

Errata

Physics and Biology

Trace Element Analysis of Heavy Metals in Perdido Bay, Florida

Sponsoring Faculty Members: Dr. Terry Austin (Physics) and Randy Colvin (Biology)

Robert Tobias (Physics) and Taylor Ray (Biology)

Introduction

The purpose of this experiment is to determine the presence of heavy metals that remains within the Gulf Coast marsh areas as a result of the British Petroleum oil spill. Core samples were acquired at multiple points along the coast before the accident. Samples were then acquired in the March of 2012 from the same coordinates, located using a GPS device. After being dried, these samples were taken to the University of Auburn Physics department for Proton-Induced X-ray Emission (PIXE) analysis using the department's Van de Graaf Pelletron linear accelerator. The accelerator uses a proton beam that collided with the samples to emit x-rays. These x-rays were then graphed as data and compared to known values to determine composition of the samples and compared to controls from before the spill at the same location. This was done to determine if any additional heavy metals were deposited into the sand as a result of the oil spill. Metals found in decrease quantities included vanadium, chromium, and silicon.

History of the PIXE Apparatus

PIXE stands for Particle-Induced X-ray Emissions which is used as a form of spectroscopy by bombarding a sample with charged particles to eject an electron. In order to return to the ground state, electrons cascade down in energy, releasing this energy in the form of an x-ray. In the early 1920's, a Swedish geologist named Hadding at the University of Lund used a low energy beam to determine the presence of some metals in a sample using x-ray spectrometry but without the ability to determine how much of each element was present [1]. In 1950, Castaing from the University of Paris used an electron microscope to bombard samples to release x-rays for a modified Geiger counter as a detector, proving that it could be used for elemental analysis [2]. In the early 1960's, a group of scientist from Livermore used 100keV protons to produce x-ray emission, but the detector lacked the resolution to identify different metals within the same sample [1].

The rise of the modern PIXE apparatus coincided with improved technology. In the later portion of the 1960's, the lithium-drifted silicon detector, or the Si(Li) detector, was first used to find high resolution differences with as low as 150 eV [1]. As the years progressed, physicists also gained greater access to higher energy accelerators [2]. The first modern PIXE device was developed in 1970 when Johansson and his fellow scientists at the Lund Institute of Technology combined a 2 MeV proton beam and a Si(Li) detector to perform a multielemental analysis of trace elements in a sample of carbon foil used to collect small amounts of air pollution [1]. The modern device works on similar principles, requiring a constant particle beam produced by an accelerator to promote electrons, a detector to determine the energies of the x-rays released from Auger electron ejection and some form of output system, usually a computer recording the data live.

Basic Concepts of PIXE

PIXE usually uses a beam of protons as the charged particles produced in the accelerator to reduce background readings in the detector which are much more prevalent with electrons [2]. The proton beam collides with the sample, interacting with the inner shells of electrons and ejecting an electron [1]. This missing electron causes instability in the atom followed by an outer electron cascading to a lower energy state to fill the "hole" in the lower shell, releasing energy in the form of an x-ray [3]. The energy released in this x-ray can be calculated by subtracting the energy of the inner shell electron from the energy of the outer shell electron [3]. These x-rays are unique to the element and can be used to determine which elements are present by using a chart such as appendix 1 [3]. While this process does not analyze every atom in the sample, it does analyze a majority and it is assumed the sample is well mixed representative sample of the whole [1]. This data can then be compared using computer software. To remove support the samples, the samples were placed between a layer of filter paper and aluminized mylar. The purpose of the aluminized mylar is to prevent an increase in charge within the sample which would result in the creating of a sparking electrical discharge. Such a spark would register with the detector as a false positive. The results in this experiment are only compared to one another to determine an increased presence of an element and not to determine the exact amount of an element in the sample. In other words, all the spectra contain aluminized mylar and filter paper so any readings created by the mylar and filter paper can be considered part of the background readings.

Characteristic X-Rays

PIXE detects the characteristic x-rays emitted when a higher energy electron enters a lower energy shell to stabilize the atom [1]. X-rays are designated after the shell from which the electron that is losing energy originated K, L, M or

N [3]. If an electron leaves the K shell, an electron from the L or M shell will replace it which are designated as either alpha or beta respectively, α and β in the figures found in the appendices [3]. Each shell contains multiple orbitals, which are designated as 1 or 2 after the designation for the shell [3]. Although multiple other x-rays could be examined from the different state changes, this experiment only studied $K\alpha_1$, $K\beta_1$, $L\alpha_1$, and $L\beta_1$ emissions.

Some electrostatic interactions do not emit x-rays because the inner electron that is excited interacts with an outer shell electron and transfers all of the additional energy to the outer electron [3]. This process causes this outer Auger electron to be ejected from the shell instead and not be replaced [3]. This interaction is much rarer than the emission of an x-ray but does occur.

The Experiment

The purpose of this experiment is to determine what, if any, elements have increased in presence in the sand of Perdido Bay after the BP oil spill. Shortly before the oil reached the bay, sand samples were taken from Bayou St. John, Orange Beach Park, Perdido Pass, North Bear Point and South Bear Point by Auburn University. In the spring of 2012, samples were taken from the same locations by LaGrange College. Also, biological samples were taken from Bayou St. John and Bear Point South. All inorganic samples were dried in an oven before the experiment.

The samples were taken to the University of Auburn Physics Department where the Van de Graaff Pelletron linear accelerator was used to create a two mega-electron volt (2MeV) proton beam. The detector used in this experiment was manufactured by Amptek, Inc. (Bedford Massachusetts). The model X-123 x-ray detector's serial number is X010228. For maximum collection efficiency, the axis of the detector was oriented approximately 45° relative to the surface of the samples. The samples were then introduced to the beam and exposed for five minutes. Samples of pure indium and pure copper were used as calibration samples to establish x-ray energy emitted as a function of detected channel number prior to the experiment. Amptek software "XRF Spectra and Analysis Software" was used to both collect and analyze the data.

The peaks of these spectra were compared using software to determine the values yielded and an increase in peak height to determine an increase or decrease in presence. Peaks for multiple values of the same element were used to ensure the accuracy of this experiment. The before and after spectra of each location were compared against each other only in order to determine changes in concentration of elements and not against each other in case the soil content of each area was polluted before sampling. Due to how broad some peaks were, however,

it is possible that some elements are present within the samples and were not detected due to the large concentration of the elements that were detected. To yield more accurate results, further studies need to be done using software that is capable of providing clear data.

The experiment showed a few different elemental increases by location, but the general trend was a decrease in presence. Elements with greatly increased or decreased presence in at least one location included S, Al, V, Si, Cr, K, Ca, Cl and Fe. Of these elements, Al, V and Cr are both dangerous and found in crude oil. In one location there was a significant decrease in Ti, but the initial presence may have been from run-off of titanium dioxide containing white paint from nearby homes. No one element was consistently greater after the oil spill.

Results

From the PIXE analysis these results were gathered. On average, at each sample site, the metals remained at the same level or slightly decreased. Some of the more toxic elements that were found in all five sample sites included Aluminum (Al), Silicon (Si), Sulfur (S), Titanium (Ti), Chromium (Cr) and Vanadium (V). The most significant spike we analyzed was a sharp decrease in the presence of Ti at Bear Point South after the oil spillage. There were in addition to decreases in Ti decreases in Al and S at the locations Perdido Pass, Orange Beach Park, Bayou St. John, and Bear Point South. There was addition elements that were detected Arsenic and Cobalt; however their amounts were not significant enough to warrant labeling on the PIXE analysis.

Our data supports the theory that the concentration of heavy metals and trace elements found in crude oil have not accumulated in the costal environments of the Gulf Coast. There seems to be support that some toxic elements were actually removed from the environment upon the oil spillage. It appears that the clean-up was a consistence project throughout the locations that sampling occurred.

Heavy Metals and Trace Elements that were found in our samples that posses treacherous effects to species within the ecosystems

There have been countless times throughout history where oil has crippled environments. Heavy metals have a detrimental effect on environments, and their inhabitants. These heavy metals accumulate, and the dosage increases as they progress through the trophic levels through terms bioaccumulation and biomagnification. Bioaccumulation is defined as, "the accumulation of contaminants by species in concentrations that are orders of magnitude higher than in the surrounding environment"[7]. One definition of biomagnifications is, "an increase

in the concentration of a chemically stable substance along a food-chain”[7] Three of many heavy metal toxicants that can be found in oil are Pd, Al, Cr along with several trace elements that can be toxic such as V, Co, and As. There are several reasons for why metals affect environments, particularly aquatic environment so violently. Metals can be found in water as *free metal ion*, combining with chloride or a variety of other anions to form *ion pairs*. Furthermore, the toxicity of these metals on the environments involves how many different species of the same metal can vary greatly in toxicity [7]. The following paragraphs are the elements and the various affect they can have on different organisms at various stages of the ecosystem.

The heavy metal Cr can accrue multiple toxic effects on the environment. These effects include changes in the growth of roots, stems, and leaves, photosynthesis, water relation, and mineral nutrition [9]. The toxic effects that Cr can cause on upper trophic level consumers (mainly mammals) include inhibition of glucose reabsorption as a result of damage to the convoluted proximal tubule [7]. This can decrease the life span of any organism that this occurs in.

The prime impacts Al toxicity can have on plants is the inhibition to grow roots, with the full extent of Al toxicity occurs in highly acidic soils. This root stun transpires through the initial uptake from the root cap and the mucilaginous secretion covering the epidermal cells. Al is also known to cause morphological damages, an example being its affect on photosynthesis by lowering the chlorophyll and decreasing the electron flow [13]. DNA binding and nuclei binding has been seen from Al although penetration of the mitotically is slow. As Al moves up the food chain it decreases the absorption of other elements in the gastrointestinal tract and can alter intestinal function. Al is known too as being a neuro toxicant, by producing accumulation of neurofibrillary tangles in the cell body, proximal axons and dendrites of neurons in many brain regions [10].

Trace elements that can be found in oil also have the potential to be potent to environments as well. Three of these elements that appear frequently in oil are V, Co, and As. Toxic effects that V can cause include decreases in stem length, number of leaves, and the total number of roots and stems. V has been shown to impersonate insulin in *in vitro* and *in vivo*. The major predicament with V is the multiple forms in which it can be in the environment; it can be either the organic compounds or the much more dangerous inorganic salt form. Side effects of this compound can be gastrointestinal discomfort and reduced body weight gain, along with severe damage to the liver and kidneys [8].

Since Co is a transition element it is a key factor in several enzymes and co-enzymes [11]. Two areas that are affected significantly by Co in plants are starch grain differentiation, and both the structure and number of chloroplasts in an area

of a leaf. In mammals, Co becomes a reproductive toxicant, that can harmfully affect spermatogenesis and accessory to sex organs function [10].

As toxicity relies heavily on the form it has in the soil, and the concentration of the metalloid. Due to how chemically similar it is to phosphorus, As is able to replace phosphorus, notably within the phosphate group on DNA molecules. Through this imitation As is able to disrupt many cellular functions involving growth. As is neurotoxicity that principally begins sensory changes, paresthesia, and muscle tenderness. Toxic effects can progress to hepatic parenchymal cells, which in turn ascend liver enzymes in the blood. There is data to suggest that damage occurs to granules and the ultrastructure of mitochondria due to the loss of glycogen. There is also substantial data to support that As has the ability to produce chromosome breaks and chromosome aberrations in DNA [10].

Silicon is bountiful within costal environment due to the fact that it is found in sand. Silicon is not by itself a very toxic element though Si has the suggested ability to raise the pH of soils, thus dwindling the affects of other toxic elements found in crude oil. Si in its elemental form does not pose any threats to many species, though in other forms it can become a serious immune toxicant [10].

Sulfur was also analyzed in our data, and although S has the ability to become toxic to organisms in ecosystem by forming into sulfur oxides. Pulmonary irritant by way of increasing airway resistance has been documented in mammals in exposure levels as low as 5 ppm of sulfur dioxide. S also has the capability of reacting with hydroxyl radicals in the environment to produce sulfuric acids, which are major components in what is known as acid rain [7]. These toxic effects require momentous amounts of S in the environment more than was detected by our analysis, so it was not one of the major elements of concern to the experiment.

Discussion

There is no reason to assume that the ecosystems that occupy that samples were gathered are not in serious danger. Many of these elements as they biomagnify up the trophic levels become more potent to the organisms they come into contact with. Not only are these elements dangerous by themselves, but in some cases can combine with other elements to become even more toxic. As the bioavailability grows with respect to each individual element amplifying presence of each element up the food chain will increase.

In recent studies done on the retention of heavy metals in maze contaminated with crude oil, when the seeds were gathered from the maze there was a significantly higher amount of heavy metals found in them when compared to the seeds that were grown in the uncontaminated soil. There is further data to suggest

that the elements that compose oil act it a either synergistic or antagonistic reactions to prevent the uptake of vital minerals for plants [4].

The affect that these elements could have on the coastal environments of the Gulf untouched could be monumental. As these elements bioaccumulate in the environments there is no valid danger to the producers and primary consumers in the ecosystems. As biomagnification occurs there is an increase contraction of these metals amassing in the predacious organisms, putting a severe strain on the population of these species.

To significantly reduce the population of these top predators in these fragile environments would have major impacts on the various trophic levels that previously followed. Many of these elements affect in superior organisms their reproductive potential as well as their overall life cycle. Clearly if there is a accelerating rate of morality among a species, and the remainder of those species are having difficulty breeding there will be a decrease of this species in the presence of lower trophic levels. From the decrease presence in the lower trophic level there will be an increase in the populations of the primary consumers, creating a massive anxiety to fall upon the primary producers. If too many primary producers leave or are killed there would be a major shift in the energy flow through the ecosystem, with the possibility that the entire ecosystem can collapse from starvation of the various communities within.

Conclusion

The data from this experiment suggests that there are no significant increases in any of the heavy metals or trace elements from oil within the area. At some samples sights there was actually a decrease in the presences of these elements. Not discussed in the section covering the elements we found in our samples was Ti (Titanium), due to its mostly non-toxic effects on the environment. The interesting fact surrounding Ti in our experiment is that out of all the elements that were seen Ti had the largest variation among the before and after samples. One possible explanation for this which has been theorized, but not experimented on could be the possibility that crude oil possess the ability known as chelate. The definition of chelate is "The formation or presence of bonds (or other attractive interactions) between two or more separate binding sites within the same ligand and a single central atom" [8]. Our data suggests that not only were the toxic elements in the crude oil liberate into the environment, the already existing elements could have been confiscated by the crude oil as well.

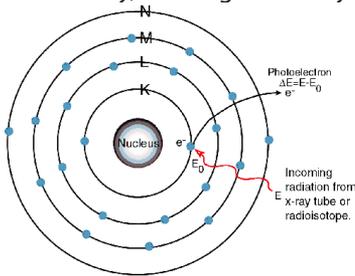
The lack of these elements advocates that the clean-up that BP did along the Gulf Coast was remarkable. The data indicates that as of this moment the costal environments are in no serious threat from any of the elements we tested

for. We should not overlook the amount of energy and time that went into the clean-up of this oil spillage, nor the potential that is there for severe health risks. However, as much as we humans want to distance ourselves from the environment, it only takes some exceptionally small particles to remind us how close we are to what is around us.

Appendix 1

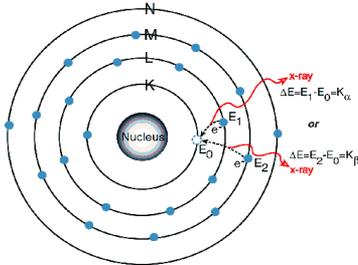
X-Ray Fluorescence Process Example: Titanium Atom (Ti=22)

1) An electron in the K shell is ejected from the atom by an external primary excitation x-ray, creating a vacancy.



The K Lines

2) An electron from the L or M shell “jumps in” to fill the vacancy. In the process, it emits a characteristic x-ray unique to this element and in turn, produces a vacancy in the L or M shell.

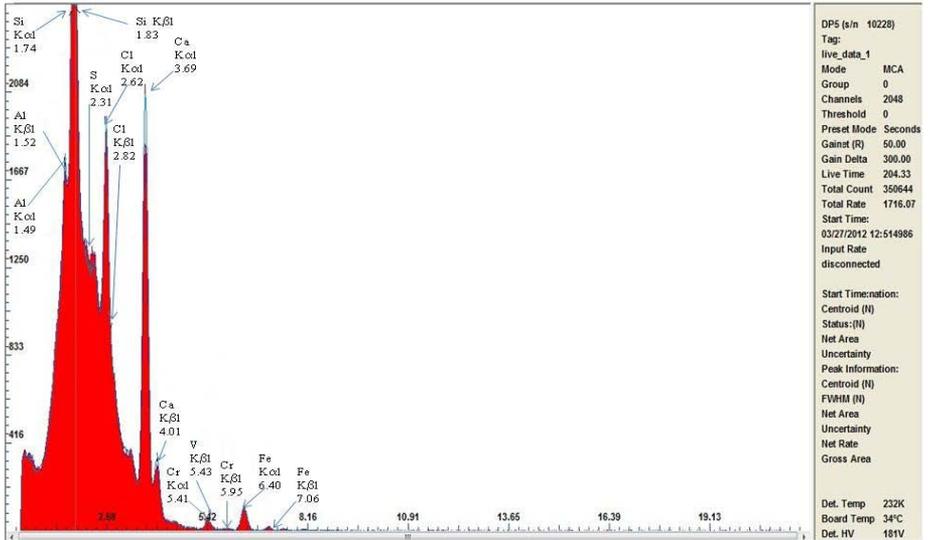


The L Lines

3) When a vacancy is created in the L shell by either the primary excitation x-ray or by the previous event, an electron from the M or N shell “jumps in” to occupy the vacancy. In this process, it emits a characteristic x-ray unique to this element and in turn, produces a vacancy in the M or N shell.

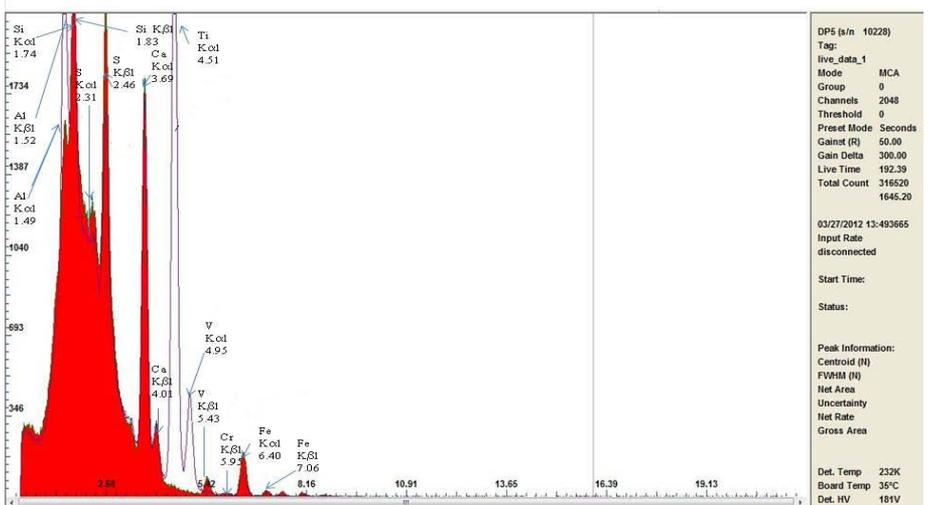
Appendix 3

Bear Point North before oil spill (outlined) and after clean up effort (red)



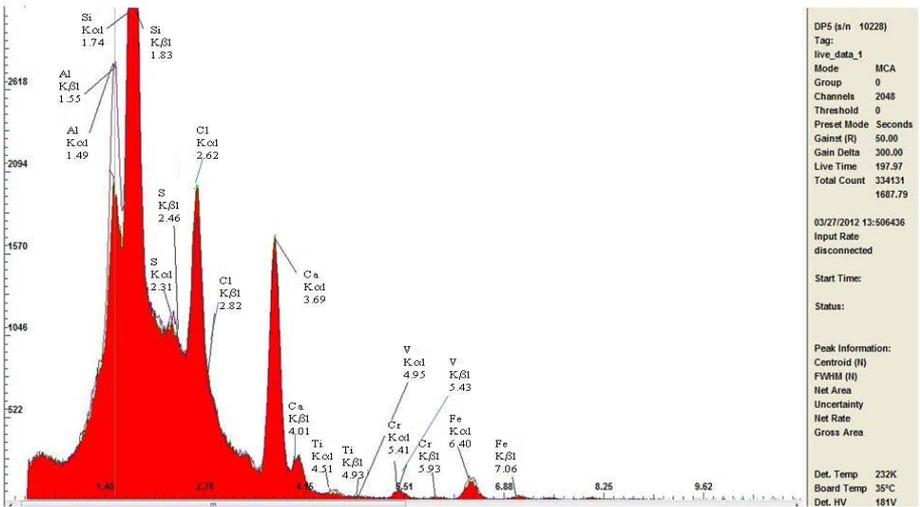
Appendix 4

Bear Point South before spill(outlined) and after clean-up efforts(red)



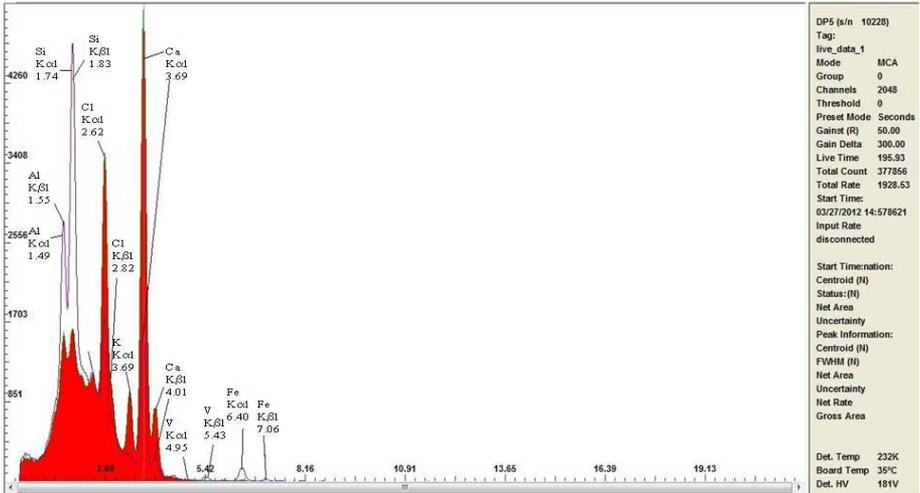
Appendix 5

Orange Beach Park before oil spill (outlined) and after clean up efforts (red)



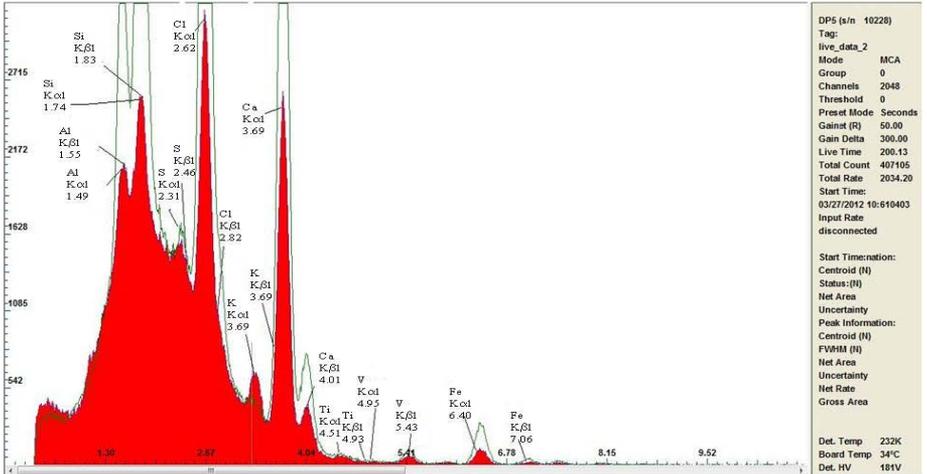
Appendix 6

A plant from St. John(Hodson Marina, red) and a fish from Bear Point South (outlined)



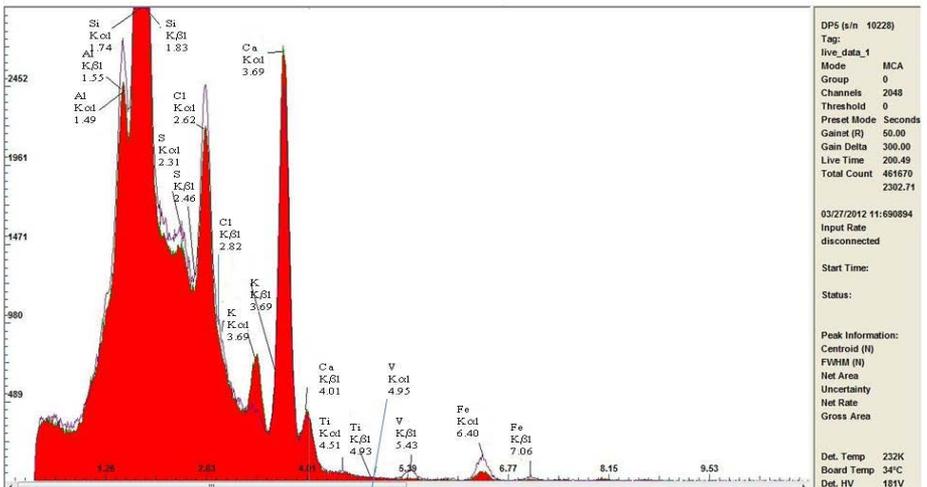
Appendix 7

Perdido Pass before the oil spill (outline) and after cleaning effort (red)



Appendix 8

Bayou St. John before the oil spill (outlined) and after cleaning efforts (red)



Work Cited

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