildlife Service purchased the mining areas and attempted to remediate the land but the residual effects of these mines are still being experienced presently. High levels of S, Cu, Pb, and Zn in soil can lead to extensive soil acidification and deplete the health of local plants. Contaminants in water did not pose a significant threat but mobilization of heavy metals in the soil does have the potential for future water contamination. Remediation of the soil through the use of bioremediation and phytoaccumulators could mitigate the environmental effects of these ancient mines.

Future work at Killarney National Park and Ross Island should include soil cores as a way to support or deny the hypothesis by Sowinski et al. that heavy metal concentrations are highest in the topsoil and decrease as depth increases. More extensive water testing and an in-depth geochemical analysis of the area could help park rangers and environmentalists further improve the park. A collaboration of geologic, botanical, and biologic studies could show the relationship between heavy metals and S in soil and the ecological effects being seen, or could be seen in the future.

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