Proton Induced X-Ray Emission (PIXE) Analysis to Measure Trace Metals in Soil Along the East River in Queens, NY

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Introduction

Heavy trace metals are found naturally on Earth. Even though found naturally, levels of trace metals can become concentrated as a result of human activities. At higher concentration, these metals are highly toxic, and can have severe health effect in the short and long terms. [1] Thus, it is vital to identify and determine the concentration of heavy metals found in our surroundings to understand their origin and monitor their deposition, transport, and uptake.

As an application, my project is to study the presence of heavy trace metals in soil samples along the eastern shoreline of the East River in Queens, NY between Astoria and Gantry State Parks. Being in a metropolitan area, there are various industrial sites, residential homes and parks nearby the shoreline. It is necessary to understand the quality of the soil since children and adults play in the park and people plant gardens at their homes.

PIXE Analysis

In order to identify the specific elements found in soil samples and thus determine their concentration, the non-destructive, highly sensitive, and accurate ion beam analysis (IBA) technique of Proton Induced X-ray Emission Spectroscopy (PIXE) was used. PIXE is the main IBA technique used for elemental analysis of soil and sediments samples in the Union College Ion-Beam Analysis Laboratory (UCIBAL) and thus it is a very useful tool for the study of environmental pollution. This technique provides information on elements ranging from Na to U with high sensitivity.

Figure 1 shows a schematic diagram of the PIXE process. The sample is bombarded with a beam of protons of a few MeV, which knocks an inner shell electron out of an atom and an x-ray is emitted characteristic to the atom as the vacancy is filled by an outer shell electron.[2] The energies of the x-rays are characteristic of the elements in the sample, allowing us to determine the elemental concentration of our sample. The concentration C_z of an element Z present in the sample is given by

$$C_z = \frac{Y_z}{Y_t \cdot H \cdot Q \cdot \varepsilon \cdot T} \quad (1)$$

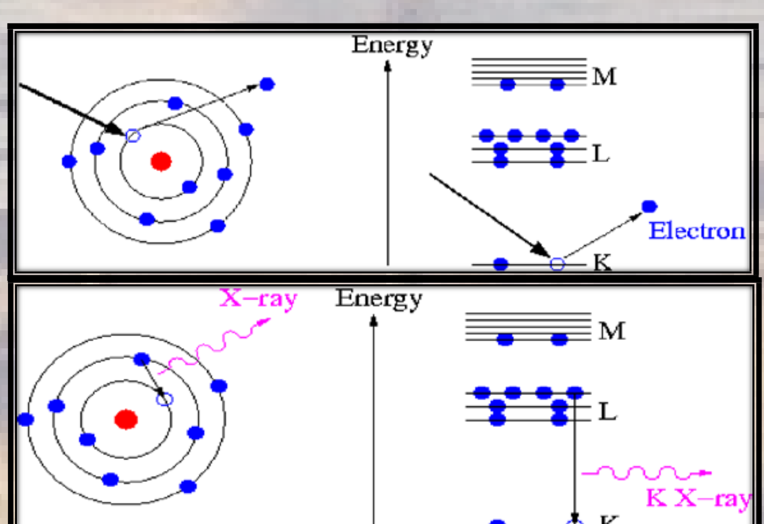

Figure 1: A schematic of the PIXE process. In the upper left, an incident proton ejects the inner shell electron. In the right, an outer-shell electron will de-excite as shown in the lower left panel, emitting an x-ray. The upper and lower right panels show an energy level diagram of the PIXE process

Where Y_z is the intensity of the principle X-ray line for element Z, Y_t is the theoretical intensity per micro coulomb of charge, H is an experimental constant determined by running on a set of standards, Q is the measured beam charge incident on the sample, ε is the efficiency of the detector, T is the transmission through any filters or absorbers between the target and detector.

Experiment

The PIXE experiments were performed in the UCIBAL using our 1.1 MV tandem Pelletron accelerator as shown in Figure 2. First, we performed PIXE analysis on 6.3µm thin target standards of Ti, Fe, Cu, Ge, Au, and Pb to determine several experimental parameters required to determine elemental concentrations in thick target soil samples using eqn 1. From fitting the x-ray energy spectra on standards, experimental values of H and T can be determined, where T is the thickness of the aluminum absorber placed in front of the detector. The values used in eqn.1 for H and T are $(1.92 \pm 0.02)x10^3$ sr and (79 ±3) µm respectively.

Ten soil samples were collected from the shoreline along the East River in Queens, NY as shown in Figure 3. The samples were dried and sifted into a fine powder. Then, about 1.4 ml of polyvinyl alcohol (PVA) was added to approximately 0.5g of powered soil. A hydraulic press applied pressure of about 5000 psi to turn the fine powder into 4-5 mm thick solid pallet as shown in Figure 4. A 2.2 MeV proton beam was produced and subsequently bombarded the target for ten minutes. The charge was integrated for five min through the hole as shown in Figure 4. We repeated the process three times and doubled the charge to find Q needed in eqn 1.

Furthermore, we used the PIXE method to analyze certified NIST [5] soil standards (Montana2710a and NYNJ 1944.) We used the NIST standards to determine the accuracy of our experimental results for the thick target soil samples.

Figure 2: A photograph of the UCIBAL's 1.1 MV tandem electrostatic accelerator showing the main components. The protons are generated in the Source and accelerated trough the accelerator tank to an final energy of 2.2 MeV. They are focused and steered toward the target using the Quadrupole and Steering magnets respectively.

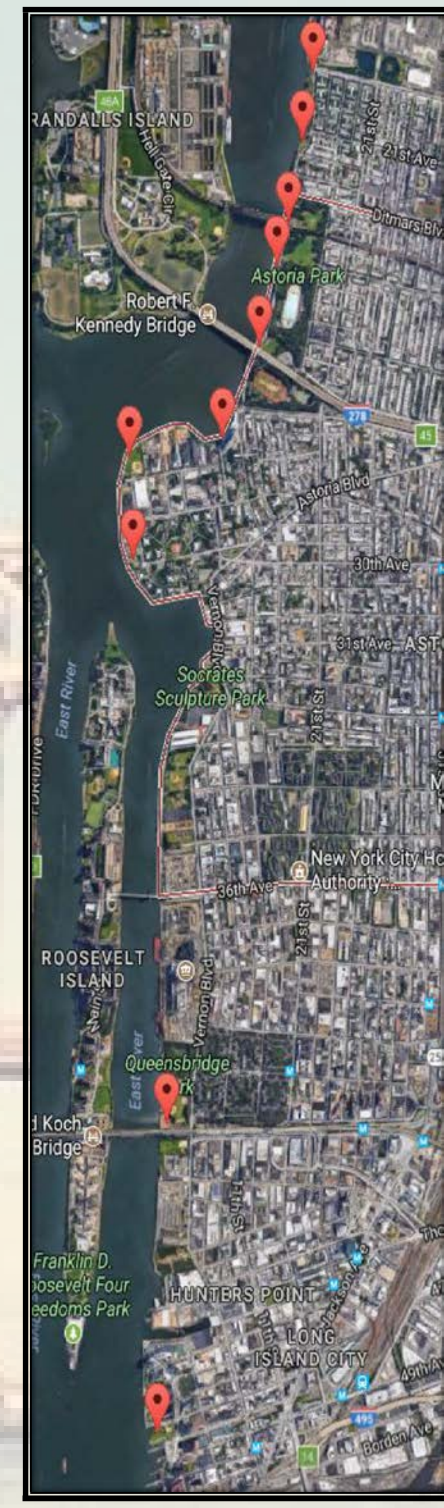

Figure 3: Google Map [4] showing the ten different sampling locations between Astoria and Gantry State Parks.

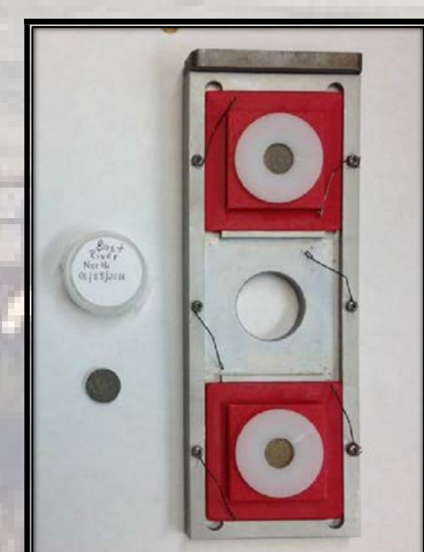

Figure 4: A photograph showing a compressed soil pellet on the left which was collected under the Hell Gate Bridge in Astoria Park. On the right, the target ladder assembly showing two mounted soil pellets in holders and a hole through which charge can be collected.

Preliminary Results

Selected results are shown in Figures 5-8. Figure 5 shows the x-ray energy spectra of the intensity versus energy (in keV) for the Hell Gate Bridge in Astoria Park, Gantry State Park, and the NIST Montana 2710a soil standard. The x-ray spectra are fit with GUPIX [3] to determine the elemental composition and concentrations of the elements. The results show the presence of metals ranging from Ti to Pb with the concentration of Pb in Astoria Park (1600 ± 200 ppm) approximately ten times that of Gantry State Park.

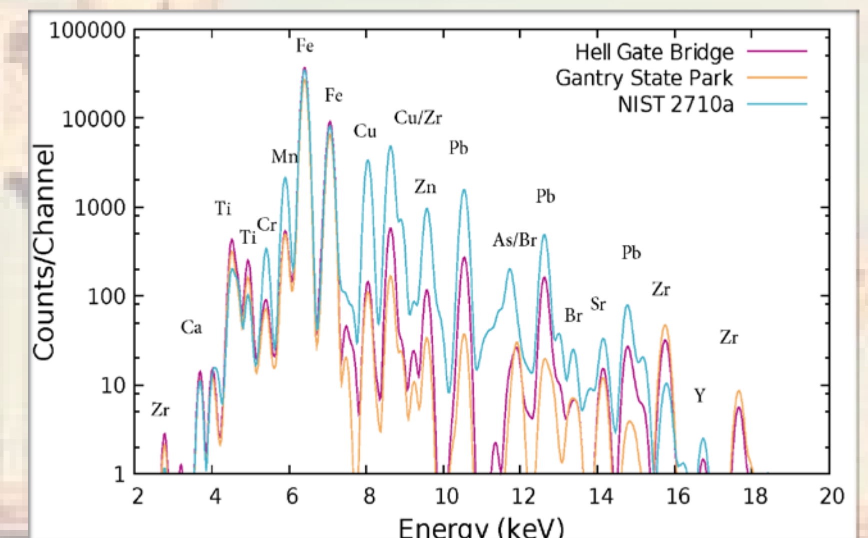

Figure 5: X-ray energy spectra of the intensity versus energy in keV for the Hell Gate Bridge in Astoria Park, Gantry State Park, and NIST Montana 2710a standard. We can see that the concentration of Pb in Astoria Park (1600 ± 200 ppm) is approximately ten times that of the Gantry State Park.

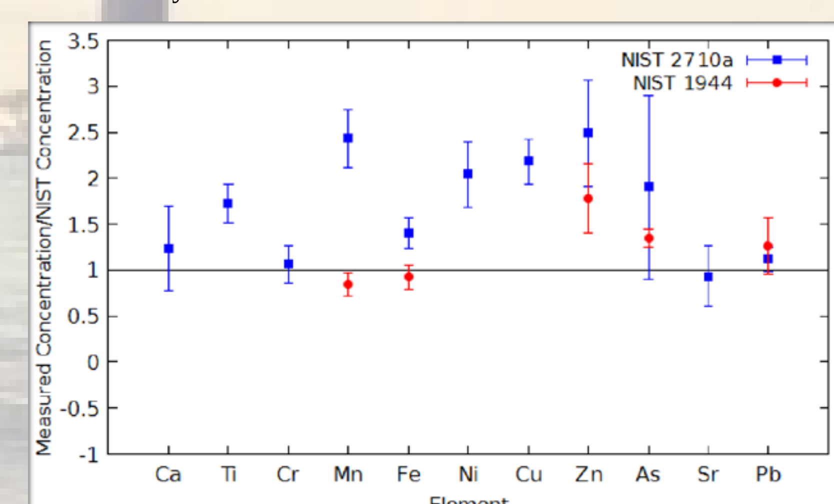

Figure 6: A plot comparing the measured GUPIX concentrations for the two NIST standards to the concentrations reported by NIST. These values are close to 1 suggesting that we can use the concentration generated by GUPIX in ppm.

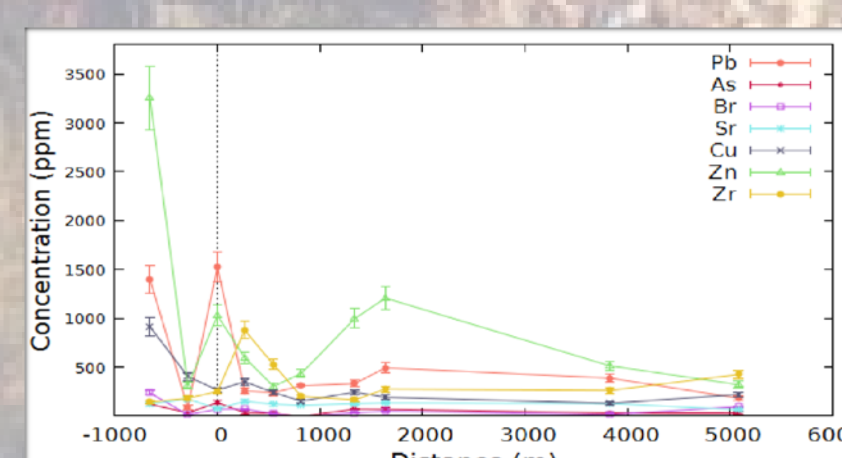

Figure 7: A plot of the distribution of metals heavier than Fe as a function of their distance from the Hell Gate Bridge. The positive numbers being distances south of the bridge and negative numbers the distances north of the bridge.

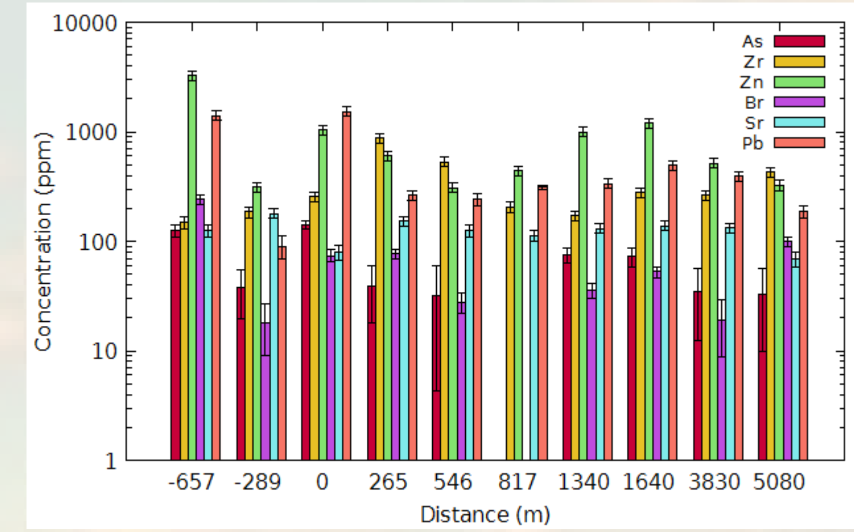

Figure 8: A bar graph of the concentrations of elements heavier than Fe as a function of distance from the Hell Gate Bridge. The sign convention used here is the same as in Figure 7.

Preliminary Results

Figure 6 is a plot comparing the measured GUPIX concentrations for the two NIST standards (Montana 2710a and NYNJ 1944) to the concentrations reported by NIST. This graph suggests that since these values are close to 1 for most elements that we can use the concentration generated by GUPIX in ppm as a good indicator of the concentration of element Z in the soil.

Our results from Figure 5 suggest that the higher concentration of lead at Astoria Park is due to repainting and sandblasting the original lead based paint on the Hell Gate Bridge as shown in Figure 7.

Figure 7 is a plot of the distribution of metals heavier than Fe as a function of their distance from the Hell Gate Bridge. We notice that the concentration of Pb decreases rapidly within a 500 m radius from the bridge and remains relatively constant. From the north of the bridge, the concentration of Pb is increasing. Thus, the source of lead is not only the repainting of the Hell Gate Bridge but there must be some unknown source farther north. To show this we need to gather more soil samples in smaller distance intervals within the 500m radius.

Figure 8 is a bar graph showing the concentration of metals heavier then Fe as a function of distance from the bridge. We see that in addition to Pb the concentrations of As and Zn are also higher near the bridge and decrease with increasing distance from the bridge. To determine the origin of the As and Zn more samples must be collected near the bridge.

References

1 "Water Treatment Solutions." Heavy Metals. Lenntech BV, n.d. Web. 18 July 2016.
2 S.A.E. Johanson, J.L. Campbell, and K.G. Malmquist, "Particle-Induced X-Ray Emission Spectrometry (PIXE)," Wiley, New York (1995)
3 GUPIX, University of Guelph. 2005.
4 Google Maps. https://www.google.com/maps/place/Astoria,+Queens,+NY/@40.7730304,-73.9367801,16z/ data=!4m5!3m4!1s0x89c25f36e7b5a553:0x9c0aafc4ac84110e!8m2!3d40.7643574!4d-73.9234619
5 Material Measurement Laboratory Standard Reference Materials." NIST -SRM Order Request System SRM 2710a - Montana I Soil.

Acknowledgement

I would like to thank my advisors Scott LaBrake and Mike Vineyard as well as my lab partners Skye Conlan and Zach Porat. Also I'd like to thank the Union College Department of Physics and Astronomy and the Davenport Fellowship for financial support.