Coal Railway Heavy Metal Contamination

By

Lauren Joyal

An Honors Project submitted to the University of Indianapolis Strain Honors College in partial fulfillment of the requirements for a Baccalaureate degree "with distinction." Written under the direction of Dr. Levi Mielke.

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Approved by:

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Dr. Levi Mielke, Faculty Advisor

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Dr. James B. Williams, Interim Executive Director, Strain Honors College

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First Reader

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Second Reader

Abstract

The Harding Street Generation Station near downtown Indianapolis is a coal-powered energy plant that could have adverse effects on the surrounding air and soil resulting from coal dust and ash. In particular, properties adjacent to the plant, such as the sampling site, could be at high risk for contamination. Dr. Mielke and I had concerns about possibly dangerous levels of heavy metals such as chromium, lead, or arsenic in soil, root, and plants. To determine the levels of heavy metals, soil, root, and plant body samples were taken in transects to quantify heavy metals and determine if these could be considered toxic. Soils were expected to have higher levels of heavy metals, while the roots of the plants, as well as the bodies, were expected to absorb a portion of the heavy metals from the soil and contain them for evaluation. Transects were predicted to contain higher concentrations of metals closest to the railroad carrying coal into the power plant, decreasing in concentration with distance. Heavy metals were examined by measuring their fluorescence using microwave-plasma atomic emission spectrometry after their digestion in strong acids as per the EPA Method 3050B. The analysis demonstrated no metals exceeding regulatory limits set by the EPA. In addition, samples did not have decreasing quantities moving away from the railroad track. Although, soil presented with the largest concentration of metals, followed by roots, and lastly, plant bodies.

Acknowledgment

List of Tables

List of Figures

Table of Contents

Statement of Purpose

Indiana is among the top 10 coal production states in the US, making it susceptible to large amounts of pollution (Nunez). As a state invested in the burning of coal, many local railroads, such as at the railroad leading into the coal-powered Harding Street Generation Station owned by the Indianapolis Power & Light company, transport large amounts of coal in order to generate power. The power plant itself releases large amounts of chemical wastes, which in 2010 totaled 1,499,059 pounds of on-site releases (Facility Report). The majority of these releases were via the air, followed by water, and lastly by land (Detail Facility Report).The railcars that transport the coal are often uncovered and leave behind coal dust along their routes as well as whole pieces of bituminous coal. The United States Department of Labor defines coal dust as "dust from the extraction or mining of coal" (United States Department). Coal dust and droppings from railcars can pollute local soils and waterway systems through leaching of heavy metals. According to the EPA (Environmental Protection Agency), heavy metals are "metallic elements with high atomic weights such as, mercury, chromium, cadmium, arsenic, and lead" that do not decompose or bioaccumulate, which even at low levels can damage living things, causing health concerns (Glossary). Soil health is an essential component of an ecosystem. It provides nutrients for plants, which then can provide shelter for other organisms in the ecosystem. It is also a natural filter that cleans water before it enters local waterways and aquifers. If soil is contaminated with heavy metals it can inhibit plant growth within the soil, which will lead to a reduction in natural wildlife in the area.

Heavy metals present in soil can also be a risk to human health. Because of this, the EPA has set standards for heavy metal soil contaminants such as lead, mercury, and arsenic, which are common products of coal combustion. These standards pinpoint the limit of acceptable amounts of heavy metals in soil, which if exceeded, begin to cause symptoms of heavy metal exposure.

The purpose of this study was to determine the amount of contamination taking place along the small section of railroad to the east of the Harding Street Generation Station in order to assess the extent of environmental damage. Figure 2 provides a photo of the section of railroad examined in this study. This study contributes to the current knowledge base on pre-combusted coal and how, or if, it leaches heavy metals into the surrounding environment. It adds to the limited amount of current research on coal dust that is emitted from railcars as they travel. Many studies investigating the contaminants produced from the combustion of coal are available; however, there is little research on the effects of coal dust originating from transportation. Also, the given effects of bituminous coal left on top of soil for an extended period have not been studied thoroughly. Coal dust and bituminous coal components were evaluated in order to assess their potential or possible current damage to the soil and plant life adjacent to the railroad tracks. My research was one of the first studies to assess the danger of transporting freshly mined coal by rail.

The research conducted contributed significantly to my skillset as an environmental science major. Previously acquired skills from my chemistry and biology background were tapped so that I could gain in-field experience with experimentation.

The study facilitated my independent research, with the aid of my research advisor, Dr. Levi Mielke. It improved my research abilities and prepared me for future studies that I hope to conduct.

Introduction

Components of Coal

Coal is a fossil fuel commonly used for energy production because of its low cost and availability. Overconsumption of coal leads to environmental damage from the mining site to the coal plant. At coal power plants, toxins, particularly heavy metals are leached into surrounding areas, polluting local air, waterways, and soil. The type of chemicals that are left behind through coal transportation and combustion are solely dependent upon the type of coal and the minerals within it. However, all coals have the same basic mineral compositions with a slight variation. Coals are mainly composed of carbon (60-95%), followed by hydrogen, oxygen, sulfur, nitrogen, organic minerals, and water (Coal).

In a study by primary researcher, Liu Guijan in the Yanzhou mining district of China, samples were taken from a local mine as well as fly ash (ash less than 100 micrometers), bottom ash (ash greater than 100 micrometers from the scrubber), and raw coal from the power plant. The chemical analysis of the sources concluded that coal ash from this region is primarily composed of SiO_2 and AlO_2 with minor amounts of FeO_2, MgO, and MnO, along with other compounds. However, it is shown that when fly ash and bottom ash are compared to raw coal, there are elevated levels of heavy metals and

harmful elements present in fly ash and bottom ash. This hints towards the "redistribution of these elements during coal combustion" that may cause them to concentrate in ash (Liu 363). The study shows that raw coal has trace amounts of thorium, vanadium, chlorine, arsenic, fluorine, lead, copper, and zinc (Liu 359-366). This indicates that coal has varying amounts of heavy metals along with other elements that are potentially harmful to ecosystems. It also confirms that raw coal does not have as many damaging chemicals and compounds as fly ash or bottom ash when burned as a result of the chemical structure of coal metamorphosing into a more toxic form during combustion.

A similar study in which samples were taken from coal ash ponds at a coal power plant was conducted in Delhi, India. The samples were collected from fly ash produced at the plant and from groundwater near the power plant and tested for chromium, nickel, and zinc (Singh 685). The instrument used to analyze the samples, the ultraviolet visible spectrophotometer Hach Model DR 4000, was approved by the EPA for reporting purposes for chromium and zinc, but not nickel, deeming the nickel measurements not EPA approved (Hach Company). This flaw can be improved upon by utilizing different analytical methods such as my intended use of the 4200 MP-AES (created by Agilent Technologies), which is approved by the EPA for nickel analysis. However, the study indicates that there is leaching of nickel, chromium, and zinc that takes place near coal power plants. This is shown by the presence of these three elements in unusually high quantities in the groundwater adjacent to the coal plant. Elements found in coal ash can have a leaching rate of approximately 8% to 17%, leaving up to 92% of the metals remaining in the soil (Singh 687). This suggests the elements found in raw coal and coal

dust deposited by rail transportation have the potential to leach and pollute the soil near the railways on which they are transported. Although pollution rates from coal are difficult to identify, as the study mostly considered coal ash, it did find a negative correlation between particle size and elemental concentration. However, this trend is only attributed to coal remnants, not raw coal itself. The research does indicate the harmful potential of coal, but raw coal is further explored in my study

Coal dust and coal ash are two very disparate entities. When coal is burned, the elements within it are chemically altered into different, more toxic chemicals that compose coal ash. This ash is seen in much higher quantities than coal dust because it is a product of coal combustion, also contributing to its harmful effects. Coal dust is simply dust that is emitted from raw coal as it is being transported. This dust has the same components as raw coal and is found in smaller quantities than coal ash. Therefore, it has not been chemically altered by the process of combustion and has a lower toxicity level than coal ash.

In order to determine the harmfulness of coal, there must a "safe" standard put forth to compare against results. When examining metals amounts that are "safe" to be present in soil, there are many specific sets of regulations, considering the many uses of soil. Soil can be used industrially, meaning that its toxin levels are able to be slightly higher. It can be used for residential purposes, in which case the quantity of allowable toxins is much smaller. Or perhaps it can be used for agricultural purposes, making it report to the most restrictive regulations. Residential soil was sampled for this research, causing it be accountable to the EPA's soil regulations for residential soils. These

regulations take into consideration the possibility of the soil being ingested by a child 6

years-old or younger. In other words, the regulations are set so that the standards allow

for children to ingest the soil without any health risks. There are different regulations

according to state and federal law. The Indiana Department of Environmental

Management (IDEM) has less severe regulations than the EPA.

Table 1. EPA and IDEM regulations for metals (ppm) in residential soils

Element	EPA Residential Soil	IDEM Residential Soil
Fe	-	77,000
Zn	23,000	32,000
Cd	70	98
Ca	-	100,000
Ag	390	550
Cu	3,100	4,300
Mg	-	-
Al	78,000	100,000
Mn	1,900	2,500
Pb	-	400
Cr	230	-
V	390	550
Ba	15,000	21,000
K	-	100,000

Units are in ppm or mg/kg
Ca is in the form of Calcium Pyrophosphate
Potassium is in the form of Potassium Tripolyphosphate

As the Table 1 demonstrates, the EPA and IDEM deem different amounts of the

same metals to be dangerous and therefore do not monitor metals at the same rates. The

quantity at which metals become toxic is determined by humans and therefore not

concrete, causing IDEM and the EPA to state different quantities of the same metal as

harmful to human health. Some particularly harmful heavy metals, such as lead, silver,

and cadmium are regulated by a distinctive set of standards known as Human Health

Screening Levels (HHSL). These standards are referenced when the EPA Regional

Screening Level results in a risk of cancer 4 times larger than HHSL (Gorospe). They are

applicable to any type of soil, although the typical amount of each element naturally

occurring in the soil is dependent upon the type of soil, regardless of its use.

Impacts of Heavy Metals on Plant Growth

Heavy metals that are leached from coal and its byproducts have a significantly

negative impact on plant growth. When heavy metals are present in soil, plant roots have

been shown to grow shorter in length. A study using the *Azolla filiculoides* water fern

was conducted to determine the effects of heavy metals on plant growth. The ferns were

dried and then stirred in a solution of 5-20 parts per million (ppm) of 5 heavy metals

salts. After they absorbed the heavy metals, they were dried and placed in nitric acid in

order to prepare the samples for analysis by a spectrophotometer. This experiment also

investigated the heavy metal content in the plants with a spectrophotometer, specifically

with the Perkin-Elmer model 2380 atomic absorption spectrophotometer. The results

show that the amount of nitrogenase enzyme (crucial to nitrogen fixation) activity was

drastically reduced by nickel, cadmium, and zinc. Nitrogen fixation decreased with a

corresponding increase of copper. *A. filiculoides* ultimately was affected by heavy metals

in several ways which included: loss of water, stunted growth rate, changes in color and

texture, and loss of cations. These symptoms of heavy metal exposure reveal that even in

heavy metal-tolerant plants (such as the water fern) biological activity suffers (Sela 7-11).

The findings indicate soluble metal salts are disruptive to plant growth in a variety of

ways. However, my study analyzed only compounds found in coal, many of which are not metal salts and therefore are not as soluble.

The manner in which heavy metals affect plant growth varies depending on the plant as well as the metal quantity. For example, Researcher Symenodois demonstrated that heavy metals actually affect the amount of chlorophyll in a plant. Chlorophyll is the unit in plants that captures sunlight in order to carry out photosynthesis, without which a plant cannot execute photosynthesis and will perish. The chlorophyll content in the leaves of *Holcus latanus* L. was observed with increasing amounts of lead and zinc. Individual plants were grown in nutrient solutions with 0.0, 3.0, 8.0, and 12.5 ppm of lead. Other plants were grown in nutrient solutions of 0.0, 9.0, 13.0, and 25.5 ppm of zinc. Conclusions established that chlorophyll decreased while lead and zinc increased. The most critical decrease of chlorophyll occurred with the first addition of lead and zinc, indicating that the initial exposure to heavy metal contaminants is the most influential to chlorophyll production. The study suggests that heavy metals may interfere with the synthesis of chlorophyll or may "reduce, indirectly the chlorophyll content by inhibition of other essential micronutrients" (Symeonidis 108-111). Once again, heavy metals clearly have a negative effect on the biological functions of plants.

Railway Transportation

Rail is often thought be a harmless means of transportation due to a focus on automobiles and their contribution to global warming through greenhouse gas emissions.

This shifts the focus away from railcars, despite their possible contribution to environmental contamination. Trains are convenient, moving massive amounts of materials across the country in a relatively short timeframe. But unfortunately, the cargo they carry causes pollution, the two most important types of which are polycyclic aromatic hydrocarbons (PAHs) and heavy metals. A study in Ilawa Glowna, Poland found increased amounts of heavy metals at sample sites near railroad tracks when soil samples were taken from four different areas. Sampling was conducted so that several samples were taken from areas between two rail ties and several were taken from areas outside of the rail ties in order to compare the two. Samples from between two tracks (the rail gauge) were expected to have higher pollution than samples from outside the tracks, and in fact, did. Inductively coupled plasma spectroscopy (ICP), the method most similar to MP-AES, was used in order to determine the amount of heavy metals in plants in the two zones mentioned above. Inductively coupled plasma spectrometer-optical emission, a form of ICP, was used for soil samples. Iron was present in the most substantial concentration, reaching up to 59,700 milligrams per kilogram (mg/kg) in one area. Overall, the lowest level of a single heavy metal deposited was molybdenum (2.00 mg/kg) and mercury (0.046 mg/kg) (Wilkomirski 333-342). Samples were also taken from different areas of the tracks which were: the loading dock, the platform, the rolling dock cleaning bay, and the siding. This enabled the researchers to study which metals occur more often in various functioning areas of the track. All four areas displayed elevated levels of heavy metals. Zinc for example, measured 60 times the control level, testifying to the tracks pollution. Knowing that railroad tracks have previously been

found to have elevated levels of heavy metals in surrounding soil, my study examined the

metals analyzed in this study closely to find similar results.

4200 MP-AES Analysis

My analytical methods for the coal research project included the use of the 4200

MP-AES. This instrument is new in its field and is comparable to the slightly older

inductively coupled plasma atomic emission spectrometer (ICP-AES) (Vlasov 444-445).

Microwave plasma spectrometers work by first introducing an aqueous sample into the

instrument in an aerosol form. This requires liquids to be nebulized by nitrogen gas,

which is magnetically ionized by the microwave. This is a key difference between ICP

and microwave plasma atomic emissions spectrometry (MP-AES). ICP uses argon gas

rather than nitrogen. Once the sample is in aerosol form, it travels to the high-temperature

plasma flame where it is dried to decompose into its atomic form in a process called

atomization. The atoms travel through the plasma until they absorb enough energy to

create an ion (ionization) or one of their valence electrons is excited to a higher energy

level. The sample then enters the interface, in which it is depressurized and the

temperature is regulated to a lower temperature. These ions and excited atoms emit

measurable light waves as they return to lower energy states. Here the wavelength of

light is a fingerprint for the identity of the atom and the amount of light emitted is related

to the concentration of the metal. The light passes through a monochromator (device that

mechanically selects certain wavelengths to transmit), then is reflected onto the charge

coupled device (measures electrical charges induced by light), which measures spectra

and background light simultaneously (Bazilio 2-8). In comparison with the MP-AES, ICPs are more expensive because of their "high cost of plasma sources and complexity of operation" (Vlasov 449). Also, ICP plasma images spread samples across a larger volume, resulting in a sensitivity decline. Lastly, the "ICP plasma density is magnitudes lower than that of the microwave-plasma discharge" (Vlasov 449). The innovative new technology of microwave plasma spectrometry improved my research greatly with more accurate readings of the amounts of heavy metals present in the soil, although the results of the MP-AES are still comparable with the older ICP methods.

4200 MP-AES Reliability

Methods for soil analysis vary; however, with the 4200 MP-AES there are several key features that provide excellent and precise analysis of soils, one of which is its analytical calibration. Calibration of the instrument is carried out using multielement standards from Agilent Technologies. These standards are diluted to known concentrations, the results of which are used to produce calibration curves that mathematically relate the intensity of light at a given wavelength to the concentration of the metal. These readings are able to be carried out using one wavelength for a sample, without any dilutions. Calibration curve correlation coefficients for the instrument are automatically set to a tolerance of 0.999 (Lowenstern 2). With such little room for error, the instrument is extremely precise. There are two calibration curves in the software, the first of which is a rational calibration fit. This is a non-linear curve fit that allows for the extended range of one-wavelength analysis. The other option for analysis is a linear

calibration fit, which does not allow for an extended concentration range. There are two examples of these calibration fits from an experiment done by Agilent to determine the amount of metals in wastewater in Figure 1 (Hettipathirana). The fitted calibration curve shows a curved line, displaying the instrument's ability to calculate for a more expansive range of data. At high concentrations fluorescence becomes nonlinear, making it very difficult to achieve a linear calibration, and proving nonlinear calibrations to be vital to data examination.

Co (340.511 nm) Calibration

Intensity = 11553.836 * Concentration - 0.259
Correlation coefficient: 0.99995
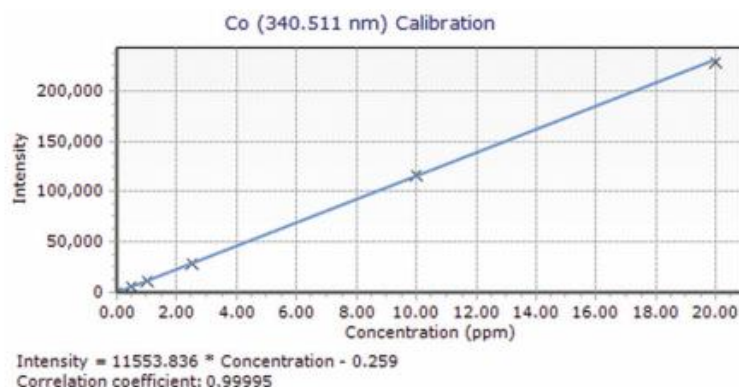
Figure 1. Typical linear calibration curve for Co at the 340.511 nm wavelength

Cu (223.009 nm) Calibration

Intensity = (1968.973 * Concentration + 0.011) / (1 + 0.001 * Concentration)
Correlation coefficient: 0.99998
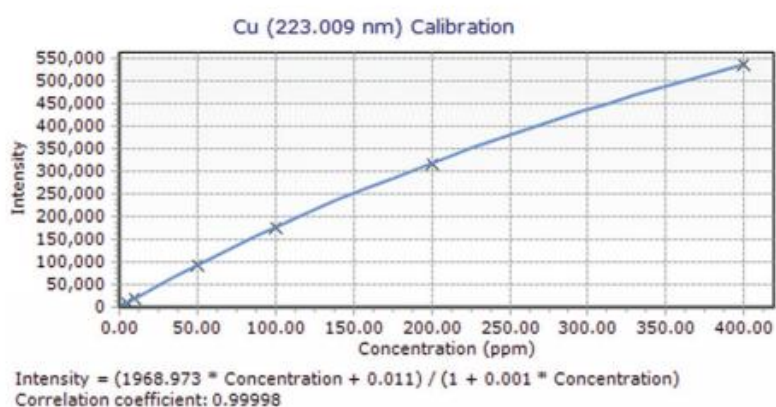
Figure 2. Typical non-linear calibration curve for Cu at the 223.009 nm wavelength. Note the extended range

Figure 1. Agilent Technologies example of a linear curve fit versus a nonlinear curve fit of copper adapted from the Terrance source

Another advantageous aspect of the 4200 MP-AES is its range of detection, yielding accurate results in samples with miniscule elemental presence. The 4200 MP-AES measures elements down to parts per billion (ppb) limits of detection (LOD) with examples given in Table 2. The table is adapted from Agilent's brochure for the 4200

MP-AES that was created in order to display the improved accuracy of the 4200 MP-AES (Lower).

Table 2. Agilent 4200 MP-AES LODs of elements in ppb

Ca	0.50
Ag	0.50
Mg	0.12
Mn	0.25
Pb	4.40
Cr	0.50
K	0.65

Agilent LODs were calculated as the concentration equal to 3 times the standard deviations of blanks. The LODs shown in Table 3 were calculated in the same manner from data in the heavy metals experiment. Three times the standard deviation of a blank's intensity was divided by the slope of a linear calibration curve. When compared to Agilent's LODs, our calculated LODs were lower and therefore more accurate in several cases. For example, the instrument used in my research can measure silver down to 0.04 ppb, while Agilent's records show they can only detect 0.50 ppb or above. The results from my experiment's calculations show a lower detection limit for lead, dropping as low as 0.05 ppb while Agilent's only reach 4.40 ppb.

Table 3. Calculated LODs of analyzed elements

Fe	0.0010
Zn	0.0030
Cd	0.1000
Ca	0.0100
Ag	0.0004
Cu	0.0800
Mg	0.0100
Al	0.0070
Mn	0.0001
Pb	0.0050
Cr	0.0010
V	0.0010
Ba	0.0001

Table 3 showcases the instrument's precision by showing its detection of elements in ppb. The ppb LODs, as well as advanced calibration of the instrument has proven the 4200 MP-AES to be an integral part of the analysis of many samples for a variety of metals.

Method/Procedure

I performed my project beginning in the summer of 2015 through February of 2016. To initiate the project, I surveyed the area of sampling, searching for any significant features. The area of interest is directly east of the Harding Street Generation Station, therefore implicating it had elevated amounts of metals in the soil and plants due to coal combustion. Dr. Mielke and I decided four transects would be taken along the fenced side of the yard facing the railroad. Each transect then had corresponding transects north, with each additional transect 25 feet further north than the previous. Each row was also 25 feet from the previous. The first two rows only contained three additional

transects heading north, while the third and fourth rows included a fourth additional transect heading north. We provided an extra transect to explore if heavy metal accumulation towards the far north end of the property's fence was present. Once the distance from one transect to another was decided, the sample sites were selected by hand measurements with a tape measure. The transect numbering system is used in the demonstrative figures and tables. The first transect was closest to Division St. and labeled T1-1. The transect 25 feet north of that, forming the first column was labeled T1-2, this continues until the last transect in the column. The second column, heading east 25 feet, or right when referencing Figure 2, is T2-1, and the pattern continues. In tables, each transect is assigned a P, R, or S to identify whether it is a plant, root, or soil sample.

Samples were then collected from each transects' position. Samples were taken with a prewashed plastic shovel to avoid any possible metal contamination. Each soil sample was approximately 3 ½ inches in depth, with any plants other than grass on the top portion of the soil being bagged and labeled as well as all roots deeper than two inches being kept intact and bagged. Any excessive soil from the plant roots was shaken off and left at the sample site. The plant and root samples were separated from one another in the lab rather than in the field. Along with plant and soil samples, pieces of bituminous coal were collected from the property from atop the soil.

Once collection was completed, the samples were moved to the lab where the plant and root samples were separated with a plastic knife. Each sample was then placed in its own weigh boat and given a wet weight using an analytical balance. To dry the samples, they were placed in a dry oven at approximately 25°C for two days. Once dry,

each sample was reweighed and its mass recorded. It should be noted that root samples

had an extensive variation of dry weight, as some sample sites did not have a notable

presence of plants other than grass. However, in the data analysis, heavy metal

concentrations were converted to milligrams of metal per dry weight gram of sample for

consistency. All soil samples had a much larger dry weight than the one gram

recommended by EPA Method 3050B for acid digestion of sediments, sludges, and soils.

In reaction to this, any samples that were significantly higher than the one recommended

gram dry weight were proportioned to approximately one gram, ready for digestion. All

dry sample weights can be found in Table 4 below.

Table 4. Final dry weight of samples before digestion (grams)

Sample	T1-1	T1-2	T1-3	T2-1	T2-2	T2-3	T3-1	T3-2	T3-3	T3-4	T4-1	T4-2	T4-3	T4-4
Plant	0.76880	1.87600	1.76970	1.36980	1.65880	1.63260	1.86700	5.44290	0.97761	1.82330	0.93380	1.12530	1.10040	2.28180
Root	0.04790	0.38560	1.00350	0.18700	1.11810	0.79880	0.47810	3.83400	2.83500	1.12900	0.01810	5.19100	0.39570	1.48120
Soil	1.06550	1.05120	1.01960	1.07620	1.00680	1.02370	1.02730	1.01620	1.10010	1.02720	1.01130	1.03110	1.00220	1.01234

Table 5. Final dry weight of coal samples before digestion (grams). Coal dilution dry
weights are calculated from original coal dry weight

Sample	Coal 1	Coal 2	Coal 3	Coal 1 dil	Coal 2 dil	Coal 3 dil
Coal	0.98730	1.03720	1.12000	0.09873	0.10372	0.11200

Dry, appropriately weighed samples were then digested according to EPA

Method 3050B. This method begins with placing the sample in 10 ml of 1:1 nitric acid

and heating for 10 to 15 minutes, then placing 5 ml of pure nitric acid in the container

and heating again. Brown fumes are typically generated, requiring an additional 5 ml to

be continuously added and refluxed for 30 minutes until brown fumes cease. Using a

ribbed watch glass, the solution was then heated until it was approximately 5 ml, or until

2 hours had passed. The sample was allowed to cool, then 2 ml of water and 3 ml of 30%

hydrogen peroxide were added. The solution was reheated, without boiling. If the sample

effervesced, 1 ml aliquots of hydrogen peroxide were added until the effervescence

ceased, or until 10 ml of hydrogen peroxide had been added. Afterwards, 10 ml of

hydrochloric acid was added and refluxed for 15 minutes. The sample cooled and was

filtered with filter paper into the desired container for analysis. Lastly, the sample was

diluted to 50 ml with nano pure water.

All glassware used in the research was first acid washed with a 1:10 solution of

aqua regia to eliminate any trace metals remaining from previous use. When digestion

was complete, the samples were allowed to cool and then diluted to 50 ml with nano pure

filtered water. All samples were stored in a refrigerator until their analysis.

Prior to any sample analysis, standards for the elements in question had to be

created. The elements that were examined were selenium, mercury, arsenic, iron, zinc,

cadmium, uranium, calcium, silver, copper, cobalt, magnesium, aluminum, manganese,

lead, chromium, vanadium, barium, sodium, and potassium. To make standards to run

with these samples, standards were purchased from Agilent Technologies. The elements

to be studied were determined by running a coal sample as well as a 1:10 dilution of a

coal sample. Whichever elements were deemed to be present and of interest were put on a

list of elements to be examined with all other samples. Standards for each element were

made of 5, 10, and 15 ppm by taking 3, 2, and 1 ml increments of the Calibration Mix

Majors standard solution containing iron, calcium, magnesium, sodium, and potassium

and diluting them to 100 ml with nano pure water. The Calibrations Mix Majors 2

standard solution contained the rest of the elements tested and had 10, 5, and 2 ml

increments diluted to 100 ml with nano pure water. Standards were run at the beginning

of every sample sequence. We attempt to run all sample types together to ensure that all

plant, root, and soil samples were tested with the same instrument conditions.

Unfortunately, this was not entirely possible due to the instrument's use of compressed

nitrogen and air tanks that did extinguish during several test sequences.

Before every sample run the instrument's housing torch was examined for cloudy

spots, and in the one instance it did present with a cloudy spot (indicating residual metals)

the torch was placed into an aqua regia bath for 24 hours before use. After the torch was

checked, the air tank pressure lines were adjusted to approximately 80 psi, if not already

there. When the instrument was initially turned on, the gas lines were typically purged 4

times before operation could proceed. For each sample run, the instrument was properly

prepared for samples by first running nano pure water (<18 Mega Ohms resistivity)

through the tubing while the torch activated for 10 minutes. The instrument was then

calibrated using a test solution as well as tested for LODs.

After all operational tests were passed, each sample sequence began with all of

the standards, followed by samples and periodic blanks of nano pure water. Blanks were

run after about every 5 samples to check for residual elements from samples presenting

themselves in the water as well as to purge the torch of residual elements, specifically

those found in extremely high concentrations such as iron and calcium. Every sequence

run terminated with a blank as well. All plant, root, and soil samples were run and

analyzed as well as coal samples and acid solutions samples. Acid solutions samples were

evaluated to determine which elements were present in the digestion solutions of the EPA

3050B Method alone, so that they may be negated in the final analysis. These solutions were simply the nitric and hydrochloric acids as well as hydrogen peroxide used to digest samples. During sample runs, each sample was shaken several times before being introduced to the instrument to create an even distribution of elements in the solution. In addition to this, each sample was run through the instrument for approximately 2 minutes before being quantified to enable the liquid from the current solution to displace the liquid of the previous solution in the torch chamber before assessment. This process provides accurate results with little to no carryover of samples. Once all samples were tested, the results were adjusted, requiring error coefficients to be adjusted from 5% to 25% which typically occurred for selenium, calcium, and potassium. Upon completion of the sample sequence, the data was converted into excel worksheets for further exploration.

The data in the excel worksheets was originally in ppm and needed to be converted to mass of element per mass of sample. This was achieved through the formula $\frac{ppm\ of\ element}{1000\ ml} X \frac{50\ ml}{dry\ weight\ of\ sample}$ .The results were used to subtract any elements found in the acid digestion. The two acid digestion blank results were averaged for each element and the average subtracted from every sample. This negates any elements added to the samples through the acids used to digest them. In total, the data was converted to milligrams of element/ kilogram of sample. The average concentration of each element present in the acid digestion was subtracted for every sample involving that element. In order to analyze data, the transects were approached in rows and columns. The same elements from different transects were always grouped together throughout this process.

The columns were the same transect, the 3 or 4 different sample sites of each. This explanation is better seen in Figure 2 below in which all transects, rows, and columns are labeled. The columns run along Division Street, while the rows are the first samples of all four transects, paralleling Hanna Street and the railroad line just outside of the sample site. In addition, Figures 3 and 4 show the ground view of the property and Harding St. Generation Station.

Figure 2. Google earth map of sample site with transects, rows, and columns labeled. Division St. runs north-south on the west edge of the property and the railroad runs east-west on south end of the property

Figure 3. Google earth ground view, looking northeast from Division St at railroad and sampling site property

Figure 4. Google earth view of Harding St. Generation Station from Division St.

Results

Tables of the results are given below. Each table's data has already been converted to mg of element per kg of sample to allow for accurate analysis. No two samples had the same dry weight and therefore mg of element per gram of sample

provides a standard analysis in which all data is consistent. All values that are shown as #### indicate that the concentration of the element was too large for the 4200 MP-AES to quantify. In addition, some elements had to be removed from the results. The removed elements were not able to be analyzed due to wavelength interference, causing inaccurate results, or the instrument's inability to calibrate for the element. Iron was present in enormous quantities and caused wavelength interferences in several elements, particularly mercury and arsenic. Selenium, however, was removed due to the lack of a standard and low raw intensity. Without a standard the results were not reliable. The standard for sodium would not calibrate, likely due to instrument error, as all the other elements from the same standard solution calibrated very well.

Table 6. Acid samples and acid averages in ppm

Element	Acid 1	Acid 2	Acid Avg
Fe	BLOD	1.44	1.44
Zn	0.14	0.19	0.165
Cd	0.04	0.17	0.105
Ca	0.17	0.2	0.185
Ag	0.01	0.00	0.005
Cu	BLOD	BLOD	N/A
Mg	0.00	0.02	0.01
Al	0.01	0.01	0.01
Mn	0.08	0.07	0.075
Pb	0.17	0.14	0.155
Cr	0.06	0.05	0.055
V	0.02	0.02	0.02
Ba	BLOD	BLOD	N/A
K	0.01	0.01	0.01

*Uncal indicates instrument did not find calibration curve for element and cannot quantify it
*BLOD signifies below detection limit of instrument
*N/A indicates average not found

Data from Table 6 was subtracted from every sample in order to assure the results only displayed what was present in the samples and not what was present in the acid digestion mix. The data in Table 7 confirms that the coal being mined and transported to the Harding St. Generation Station contains all of the elements selected for analysis and all elements in Table 7 were therefore analyzed in the conclusion. All results from the 4200 MP-AES can be found in Appendix B.

Table 7. Coal and coal dilution mg of element/gram of coal with averages of coal and coal dilution samples. Elements not analyzed were removed

Element	Coal 1	Coal 2	Coal 3	Avg Coal	Coal Dil 1	Coal Dil 2	Coal dil 3	Avg Dil
Fe	4.301	3.433	4.623	4.119	0.456	0.371	0.582	0.470
Zn	0.010	0.007	0.003	0.007	BDL	BDL	BDL	N/A
Cd	0.036	0.010	0.035	0.027	0.001	BDL	BDL	0.001
Ca	0.464	0.619	0.285	0.456	0.011	0.019	0.001	0.010
Ag	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cu	0.015	0.033	0.008	0.019	0.002	0.003	0.001	0.002
Mg	BDL	0.578	BDL	0.578	BDL	0.046	BDL	0.046
Al	0.352	1.956	0.243	0.850	0.034	0.205	0.041	0.093
Mn	0.003	0.020	0.001	0.008	BDL	0.001	0.000	0.000
Pb	0.077	0.017	0.004	0.032	0.010	0.004	0.003	0.006
Cr	0.001	0.003	BDL	0.002	BDL	BDL	BDL	N/A
V	0.005	0.013	0.003	0.007	0.001	0.001	0.001	0.001
Ba	0.005	0.027	0.002	0.011	0.000	0.002	0.000	0.001
K	0.282	0.924	0.015	0.407	0.016	0.102	0.001	0.040

Coal 1, 2, and 3 are all separate coal samples. Coal dilutions 1, 2, and 3 are all 1:10 dilutions of the corresponding coal samples.

Analysis/Conclusion

To begin, samples were examined in transects in order to determine if heavy metals decreased as they moved further away from the railroad track. This was an expected result, as the samples move further away from the tracks, there should be a

lower quantity of heavy metals from coal dust. Due to its proximity, heavy metals are less likely to reach the more distal sample sites. In a general consensus, the opposite appeared to be true. When examining the transects, there are 32 separate column transects to analyze due to each column having 3 types of samples. Each row sample type also has 13 elements that were tested. However, silver, for the roots and calcium, for the plants were not examined due to lack of calibration. This leaves 148 separate transects that could possibly decrease as they go north, away from the railroad. Of the 148 possible transects, 34 increased as they progressed north. Eleven of the transects decreased, leaving 103 with no particular pattern. There are examples of each trend given below in Figures 5, 6, and 7.
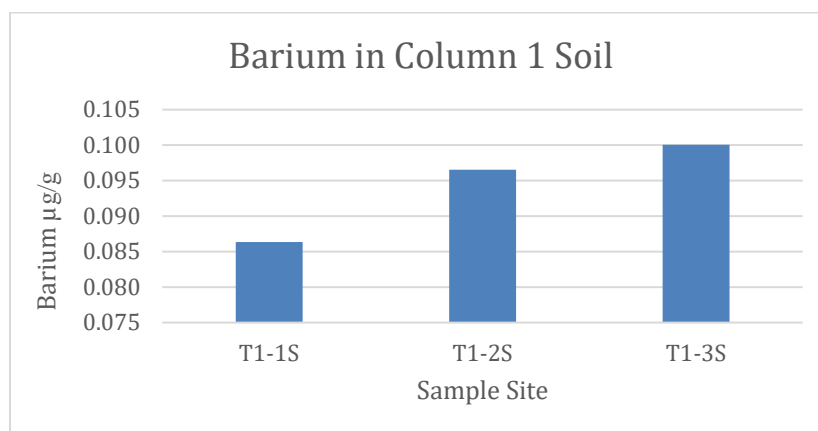
Figure 5. Barium in soil column 1 in mg/g showing general increasing trend
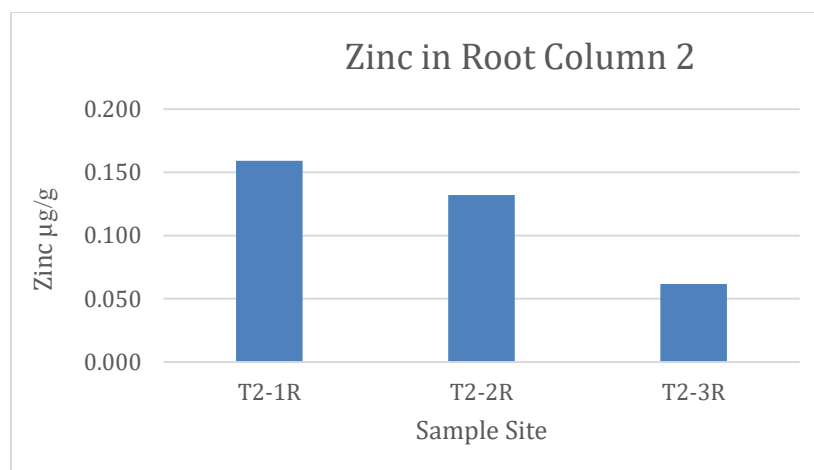
Figure 6. Zinc in root column 2 in m/g, showing general decreasing trend
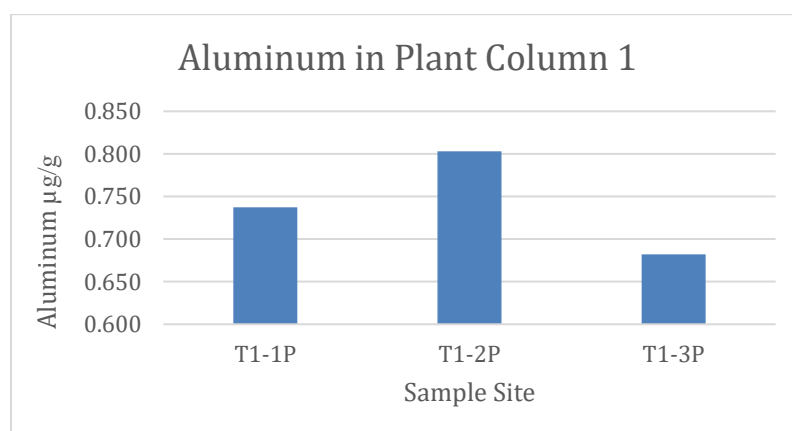
Figure 7. Aluminum in plant column 1 (mg/g) displaying no general trend

Overall, only 7.4% progressively decreased leaving the railroad and 23.0% increased. The large majority, 69.6%, had no pattern. The bulk of the samples that escalated with distance from the railroad were soil samples, with 16 examples, followed by roots with 12, and plants with 10. This could be due to the plants' abilities to absorb nutrients. Or. the density and type of plants at the sample site could attribute to this. Not all nutrients present in the soil are absorbed in the roots and plant body at the same rate, which would cause an uneven distribution pattern.

This phenomenon could be incited by the closeness of the sample sites to the actual power plant. The proximity could allow for contaminants from the scrubber to be released and settle into the soil in the yard, causing a random interference in the transects. Both forces, the railroad and the power plant, working in collaboration would produce a random pattern of metals in the samples.

Further investigation of the samples demonstrated there was a trend in the elements with the three sample types. When the average quantity of each element was established, it was apparent that typically the largest quantity of an element was present in the soil, then the root, and lastly, the plant body. An example of this is given below with manganese in Figure 8. Only 11 elements were eligible for this analysis, and out of these seven showed a clear trend of increasing quantities from plant to root to soil.
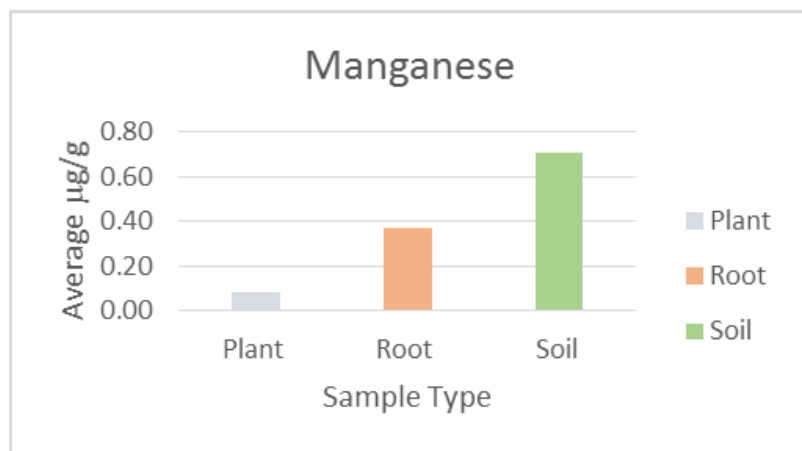
Figure 8. Average of manganese for plant, root, and soil samples

This trend continued when samples were broken down into rows. Although, sample TR1-1 appeared to have unusually inflated measures of metals, causing the overall trend to be broken by row 1. A visual of this is shown below, in Table 9, as the

root of row 1 spikes, destroying the overall trend. This graph is representative of all
graphs when comparing the abundance of metals in each sample type. There is no
correlation between the trends of the transects and the other sample types of that transect.
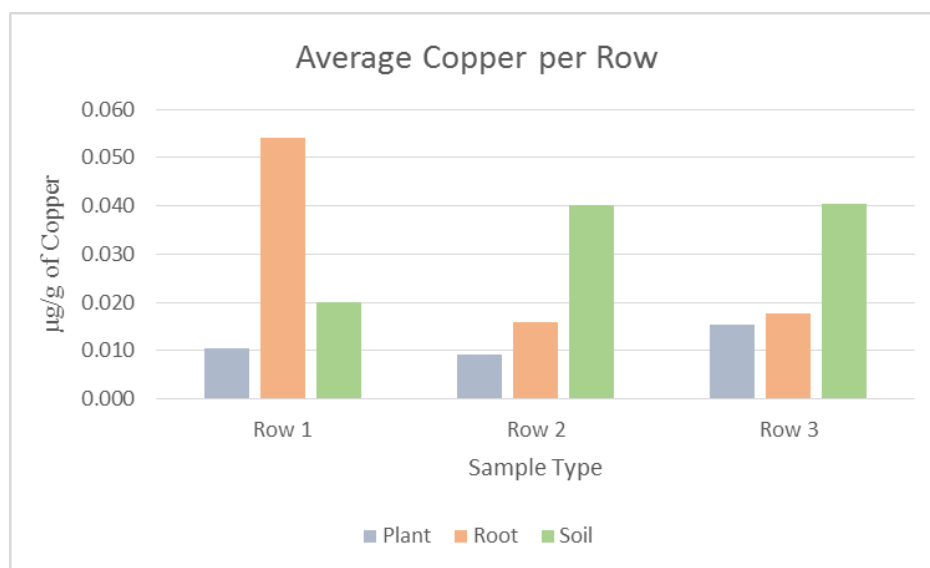
Figure 9. Average copper in mg/g of each row

The final work conducted was a health hazard check utilizing EPA regulations
for residential soils. However, the EPA has different regulations than the state of Indiana.
In the case that both have standards for the same element, the EPA standard was applied.
However, if there was an HHSL quantity given, this regulation was abided by in spite of
other regulations.

In regards to the EPA regulations for all metals, none were broken. In order to
reveal this, the average for each element was calculated for the three different sample
types. This chart can be found in Appendix B, Table B16. An overall average for every
element was also calculated and none were noted to be hazardous to human health. In

fact, no regulations were surpassed for any elements. This was an unexpected result, as

sitting within a mile of the Harding St. Generation Station, the soil, at minimum, was

thought to be contaminated. Not only were the regulations not exceeded, but the samples

had drastically lower concentrations than the regulations allowed. For example, zinc,

which can be present up to 23,000 ppm without posing a threat to a child 6 or under

ingesting it, averaged 10.7 ppm. This is several orders of magnitude lower than the health

risk for children. Other elements were closer to the health hazard amount, for instance

lead. Lead was averaged at 36.89 ppm overall, while the HHSL is 400 ppm. While this is

only 9.22% of the 400 ppm, it has a much higher percentage in comparison to aluminum

which only consist of 0.047% of the health hazard quantity. Table 8 displays the final

averages of all transects for each element, converted into ppm so that they can be

compared to governmental regulations. Manganese is the closest to threatening regulation

standards composing 20.34% of the regulation, although this is a typical element of soil

in this region and therefore may be attributed to this.

Table 8. Overall average of each element in ppm, compared to governmental regulations

Element	Overall Average	EPA Residential Soil	IDEM Residential Soil	HHSL	Percent of Regulation
Fe	5098	-	77,000	-	6.62
Zn	106.9	23,000	32,000	-	0.33
Cd	-39.87	70	98	1.7	N/A
Ca	5176	-	100,000		5.18
Ag	0.2990	390	550	380	0.08
Cu	23.53	3,100	4,300	-	0.76
Mg	1671	-	-	-	N/A
Al	3206	78,000	100,000		4.11
Mn	386.4	1,900	2,500	-	20.34
Pb	36.88	-	400		9.22
Cr	-2.087	230	-	-	N/A
V	11.21	390	550	-	2.87
Ba	54.51	15,000	21,000	-	0.36
K	6099	-	100,000	-	6.10

The symbol – indicates no regulations are provided
N/A indicates no calculations could be made

Although large infractions upon the regulations were not anticipated, some elements were expected to approach or perhaps surpass regulatory standards. The soil may not have been as contaminated as predicted due in part to the site it occupies. The field in which samples were taken has residential horses, eating some of the vegetation, perhaps ingesting some of the metals into their bodies. Another explanation could be possible wind patterns. The wind may not carry any coal ash or coal dust to the property where the samples were collected, but blow them in other directions.

Pollution can also be evaluated by inspecting the components of coal and their corresponding presence in the samples. Table 9 exhibits the calculated percentages of available elements. The averages of all plant, soil, and root samples for each element were used to gauge what percentage each element comprises of the sample total. It should

be noted that potassium is as high as 66.85% in the root samples. Although it is helpful to analyze the components of each sample type to determine if they correspond with raw coal samples, it should be noted that potassium is a natural element in soil. It usually is found in high quantities due to plants' nutritional needs. Other elements, specifically calcium, magnesium, and iron are fairly abundant naturally and cannot easily be contributed to coal dust pollution. However, upon examination many of the elements are in similar proportions to those in coal. Iron, the largest concentrated element in coal, is 42.92% of the soil samples and 23.29% overall.

Some elements, considerably lead, which is an element of high concern given its potential for adverse human health impacts, could possibly be attributed to the coal dust blown in from the plant. At 0.53% of coal composition, it is not a sizable percentage. However, there is about 1/3rd as much lead present in the overall samples as there is in coal. Further inquiry would be needed to prove a correlation, but there is a possible connection. The same could said for copper, as this is not a commonly occurring element such as calcium or potassium, and can be sourced more easily.

Table 9. Calculated percentages of each analyzed element in coal, plant, root, soil, and overall average

Element	% of Coal	% of Plant	% of Root	% of Soil	% Overall
Fe	67.27	9.77	15.62	42.92	23.29
Zn	0.11	0.59	0.54	0.49	0.49
Cd	0.44	-	-	-	-
Ca	7.45	-	23.70	16.23	23.65
Ag	0.00	-	-	0.00	0.00
Cu	0.30	0.11	0.10	0.13	0.11
Mg	2.92	13.68	7.59	6.97	7.63
Al	13.89	7.77	11.59	24.26	14.65
Mn	0.13	0.90	1.33	3.02	1.77
Pb	0.53	0.10	0.15	0.26	0.17
Cr	0.01	-	-	0.07	0.08
V	0.11	0.02	0.03	0.10	0.05
Ba	0.19	0.21	0.21	0.36	0.25
K	6.65	66.85	39.14	5.19	27.86

The research produced an unforeseen result, exhibiting no contamination levels above regulatory limits for any of the governmental agencies. This is a positive finding for the neighborhood the samples were taken from as well as the owner of the sample site. However, this study does not confirm there is not contamination surrounding the Harding St. Generation Station. Further studies, spanning more acreage and perhaps larger sample ranges, such as volatile organic compounds, may give more concrete evidence of pollution. A future study would need several control soils to examine the typical amounts of heavy metals in the Indianapolis area that are comparable to the findings from the samples near the plant.

Although the samples were not found to be toxic, there was a correlation between the quantities of metals in the plant, root, and soil samples. It was hypothesized that soil samples would have the highest concentrations of metals, as soils are the first subject to

anything in the environment. Plants then absorb many elements, particularly potassium, magnesium, and calcium into their roots, causing the roots to have the second highest concentration of metals. Lastly, the plant bodies contained the lowest concentration of elements, as was anticipated. Roots absorb the first of the metals out of the soil and then distribute them to the plant body. This was likely to dilute the metals concentrations. However, in the future it would favorable to gather identical kinds of plant to examine for plant testing. Options for this study were limited to whichever plants were on the sample site, which did vary slightly.

Similar studies need to be conducted in order to confirm results from this research. Perhaps groundwater could be inspected as well. There are many different outlets for pollution, making it difficult to pinpoint sources and concentrations.

Reflection

Through my research, I have come to understand a great deal more about the 4200 MP-AES instrument. I feel my abilities in running the instrument have improved significantly. I now understand how the instrument works and also how incredibly sensitive it can be. The 4200 MP-AES has taught me patience as well as given me a thirst to learn more about such a precise measurement technique.

Although, the scientific process has always seemed somewhat vague and not particularly important to me, I now understand the importance of creating a hypothesis and researching the idea. Without my research, I never would have fully understood the 4200 MP-AES or how coal combustion affects the surrounding environment. The

scientific process also seems vital when looking back at the original question and hypothesis. My project had a massive amount of data that could be presented in many different ways. I now understand how to hone in on my exact question and analyze my data accordingly. Through the process of research, I realized there are hundreds of ways to do any experiment and the way you choose to do your experiment should be directly dependent on what it is you are trying to understand. There are also hundreds of sources you can utilize for a project. I learned to focus on research relevant to my own and even improve upon the previous research. This is particularly true when I was reading the Liu Guijan research on coal ash. The experiment used an instrument that was not approved by the EPA to measure nickel concentrations. In reading this, I was sure to use elements that had approved testing standards.

From beginning to end, my honor's project has given me a greater sense of confidence. Although my results did not turn out as I expected, I already know what I would do differently in the future to improve upon the project. I now have ingrained in me a sense of accomplishment and eagerness for more research to come.

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"3535 Division St Indianapolis, IN 46227" Map. Google Maps. Google, 2016. Web. 29 January 2016.

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Appendices

Appendix A: Style Guidelines

MLA format was used in the creation of this research. To access MLA style guidelines go to the website provided-https://owl.english.purdue.edu/owl/resource/747/01/. Purdue Owl is a widely known and accepted style guideline for all styles of writing and was referenced frequently throughout this project.

Appendix B: Raw Data in mg/g from 4200 MP-AES Analysis

All data was provided by the MP-AES software. Every element that was not suitable for analysis were removed from the tables. Raw data was in ppm, however, to be consistent, all numbers were converted to mg/g due to the different original dry weights of samples. After this, the quantities of elements were calculated by subtracting the average of the two acid samples from each and every sample. The following tables are in the resulting form. Tables often present with ####, signifying the quantity of the element was too large to be quantified with the given calibrations. BLOD signifies below detection limit, meaning the element was in such small quantities the instrument could not measure it. N/A indicates the quantity could not be calculated due to a lack of data. In addition, samples T3-3P and T4-1R were not run due to human error and after discovery were not able to be run because of instrument dysfunction.

Table B1. Plant samples mg/g with averages for column 1 and 2

Element	T1-1P	T1-2P	T1-3P	Average	T2-1P	T2-2P	T2-3P	Average
Fe	0.906	1.132	0.881	0.973	0.454	0.485	1.893	0.944
Zn	0.103	0.036	0.052	0.064	0.057	0.025	0.036	0.039
Cd	0.005	0.004	0.001	0.003	BDL	BDL	BDL	N/A
Ca	####	####	####	####	####	####	####	####
Ag	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cu	0.013	0.014	0.017	0.015	0.011	0.008	0.015	0.011
Mg	1.259	1.338	1.468	1.355	0.811	0.904	1.667	1.128
Al	0.737	0.803	0.682	0.741	0.287	0.345	1.334	0.655
Mn	0.092	0.096	0.079	0.089	0.055	0.053	0.158	0.089
Pb	0.010	0.013	0.009	0.011	0.007	0.007	0.018	0.011
Cr	BDL	BDL	BDL	N/A	BDL	BDL	0.001	0.001
V	0.002	0.002	0.002	0.002	0.001	0.001	0.004	0.002
Ba	0.026	0.018	0.037	0.027	0.020	0.014	0.021	0.018
K	####	####	####	N/A	10.164	8.812	6.917	8.631

Table B2. Plant samples mg/g and averages of column 1 and 2

Element	T3-1P	T3-2P	T3-3P	T3-4P	Average	T4-1P	T4-2P	T4-3P	T4-4P	Average
Fe	0.342	0.104		0.261	0.236	2.758	1.493	1.579	0.213	1.511
Zn	0.096	0.004		0.023	0.041	0.195	0.056	0.047	0.012	0.077
Cd	BDL	BDL		BDL	N/A	0.002	BDL	BDL	BDL	0.002
Ca	####	####		3.915	N/A	1.821	3.766	9.870	1.406	4.216
Ag	0.000	0.000		0.000	0.000	0.001	0.000	0.000	0.000	0.000
Cu	0.005	0.002		0.007	0.005	0.012	0.013	0.014	0.005	0.011
Mg	0.720	0.333		1.380	0.811	0.835	3.157	2.493	0.862	1.837
Al	0.263	0.232		0.204	0.233	2.366	1.268	1.322	0.176	1.283
Mn	0.046	0.009		0.032	0.029	0.229	0.131	0.139	0.029	0.132
Pb	0.005	0.002		0.005	0.004	0.013	0.010	0.017	0.003	0.011
Cr	BDL	BDL		BDL	N/A	BDL	BDL	0.000	BDL	0.000
V	0.001	0.000		0.001	0.000	0.006	0.004	0.004	0.000	0.004
Ba	0.019	0.004		0.005	0.009	0.030	0.027	0.030	0.010	0.024
K	7.309	2.538		####	4.923	2.802	18.247	16.005	9.049	11.526

Table B3. Root samples mg/g and averages of column 1 and 2

Element	T1-1R	T1-2R	T1-3R	Average	T2-1R	T2-2R	T2-3R	Average
Fe	24.504	1.015	1.202	8.907	3.683	4.575	2.572	3.610
Zn	1.185	0.038	0.028	0.417	0.159	0.132	0.062	0.118
Cd	0.057	BDL	0.000	0.029	BDL	BDL	BDL	N/A
Ca	29.071	4.615	7.565	13.750	2.374	5.141	6.776	4.764
Ag	BDL	uncal	uncal	N/A	uncal	uncal	uncal	N/A
Cu	0.125	0.017	0.010	0.051	0.029	0.030	0.023	0.027
Mg	9.348	1.328	1.421	4.032	1.346	1.636	2.634	1.872
Al	15.966	0.890	0.857	5.904	2.873	3.534	2.179	2.862
Mn	2.140	0.089	0.086	0.772	0.286	0.372	0.225	0.294
Pb	0.172	0.015	0.011	0.066	0.025	0.038	0.027	0.030
Cr	BDL	BDL	BDL	N/A	BDL	0.008	0.001	0.005
V	0.042	0.001	0.002	0.015	0.005	0.010	0.006	0.007
Ba	0.324	0.022	0.027	0.124	0.045	0.059	0.037	0.047
K	52.662	12.210	7.715	24.195	14.984	7.151	8.270	10.135

Table B4. Root samples mg/g and averages of column 3 and 4

Element	T3-1R	T3-2R	T3-3R	T3-4R	Average	T4-1R	T4-2R	T4-3R	T4-4R	Average
Fe	12.834	0.368	1.102	2.009	4.078	BDL	0.430	2.228	1.588	1.415
Zn	0.373	0.012	0.066	0.157	0.152	BDL	0.018	0.088	0.060	0.055
Cd	BDL	BDL	0.000	BDL	0.000	BDL	BDL	BDL	BDL	N/A
Ca	15.041	3.381	1.154	4.469	6.011	BDL	2.400	5.270	1.819	3.163
Ag	uncal	uncal	uncal	uncal	N/A	BDL	uncal	uncal	uncal	N/A
Cu	0.089	0.007	0.013	0.021	0.033	BDL	0.009	0.025	0.010	0.015
Mg	4.660	0.902	0.478	1.450	1.872	BDL	0.596	1.416	0.852	0.955
Al	10.328	0.298	0.657	1.773	3.264	BDL	0.292	1.944	1.038	1.091
Mn	1.044	0.037	0.094	0.151	0.331	BDL	0.040	0.187	0.114	0.114
Pb	0.107	0.005	0.013	0.012	0.034	BDL	0.005	0.026	0.008	0.013
Cr	0.020	0.000	0.001	BDL	0.007	BDL	0.000	BDL	BDL	0.000
V	0.030	0.001	0.002	0.006	0.010	0.000	0.001	0.005	0.003	0.002
Ba	0.174	0.014	0.015	0.020	0.056	BDL	0.015	0.037	0.016	0.022
K	10.203	2.916	2.141	6.712	5.493	BDL	2.348	8.022	4.523	4.965

Table B5. Soil samples mg/g and averages of column 1 and 2

Element	T1-1S	T1-2S	T1-3S	Average	T2-1S	T2-2S	T2-3S	Average
Fe	11.232	11.284	10.927	11.148	9.663	11.526	9.867	10.352
Zn	0.099	0.142	0.145	0.129	0.083	0.169	0.131	0.128
Cd	BDL	BDL	BDL	N/A	BDL	BDL	BDL	N/A
Ca	2.911	3.198	6.166	4.092	1.941	3.546	6.566	4.018
Ag	0.000	0.001	0.001	0.001	0.000	0.002	0.001	0.001
Cu	0.025	0.043	0.040	0.036	0.022	0.048	0.040	0.037
Mg	1.412	1.535	2.110	1.686	1.255	1.684	1.953	1.631
Al	BDL	7.336	7.678	7.507	7.043	BDL	7.084	7.063
Mn	0.860	0.759	0.721	0.780	0.788	0.798	0.755	0.780
Pb	0.046	0.081	0.074	0.067	0.049	0.092	0.081	0.074
Cr	0.014	0.024	0.020	0.019	0.013	0.030	0.021	0.021
V	0.027	0.023	0.025	0.025	0.021	0.029	0.022	0.024
Ba	0.086	0.097	0.100	0.094	0.072	0.122	0.096	0.096
K	1.629	1.295	1.508	1.477	1.178	1.344	0.977	1.166

Table B6. Soil samples mg/g and averages of column 3 and 4

Element	T3-1S	T3-2S	T3-3S	T3-4S	Average	T4-1S	T4-2S	T4-3S	T4-4S	Average
Fe	9.525	10.129	10.875	8.181	9.677	6.953	9.889	10.007	9.500	9.087
Zn	0.113	0.122	0.155	0.063	0.113	0.055	0.132	0.125	0.055	0.092
Cd	BDL	BDL	BDL	BDL	N/A	BDL	BDL	BDL	BDL	N/A
Ca	1.765	2.945	7.433	3.430	3.894	1.942	3.798	4.878	2.259	3.219
Ag	0.000	0.001	0.002	0.000	0.000	0.000	0.001	0.001	0.000	0.000
Cu	0.018	0.034	0.045	0.014	0.028	0.015	0.035	0.037	0.014	0.025
Mg	1.302	1.434	2.813	1.204	1.688	0.951	1.591	2.220	1.364	1.531
Al	6.836	7.024	7.546	5.097	6.626	5.037	6.799	7.020	6.825	6.420
Mn	0.705	0.689	0.745	0.443	0.646	0.528	0.691	0.713	0.561	0.623
Pb	0.032	0.070	0.086	0.024	0.053	0.025	0.068	0.073	0.024	0.047
Cr	0.011	0.021	0.024	0.005	0.015	0.005	0.019	0.019	0.008	0.013
V	0.022	0.024	0.025	0.017	0.022	0.015	0.022	0.022	0.024	0.021
Ba	0.065	0.093	0.105	0.041	0.076	0.049	0.093	0.092	0.051	0.071
K	1.063	1.066	1.527	0.948	1.151	0.848	1.328	1.039	1.098	1.078

Table B7. Averages of plant elements per column in mg/g

Element	P1	P2	P3	P4
Fe	0.973	0.944	0.236	1.511
Zn	0.064	0.039	0.041	0.077
Cd	0.003	N/A	N/A	0.002
Ca	####	####	N/A	4.216
Ag	0.000	0.000	0.000	0.000
Cu	0.015	0.011	0.005	0.011
Mg	1.355	1.128	0.811	1.837
Al	0.741	0.655	0.233	1.283
Mn	0.089	0.089	0.029	0.132
Pb	0.011	0.011	0.004	0.011
Cr	N/A	0.001	N/A	0.000
V	0.002	0.002	0.000	0.004
Ba	0.027	0.018	0.009	0.024
K	N/A	8.631	4.923	11.526

Table B8. Averages of root elements in columns in mg/g

Element	R1	R2	R3	R4
Fe	8.907	3.610	4.078	1.415
Zn	0.417	0.118	0.152	0.055
Cd	0.029	N/A	0.000	N/A
Ca	13.750	4.764	6.011	3.163
Ag	N/A	N/A	N/A	N/A
Cu	0.051	0.027	0.033	0.015
Mg	4.032	1.872	1.872	0.955
Al	5.904	2.862	3.264	1.091
Mn	0.772	0.294	0.331	0.114
Pb	0.066	0.030	0.034	0.013
Cr	N/A	0.005	0.007	0.000
V	0.015	0.007	0.010	0.002
Ba	0.124	0.047	0.056	0.022
K	24.195	10.135	5.493	4.965

Table B9. Averages of soil elements per column in mg/g

Element	S1	S2	S3	S4
Fe	11.148	10.352	9.677	9.087
Zn	0.129	0.128	0.113	0.092
Cd	N/A	N/A	N/A	N/A
Ca	4.092	4.018	3.894	3.219
Ag	0.001	0.001	0.000	0.000
Cu	0.036	0.037	0.028	0.025
Mg	1.686	1.631	1.688	1.531
Al	7.507	7.063	6.626	6.420
Mn	0.780	0.780	0.646	0.623
Pb	0.067	0.074	0.053	0.047
Cr	0.019	0.021	0.015	0.013
V	0.025	0.024	0.022	0.021
Ba	0.094	0.096	0.076	0.071
K	1.477	1.166	1.151	1.078

Table B10. Averages of elements in mg/g across rows with averages of rows

Element	T1-1P	T2-1P	T3-1P	T4-1P	Avg Row 1 P	T1-1R	T2-1R	T3-1R	T4-1R	Avg Row 1 R
Fe	0.906	0.454	0.342	2.758	1.115	24.504	3.683	12.834	BDL	13.674
Zn	0.103	0.057	0.096	0.195	0.113	1.185	0.159	0.373	BDL	0.572
Cd	0.005	BDL	BDL	0.002	0.003	0.057	BDL	BDL	BDL	0.057
Ca	####	####	####	1.821	N/A	29.071	2.374	15.041	BDL	15.495
Ag	0.000	BDL	BDL	0.001	0.001	BDL	uncal	uncal	BDL	N/A
Cu	0.013	0.011	0.005	0.012	0.010	0.125	0.029	0.089	BDL	0.081
Mg	1.259	0.811	0.720	0.835	0.906	9.348	1.346	4.660	BDL	5.118
Al	0.737	0.287	0.263	2.366	0.913	15.966	2.873	10.328	BDL	9.722
Mn	0.092	0.055	0.046	0.229	0.105	2.140	0.286	1.044	BDL	1.157
Pb	0.010	0.007	0.005	0.013	0.009	0.172	0.025	0.107	0.097	0.100
Cr	BDL	BDL	BDL	BDL	N/A	BDL	BDL	0.020	BDL	0.020
V	0.002	0.001	0.001	0.006	0.002	0.042	0.005	0.030	0.000	0.019
Ba	0.026	0.020	0.019	0.030	0.024	0.324	0.045	0.174	BDL	0.181
K	####	10.164	7.309	2.802	6.758	52.662	14.984	10.203	BDL	25.950

Table B11. Averages of elements in mg/g across rows with averages

Element	T1-1S	T2-1S	T3-1S	T4-1S	Avg Row 1 S	T1-2P	T2-2P	T3-2P	T4-2P	Avg Row 2P
Fe	11.232	9.663	9.525	6.953	9.343	1.132	0.485	0.104	1.493	0.803
Zn	0.099	0.083	0.113	0.055	0.087	0.036	0.025	0.004	0.056	0.030
Cd	BDL	BDL	BDL	BDL	N/A	0.004	BDL	BDL	BDL	0.004
Ca	2.911	1.941	1.765	1.942	2.140	####	####	####	3.766	N/A
Ag	0.000	0.000	BDL	0.000	0.000	0.000	BDL	BDL	BDL	0.000
Cu	0.025	0.022	0.018	0.015	0.020	0.014	0.008	0.002	0.013	0.009
Mg	1.412	1.255	1.302	0.951	1.230	1.338	0.904	0.333	3.157	1.433
Al	####	7.043	6.836	5.037	6.305	0.803	0.345	0.232	1.268	0.662
Mn	0.860	0.788	0.705	0.528	0.720	0.096	0.053	0.009	0.131	0.072
Pb	0.046	0.049	0.032	0.025	0.038	0.013	0.007	0.002	0.010	0.008
Cr	0.014	0.013	0.011	0.005	0.011	0.000	BDL	BDL	BDL	0.000
V	0.027	0.021	0.022	0.015	0.021	0.002	0.001	0.000	0.004	0.002
Ba	0.086	0.072	0.065	0.049	0.068	0.018	0.014	0.004	0.027	0.016
K	1.629	1.178	1.063	0.848	1.180	####		8.812	2.538	18.247	9.866

Table B12. Averages of elements in mg/g across rows with averages

Element	T1-2R	T2-2R	T3-2R	T4-2R	Avg Row 2 R	T1-2S	T2-2S	T3-2S	T4-2S	Avg Row 2 S
Fe	1.015	4.575	0.368	0.430	1.597	11.284	11.526	10.129	9.889	10.707
Zn	0.038	0.132	0.012	0.018	0.050	0.142	0.169	0.122	0.132	0.141
Cd	BDL	BDL	BDL	BDL	N/A	BDL	BDL	BDL	BDL	N/A
Ca	4.615	5.141	3.381	2.400	3.884	3.198	3.546	2.945	3.798	3.372
Ag	uncal	uncal	uncal	uncal	N/A	0.001	0.002	0.001	0.001	0.001
Cu	0.017	0.030	0.007	0.009	0.016	0.043	0.048	0.034	0.035	0.040
Mg	1.328	1.636	0.902	0.596	1.116	1.535	1.684	1.434	1.591	1.561
Al	0.890	3.534	0.298	0.292	1.254	7.336	####	7.024	6.799	7.053
Mn	0.089	0.372	0.037	0.040	0.134	0.759	0.798	0.689	0.691	0.734
Pb	0.015	0.038	0.005	0.005	0.016	0.081	0.092	0.070	0.068	0.078
Cr	BDL	0.008	BDL	0.000	0.004	0.024	0.030	0.021	0.019	0.024
V	0.001	0.010	0.001	0.001	0.003	0.023	0.029	0.024	0.022	0.025
Ba	0.022	0.059	0.014	0.015	0.028	0.097	0.122	0.093	0.093	0.101
K	12.210	7.151	2.916	2.348	6.156	1.295	1.344	1.066	1.328	1.258

Table B13. Averages of elements in mg/g across rows with averages

Element	T1-3P	T2-3P	T3-3P	T4-3P	Avg Row 3 P	T1-3R	T2-3R	T3-3R	T4-3R	Avg Row 3 R
Fe	0.881	1.893		1.579	1.451	1.202	2.572	1.102	2.228	1.776
Zn	0.052	0.036		0.047	0.045	0.028	0.062	0.066	0.088	0.061
Cd	0.001	BDL		BDL	0.001	BDL	BDL	0.000	BDL	0.000
Ca	####	####		9.870	N/A	7.565	6.776	1.154	5.270	5.191
Ag	0.000	0.000		BDL	0.000	uncal	uncal	uncal	uncal	N/A
Cu	0.017	0.015		0.014	0.015	0.010	0.023	0.013	0.025	0.018
Mg	1.468	1.667		2.493	1.876	1.421	2.634	0.478	1.416	1.487
Al	0.682	1.334		1.322	1.112	0.857	2.179	0.657	1.944	1.409
Mn	0.079	0.158		0.139	0.125	0.086	0.225	0.094	0.187	0.148
Pb	0.009	0.018		0.017	0.015	0.011	0.027	0.013	0.026	0.019
Cr	BDL	0.001		BDL	0.001	BDL	0.001	0.001	BDL	0.001
V	0.002	0.004		0.004	0.003	0.002	0.006	0.002	0.005	0.004
Ba	0.037	0.021		0.030	0.029	0.027	0.037	0.015	0.037	0.029
K	####	6.917		16.005	11.461	7.715	8.270	2.141	8.022	6.537

Table B14. Averages of elements in mg/g across row 3 of soil with average

Element	T1-3S	T2-3S	T3-3S	T4-3S	Avg Row 2 S
Fe	10.927	9.867	10.875	10.007	10.419
Zn	0.145	0.131	0.155	0.125	0.139
Cd	BDL	BDL	BDL	BDL	N/A
Ca	6.166	6.566	7.433	4.878	6.261
Ag	0.001	0.001	0.002	0.001	0.001
Cu	0.040	0.040	0.045	0.037	0.040
Mg	2.110	1.953	2.813	2.220	2.274
Al	7.678	7.084	7.546	7.020	7.332
Mn	0.721	0.755	0.745	0.713	0.734
Pb	0.074	0.081	0.086	0.073	0.078
Cr	0.020	0.021	0.024	0.019	0.021
V	0.025	0.022	0.025	0.022	0.024
Ba	0.100	0.096	0.105	0.092	0.098
K	1.508	0.977	1.527	1.039	1.263

Table B15. Averages in mg/g of each row broken into sample types

Element	Avg Row 1 P	Avg Row 1 R	Avg Row 1 S	Avg Row 2 P	Avg Row 2 R	Avg Row 2 S	Avg Row 3 P	Avg Row 3 R	Avg Row 3 S
Fe	1.115	13.674	9.343	0.803	1.597	10.707	1.451	1.776	10.419
Zn	0.113	0.572	0.087	0.030	0.050	0.141	0.045	0.061	0.139
Cd	0.003	0.057	N/A	0.004	N/A	N/A	0.001	0.000	N/A
Ca	N/A	15.495	2.140	N/A	3.884	3.372	N/A	5.191	6.261
Ag	0.001	N/A	0.000	0.000	N/A	0.001	0.000	N/A	0.001
Copper	0.010	0.081	0.020	0.009	0.016	0.040	0.015	0.018	0.040
Mg	0.906	5.118	1.230	1.433	1.116	1.561	1.876	1.487	2.274
Al	0.913	9.722	6.305	0.662	1.254	7.053	1.112	1.409	7.332
Mn	0.105	1.157	0.720	0.072	0.134	0.734	0.125	0.148	0.734
Pb	0.009	0.100	0.038	0.008	0.016	0.078	0.015	0.019	0.078
Cr	N/A	0.020	0.011	0.000	0.004	0.024	0.001	0.001	0.021
V	0.002	0.019	0.021	0.002	0.003	0.025	0.003	0.004	0.024
Ba	0.024	0.181	0.068	0.016	0.028	0.101	0.029	0.029	0.098
K	6.758	25.950	1.180	9.866	6.156	1.258	11.461	6.537	1.263

Table B16. Overall averages in mg/g of each sample type and total overall average of each analyzed element

Element	Plant	Root	Soil	Overall Avg
Fe	0.916	4.503	10.066	5.161
Zn	0.055	0.185	0.115	0.119
Cd	0.003	0.014	N/A	0.008
Ca	N/A	6.922	3.805	5.364
Ag	0.000	N/A	0.001	0.000
Cu	0.010	0.031	0.031	0.024
Mg	1.283	2.183	1.634	1.700
Al	0.728	3.280	6.904	3.637
Mn	0.085	0.378	0.707	0.390
Pb	0.009	0.036	0.060	0.035
Cr	0.000	0.004	0.017	0.007
V	0.002	0.009	0.023	0.011
Ba	0.020	0.062	0.085	0.056
K	8.360	11.197	1.218	6.925

Appendix C: Budget

Heavy Metals Soil Analysis Budget

Soil Sampling ($25 EST)

- Small plastic shovel
- 10 ziploc bags
- 3 meter tape measure
- Black sharpie
- Cooler or refrigerator for samples

Soil Digestion ($221 EST)

- 500 mL Hydrochloric acid ($62 sigma-aldrich)
- 500mL Nitric Acid ($68 sigma-aldrich)
- 500mL 30% Hydrogen Peroxide ($91 sigma-aldrich)

Analysis with MP-AES ($460)

- 99.5% Size T Nitrogen Cylinders ($60 per cylinder - Airgas)
- Zero Air Size T Cylinders ($40 per cylinder - Airgas)

Actual Cost of Project

Soil Sampling ($5.37)

- 28 ziploc bags ($5.37)

Soil Digestion ($91)

- 500mL 30% Hydrogen Peroxide ($91 sigma-aldrich)

Analysis with MP-AES ($460)

- 99.5% Size T Nitrogen Cylinders ($60 per cylinder - Airgas)
- Zero Air Size T Cylinders ($40 per cylinder – Airgas)

Appendix D: CITI Training

Group 2

COLLABORATIVE INSTITUTIONAL TRAINING INITIATIVE (CITI PROGRAM)

COURSEWORK REQUIREMENTS REPORT*

* NOTE: Scores on this Requirements Report reflect quiz completions at the time all requirements for the course were met. See list below for details.

See separate Transcript Report for more recent quiz scores, including those on optional (supplemental) course elements.

- **Name:** Lauren Joyal (ID: 4458701)
- **Email:** joyall@uindy.edu
- **Institution Affiliation:** University of Indianapolis (ID: 473)
- **Institution Unit:** College of Arts and Sciences
- **Phone:** 8128782281
- **Curriculum Group:** Human Research
- **Course Learner Group:** Group 2.Social / Behavioral Research Investigators and Key Personnel.
- **Stage:** Stage 1 - Basic Course
- **Description:** The social behavioral track is applicable when you conduct epidemiologic, genetic, prevention/ screening, psychosocial and/or quality of life studies.
- **Report ID:** 14288921
- **Completion Date:** 10/13/2014
- **Expiration Date:** 10/12/2016
- **Minimum Passing:** 75
- **Reported Score*:** 92

REQUIRED AND ELECTIVE MODULES ONLY DATE COMPLETED

Introduction 10/11/14

Students in Research 10/13/14

History and Ethical Principles - SBE 10/13/14
Defining Research with Human Subjects - SBE 10/13/14
The Federal Regulations - SBE 10/13/14
Assessing Risk - SBE 10/13/14
Informed Consent - SBE 10/13/14
Privacy and Confidentiality - SBE 10/13/14
Research and HIPAA Privacy Protections 10/13/14
Conflicts of Interest in Research Involving Human Subjects 10/13/14
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Email: citisupport@miami.edu
Phone: 305-243-7970

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Group 3

COLLABORATIVE INSTITUTIONAL TRAINING INITIATIVE (CITI)
HUMAN RESEARCH CURRICULUM COMPLETION REPORT
Printed on 10/13/2014
LEARNER
Lauren Joyal (ID: 4458701)
3285 Glenwillow Ct.
Bargersville
Indiana 46106
United States
DEPARTMENT College of Arts and Sciences
PHONE 8128782281
EMAIL joyall@uindy.edu
INSTITUTION University of Indianapolis
EXPIRATION DATE 10/10/2016
GROUP 3 HEALTH INFORMATION PRIVACY AND SECURITY
COURSE/STAGE: Basic Course/1
PASSED ON: 10/11/2014
REFERENCE ID: 14288889
REQUIRED MODULES DATE COMPLETED
Belmont Report and CITI Course Introduction 10/11/14
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Independent Learner. Falsified information and unauthorized use of the CITI Program course site is unethical, and may be considered
research misconduct by your institution.
Paul Braunschweiger Ph.D.
Professor, University of Miami
Director Office of Research Education

CITI Program Course Coordinator