Environmental Impact of Heavy Metal Composition and Iron Speciation in Soils

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ABSTRACT

It is well known that heavy metals are naturally present in soil, but the soil composition of these metals in differing environments is not fully understood. In addition, significant quantities of iron in soil negatively affects soil restoration and the valence state of iron that is present may be correlated to both soil pH and its ability to breakdown inorganic compounds. In this experiment, x-ray spectroscopy will be used to determine the valence states of iron in soil, which serve as indicators of several environmental factors. X-ray diffraction will be used to investigate the presence and abundance of heavy metals in soil samples from various locations across northern Illinois. The samples will be taken in three subgroups: (1) agricultural vs. non-agricultural, (2) rural vs. suburban vs. urban, and (3) variable distances from a central body of water. A total of 36 soil samples will be collected and analyzed to compare the presence of heavy metals as well as the iron speciation. In addition, soil pH will be measured for each soil environment. Analysis of such samples may reveal trends regarding the effect that soil environments have on the presence of heavy metals and the different valence states of iron that are present.

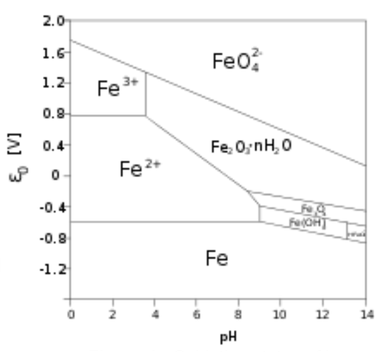


Figure 1. Oxidation states of iron for a range of soil pH values.

MOTIVATION

The accumulation of heavy metals and metalloids--due to emissions from fertilizer, industrial areas, manure, pesticides, wastewater irrigation, and atmospheric deposition--creates soil pollution that contaminates both drinking water and the food chain. This poses major risks to both humans and the ecosystem. The adequate protection and restoration of these polluted soil ecosystems first require their characterization. The study of environmental factors that may facilitate heavy metal accumulation is a part of this research's purpose.

Significant quantities of iron in soil negatively affects soil restoration as flooding-induced iron reduction (Fe^{3+} to Fe^{2+}) causes a disproportionate breakdown of organic matter and a release of inorganic compounds.

Figure 2. This experiment investigates the iron speciation of soils. Iron deficiency in soybean (left), sorghum (middle), and wheat (right) are shown above. While most soils contain adequate Fe for plant nutrition, chemical and environmental factors restrict plant uptake. Iron deficiencies are commonly observed in soils with elevated pH (>7.5). When soils become saturated, Fe^{3+} becomes converted to Fe^{2+} by microbial action. The Fe^{2+} form is much more soluble and can even result in toxicity for some rice varieties in flooded soils under strongly acid conditions.

DATA COLLECTION & EXPERIMENTS

Three sub-experiments were conducted with the purpose of finding differences in composition in various types of soil: Group A compared non-agricultural vs. agricultural soil, Group B compared rural vs. urban vs. suburban soil, and Group D sought to determine if the distance to a body of water affected soil composition. 36 samples (12 per group) were collected. During sample collection, groups recorded the coordinates of the sites where they obtained the soil. The pH level was also recorded for each sample before they were sent to Argonne for experimentation with APS. After a few issues with the on-site machinery, all the sample data were collected using x-ray fluorescence and absorption spectroscopy to investigate the soil composition - more specifically, for the presence of heavy metals and variances in the valence state speciation of iron. The results were compared with the previously measured pH to determine if there was a correlation between them.

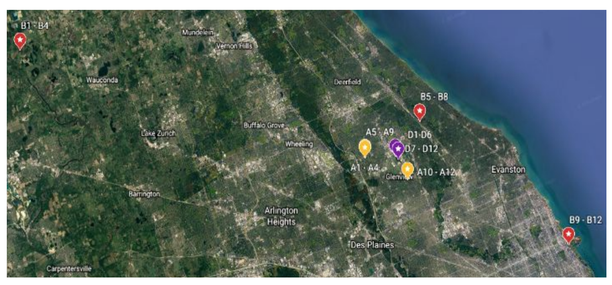
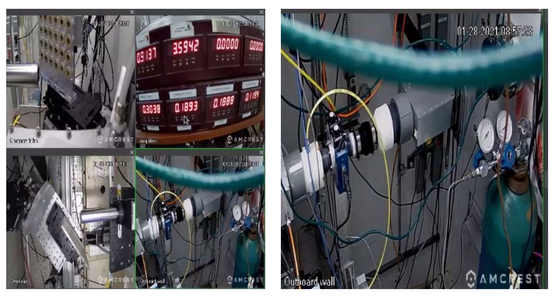


Figure 6. This map displays the locations where each sample was collected. Red is agricultural vs. non-agricultural. Yellow is rural vs. urban vs. suburban. Purple is distance from a body of water.



Figures 3, 4, and 5 (left, right, and below). The remotely run experiment was watched by the ESRP team. These images are from inside the hutch as the experiment was taking place, and Figure 5 displays soil samples in the sample holder.

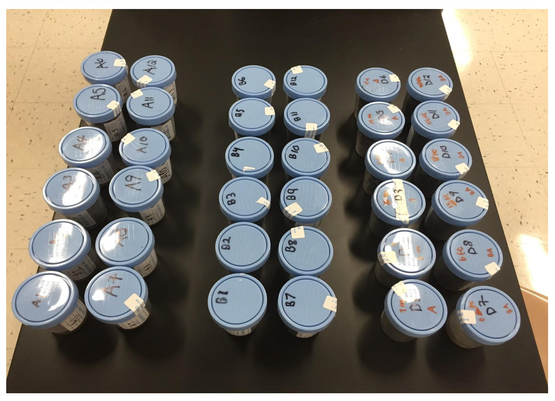


Figure 7. Sample collection cups for 36 soil samples.

RESULTS

There appears to be many similarities between the samples with the biggest differences coming from the amounts of zirconium and copper that are present.

Heavy Metal Composition

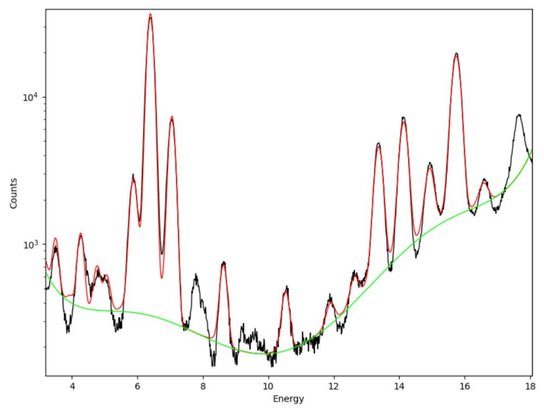


Figure 8. Sample A4 PyMca plot above illustrating energy spectrum (black), fitted metal composition (red), and background (green). Similar plots were made for all samples to determine each soil sample metal composition.

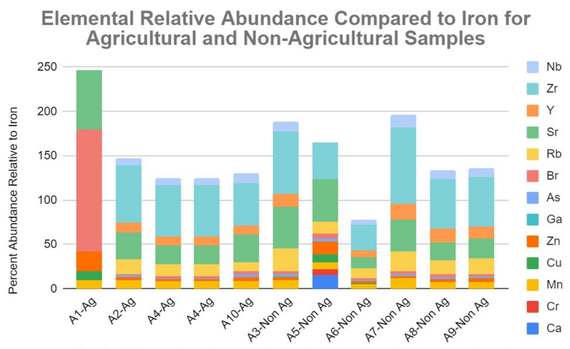


Figure 9. Relative abundance of metals present compared to the soil's iron content was determined for each sample. Shown above is comparison for one study which investigated metal composition for agricultural vs. non-agricultural soils.

There appears to be no correlation between the soil pH and valence state of the iron. This could be due to a high concentration of pure iron in the samples.

Iron Speciation Study

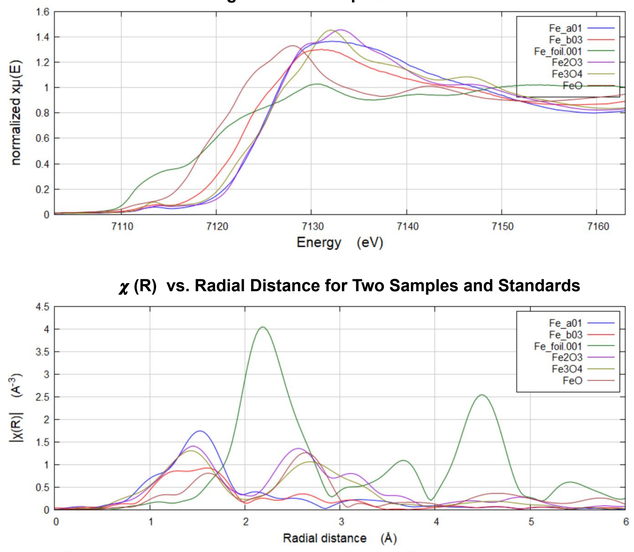


Figure 10. Iron K-edge for samples A1 and B3 compared to common iron compound standards and pure iron in order to determine iron valence state of samples (top). Radial distance to nearest atoms for the same samples illustrates atoms nearest to the sample iron are closer than for pure iron. This was expected since iron atoms that have lost electrons will have nearest neighbor atoms (often oxygen) closer.

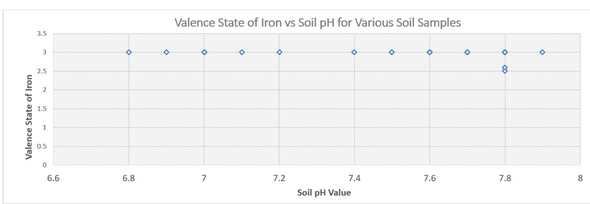


Figure 11. Each sample's iron valence state was determined and plotted as a function the soil's pH. There did not appear to be any significant correlation between valence state and pH for the samples collected in this study.

CONCLUSIONS

The high concentrations of copper present in the various soil samples indicate that the different soils are relatively healthy, given that Cu is a naturally occurring metal that is essential to plant growth. However, the high concentrations of zirconium, though itself also a naturally occurring metal, may indicate unhealthy soil due to the fact that it could cause phototoxicity within plants. In addition to the heavy metal composition in the soils, no noticeable change in the valence states of Fe was observed relative to soil pH. More data may need to be collected in order to make conclusions about the effect of iron speciation on the health of soil.

ACKNOWLEDGEMENTS

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