

Determining and Analyzing Lead Concentrations in Urban Areas with Philadelphia Based Soils

MASTERS RESEARCH PROJECT

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Abstract:

Lead is a known neurological toxin that causes permanent damage especially to developing children as well as in utero even with a one time, very low exposure. This study was completed in order to identify the presence of lead in contaminated soil samples and the associated hazard of bioaccessibility to children especially those that live in urban areas. The concentration and spatial distribution of lead in soil from samples taken in the city of Philadelphia were studied using various analytical equipment. The top 1 to 2 inches of soil were collected at locations where there were suspected former lead smelting sites. The top soil is where the main interaction of children and soil occurs. A handheld X-ray Fluorescence (XRF) detector was used to identify lead contaminated soils and provide a baseline measurement in parts per million. Soil samples were sieved into size fractions and retested by the XRF for concentrations. The finest fraction of soil (32 μ m) was prepared for Scanning Electron Microscopy (SEM) in order to visibly locate lead particles and how they interact with soil. A survey of the 32 μ m soil sample was completed to measure the elemental composition of the particles which correspond to the heavier elements in the soil. The use of Phytoremediation as a cheap and effective method of soil remediation is discussed since many cities do not have the resources to clean up all contaminated sites especially since many of the former industries that should be held responsible no longer exist.

Introduction:

Lead contamination and exposure in urban soils is a major concern for the public health of city populations. Developing children are especially at risk due to their sensitivity to lead during critical early life neurological development. Lead can cause permanent neurological damage to exposed children while developing in their mother's womb or during childhood even at blood lead levels below the Centers for Disease Control (CDC) "action level" (Senut et al. 2013). Lead has been proven to affect the following parts of the human body: the reproductive system, Neurological system, it is a known carcinogen, hypertension and other heart issues, renal failure, impairs the immune system and can affect pharmaceutical effectiveness of medications (Gidlow 2004). The CDC places the action level of lead in blood for children at 5 µg/deciliter which is down from 10 µg/deciliter when the standard was originally made back in the 1960's (CDC.gov 2007). Due to the hypersensitivity of children to permanent lead related brain damage, finding sources of lead contamination is extremely important in order to prevent children from lead exposure. Unfortunately due to the use of lead during the industrial revolution era as well as gasoline in automobiles, lead contamination is widespread and can be found in many urban soils.

Lead contamination comes from a variety of sources, most of which have been eliminated, but the former smelting and combustion of lead has a long lasting effect. The primary source of lead contamination is derived from leaded gasoline in the form of tetraethyl lead from the early 1920's until the mid-1970's (Hurst 2011). When lead is burned in gasoline it forms very fine particulate and can travel great distances with the assistance of the wind. Lead from the combustion of leaded gasoline can travel over 600 feet from car exhaust and about 11% of households in the United States are within

300 feet of four lane highways (Brugge 2007). Fine lead particulate sorbs very easily to soil and can stay in the soil for many years which generates bioaccessibility through oral and inhalation pathways (Ruby 1999). This poses a long term danger to anyone who is exposed to the fine dust from the soil. On a very hot and dry day soil readily and easily become airborne, enter the lungs of a person and the lead can enter the bloodstream. Fine particulate dust from lead contaminated dirt can pose the greatest threat to exposure to children (Gulson 1995). There is not only one source that contributed to the presence of lead in soil, leaded gasoline is not the sole source in urban areas especially in a city like Philadelphia.

There are 36 former suspected lead smelting site within the city limits of Philadelphia, all of which are no longer in operation. During the industrial revolution there were many industries that were using lead, such as paint producers, and contaminating the soils with gross quantities of lead due to the lack of environmental laws and exposure limits. Lead was being introduced into urban soils from previous industrial production, but now many of the areas where these industries existed are now residential housing and neighborhoods. Lead has a very high adsorption rate (K_d) of 900 in soils which means that it stays attached to the soil and is not easily removed (PA DEP). This means that soils that were contaminated in the mid 1900's that contain lead levels that exceed EPA and OSHA permissible exposure levels still are just as contaminated today as when the industries were smelting lead (Thomas 1995).

Figure 1 (Above): A map of the city of Philadelphia and the suspected former lead smelting sites throughout the city. Not all of the sites can be confirmed that they were smelting lead due to the lack of laws on the reporting and restriction of the hazardous metal. Locations with asterisks in the addresses are approximate locations since the areas have been redeveloped and changed into residential neighborhoods since the former industries have been removed. (Map Source: PA Bureau of Health Statistics and Research, August 2004)

A third source of lead contamination in soils as well as residential houses is from lead based paints as well as lead pipes used in the plumbing systems. Lead paint was used in residential houses until 1978 when the U.S. Consumer Product Safety Commission (CPSC) placed a final ban on it which prohibited the sales and use of lead paint in homes. Most of the lead paint has been removed in residential houses, but even after its removal lead can still be detected in high levels in dust in houses (Laidlaw 2011). Lead cannot exceed 40 micrograms in dust per square foot on the floors of a house and lead cannot exceed 250 micrograms in the dust on window sills per square foot (EPA 2001). Many houses that contained lead based paints have been remediated, but there is another major source of lead contamination that children interact with such as public parks and playgrounds.

Some of the areas in Philadelphia that were former suspected lead smelting sites were located on or nearby areas that are currently public parks, playgrounds or schools. In these locations the concentrations of lead can exceed the EPA limit which can be hazardous to the health of children. The EPA exposure limit for lead concentrations in bare soil in a yard is 1,200 ppm measured by average and only 400 ppm in children's

play areas (EPA 2001). It is imperative that we determine the concentrations of lead that are present in soil samples from urban areas. This is an especially important task in order to remediate or remove lead from soils and reduce the amount of exposure to urban populations, especially children which are more sensitive due to their on-going neurological development.

Materials and Methods:

Soil samples were taken throughout the city of Philadelphia in areas that already were suspected to have high levels of lead due to the former presence of suspected lead smelting industries. Also soil samples were collected in areas that could be hazardous to children or other individuals such as school yards and public playgrounds in parks. A handheld X-ray fluorescence detector (Innov-X-Systems) was used to determine the concentrations of lead at or near the surface of the soil. Once a location tested positive for a high lead concentration, a shovel was used to remove the top 1 to 2 inches of soil. The soil sample was placed in a bag, labeled and brought back to the lab for further processing and testing. A control sample was taken outside of the main door of Merion Hall in West Chester, PA by the footpath that leads up to the stairs. For the control sample the top inch of exposed soil was collected and tested by the handheld X-ray Fluorescence detector. This control sample should not contain high levels of lead unless there was a source of contamination on the soil. The control soil was never used for lead smelting or processing and is located far enough away from a road that combustion from leaded gasoline should not be present in the sample.

X-ray Fluorescence (XRF) is used for determining the bulk composition of a sample, in this case soil, in a nondestructive manner (Shackley 2011). The X-ray

Fluorescence detector emits a concentrated X-ray beam that bombards the elements that are present in the sample. The elements in the sample give off specific wavelengths that correspond to their valence electron shells. The intensity of the fluorescence X-rays that are emitted from the sample determines the concentrations of the elements that are present (Kawai 1998). The readings of the concentrations are in real time on the display screen on the device. These readings are used to determine the level of contamination and are compared to the EPA standard which can be used to determine if future steps are necessary for soil remediation.

Some of the samples were further processed after being collected in the field. One specific sample, from Greensgrow Farm at 2501 East Cumberland St, Philadelphia, PA 19125, is located only 300 feet away from a former suspected lead smelting site. The Greensgrow Farm sample was collected the same way that the others were, but in the lab the sample was sieved into four size fractions. The largest fraction contained particles that are 2mm or larger, the next largest fraction contained particles less than 2mm to 500 μm , the third fraction contained particles less than 500 μm to 250 μm and the smallest fraction contained particles less than 250 μm to 32 μm . Each bag containing a fraction size was measured using the handheld XRF detector to determine if there were differences in concentrations changed according to the size of the soil particles. These samples were then compared to the whole soil control sample that was taken outside of Merion Hall. The concentrations for each soil fraction size were recorded and can be seen in Table 1 in the results section along with the other samples used in this project.

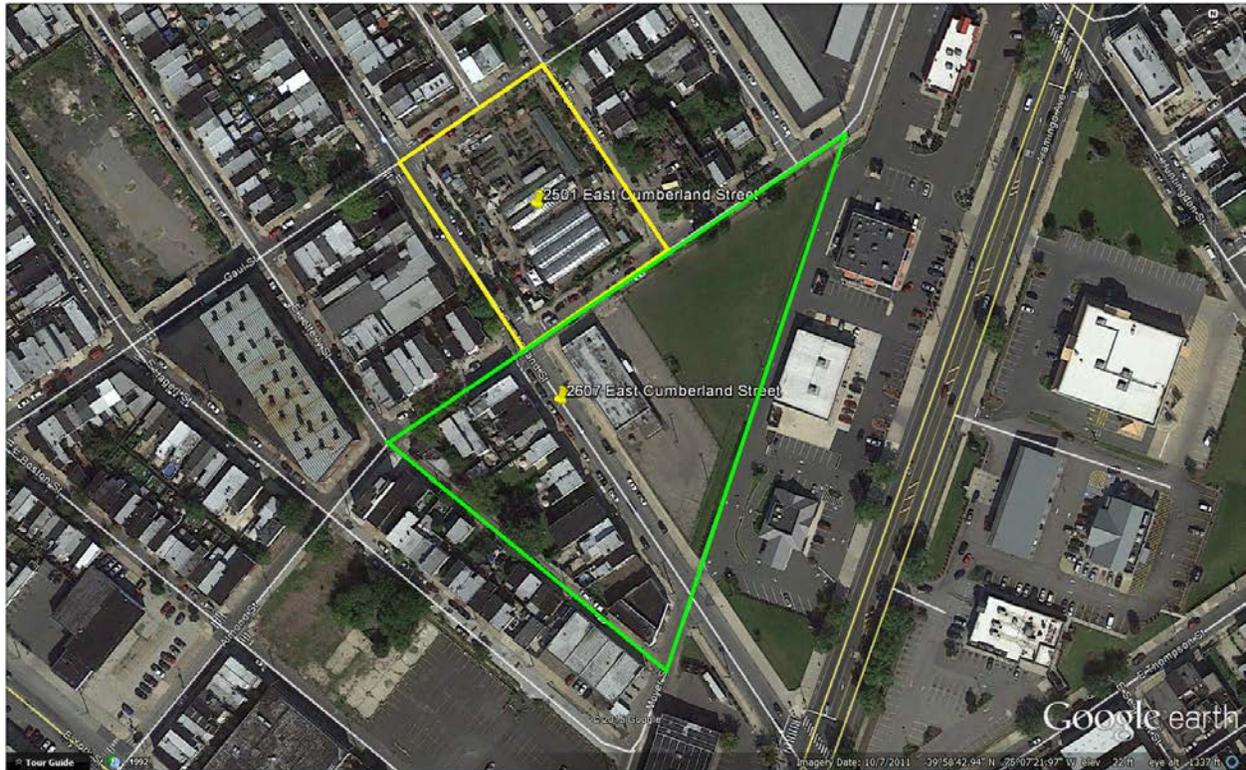


Figure 2: Shows an aerial view of Greensgrow Farms in northeast Philadelphia along East Cumberland Street. 2501 East Cumberland Street is the address for Greensgrow Farms which is an urban farm and nursery. 2607 East Cumberland Street is a former suspected lead smelting site. The proximity of the smelting site to the nursery/farm is concerning since certain plants readily absorb lead from soil.

Once the concentrations of lead in the soil using the XRF were determined, the next step was to prepare the soil fraction samples for the Scanning Electron Microscope (SEM). A large pin stub mount used for the SEM and double side tape were used to apply the soil samples to the stubs for the analysis. The soil samples were spread out over the tape so that the particles were barely touching or not touching at all. The spacing of particles is important for two reasons. The first is that if smaller soil particles are being blocked by larger ones then the electron beam may not come into contact

with them unless a higher voltage across the filament is used. Secondly, X-ray emissions that are being reported as a function of wavelength, which are specific to elements that are emitted by particles, can be blocked by adjacent soil particles. This can affect the reporting of the actual soil composition by Energy Dispersive Spectroscopy (EDS) (Manceau 1996). In order to make the soil particles spread out so that they could be applied to the stub, the soil was placed on a thin rubber sheet. A small scoop of about 0.2 grams of the 32 μm soil fraction was weighed out using an analytical scale on a piece of weigh paper. A hollow PVC tube was sanded down to make the edges of the pipe as smooth as possible. Petroleum jelly was applied to the sanded down tube which is used to decrease the friction of the rubber sheet against the sanded down PVC tube. The rubber sheet was placed on top of the PVC tube, and the soil was applied to the rubber sheet. The rubber sheet was then pulled and stretched out over the pipe as tight as possible which effectively spread out the soil particles. While holding the rubber sheet taut with one hand, the other free hand could be used to pick up the stub containing the double sided tape, and the stub was pressed against the soil on the rubber sheet. This process allowed for wide spacing of the soil particles for more accurate analysis using the SEM. For further information of the PVC tube device that was used for this process; personal Communication: Dr. Ulrich Klabunde.

Scanning Electron Microscopy was used to determine the bulk composition of soil particles, and also to determine possibly what the lead particles were binding to or associated with. The prepared sample stub of spread out soil from above was loaded into the SEM on a single position stage and the chamber was pumped using low vacuum mode which has a pressure of around 75.0 to 100.0 Pascal. Once the chamber

reached the working pressure, the high voltage current was turned on to 20.00 kV and a spot size of 5.0 was used for EDS analysis. Lead appears as brighter particles on the electron microscope due to its heavy elemental weight. This is compared to the rest of the soil particles' composition which is much lighter elements in atomic weight and therefore have a darker appearance on the SEM. After searching for particles on the sample that appear much brighter than the main soil composition, EDS was completed using the INCA software to determine the absorbance spectra of the particles. The length of the particle sizes were measured from the SEM software using the scale bar. A survey of the 32 μm sample from Greensgrow Farms in Philadelphia was run on the SEM in order to provide the overall bulk composition of soil particles that were in the same threshold region of brightness as the lead particles are. As an overall montage image of the sample was completed to show what the sample looks like at a magnification of 75x on the computer for the microscope.

Results:

The handheld XRF spectrometer gives the most accurate readings of the metals present in soil samples. Table 1 shows the lead concentration results from the XRF readings that were recorded. Three replicates were recorded for each sample, averaged and standard deviations were calculated below. Each soil fraction size: >2mm, 500 μm , 250 μm and 32 μm , were measured separately from one another in order to determine if and where the primary concentrations of lead are located in the soil. The results from the three samples from the Greensgrow location varied slightly in lead concentrations, but they are all above the EPA's upper limit for children's playgrounds. Sample 1 from Greensgrow Farms contained the highest amounts of lead in the soil from the samples

that were measured in Table 1, which is why further analysis was completed on this sample using the SEM.

Table 1. Soil Sample Concentrations by address of collection

Sample #2: Greensgrow, flower bed on left middle of bed 3/20/2012		Sample #3: Greensgrow, back of bed flower bed on left 3/20/2012	
XRF Sample #		XRF Sample #	
Lead (Pb) concentration		Lead (Pb) concentration	
6	768 ppm	8	552 ppm
7	776 ppm	9	428 ppm
8	839 ppm	10	604 ppm
Average:	794	Average:	528
Standard Deviation	39.1	Standard Deviation	89.9
Sample #1: >2 mm Fraction: Greensgrow, flower bed on left front of bed 3/20/2012		Sample #1: 500 µm Fraction: Greensgrow, flower bed on left front of bed 3/20/2012	
XRF Sample #		XRF Sample #	
Lead (Pb) concentration		Lead (Pb) concentration	
11	1000 ppm	14	1021 ppm
12	1024 ppm	15	997 ppm
13	1158 ppm	16	1071 ppm
Average:	1081	Average:	1030
Standard Deviation	85.1	Standard Deviation	37.8
Sample #1: 250 µm Fraction: Greensgrow, flower bed on left front of bed 3/20/2012		Sample #1: 32 µm Fraction: Greensgrow, flower bed on left front of bed 3/20/2012	
XRF Sample #		XRF Sample #	
Lead (Pb) concentration		Lead (Pb) concentration	
18	1087 ppm	21	1090 ppm
19	1073 ppm	22	1080 ppm
20	1040 ppm	23	1115 ppm
Average:	1067	Average:	1095
Standard Deviation	24.1	Standard Deviation	18.0
Ashland #: 5843 Ashland, Behind house in front of cellar 3/20/2012		Control Sample: Footpath by main door of Merion Hall, West Chester, PA 10/08/2015	
XRF Sample #		XRF Sample #	
Lead (Pb) concentration		Lead (Pb) concentration	
24	828 ppm	27	23 ppm
25	825 ppm	28	17 ppm
26	950 ppm	29	18 ppm
Average:	867	Average:	18.7
Standard Deviation	71.9	Standard Deviation	3.8

Table 1: Shows the lead metal concentrations in parts per million (ppm) in each sample that was measured using the XRF. Each sample was measured three times to generate an average concentration. Also the standard deviation was calculated between the replicates of measurements. These concentrations were used to determine if the SEM would be sensitive enough to detect the presence of lead since it has a detection limit of about 1000 ppm.

The first time the soil samples were prepped for the SEM, each soil fraction was prepared on separate small size pin stubs using the 500 μm , 250 μm and the 32 μm soil fractions. The soil particles were not spread out using the method described above in the Methods section. This caused a problem on the first survey when looking for lead particles in the samples. The larger particle size of 500 μm was too large and no lead particles were detectable. Only 2 particles were detected overall throughout the three sample fractions, which lead to the spread out method. After the 32 μm soil fraction was spread out on the double sided tape, there was enough spacing between the particles that the X-rays generated by the back scatter electrons were not inhibited on their path to the back scatter electron detector. After the spread out method was used to generate a 32 μm fraction sample, manual Point & ID analysis was used in order to locate particles of lead in the soil. This took about half an hour to locate the first lead particle that is shown in figure 3 below. The brightest particles were sought out and the Point and ID analysis on the INCA software was run to generate an EDS plot to determine if the particle that was located in figure 3 was in fact a lead particle. Some of the EDS plots that were measured on the SEM are attached in Appendix C section in order to show the elements related to lead. After the EDS returned positive signals of lead on a

particle, a length measurement was taken which ranged in lengths from 1 μm to 20 μm . The larger measurements usually occurred on the on the coated soil particles. Also, particles are usually in the form of a lead oxide which makes determining the source of the lead very difficult. More manual Point & ID analysis was completed in order to find more lead particles and to obtain measurements of lead particle sizes.

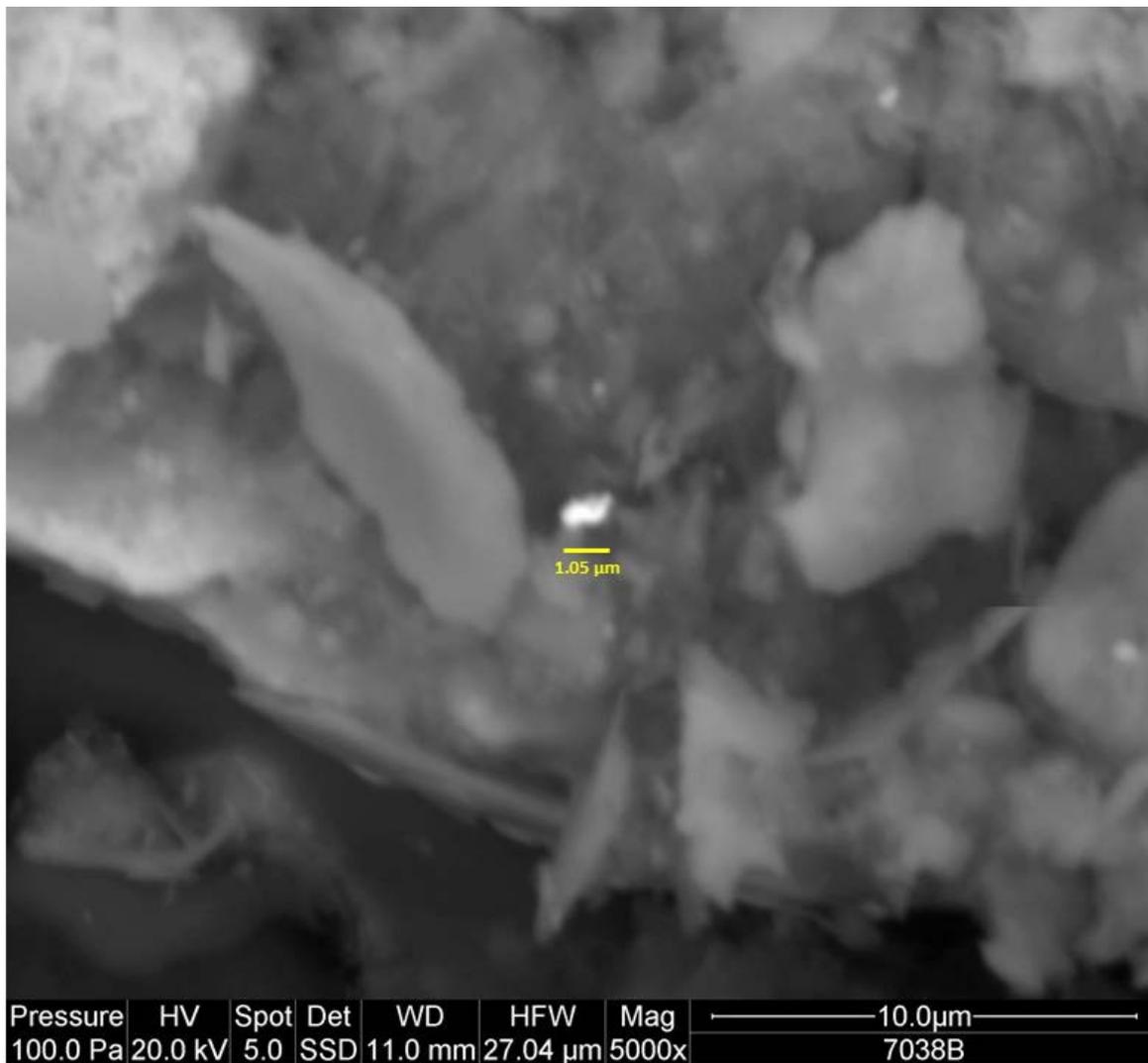


Figure 3: The image above shows the first lead particle identified by Point & ID on the INCA software. The length of the particle is shown above on the image in yellow which is about 1.05 μm . The length of the particle was measured using the scale bar provided

in the bottom right corner of the image. This is one very small particle of many particles that composes this aggregation of soil.

Spectrum	In stats.	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Pb	O	Total
Spectrum 1	Yes	0.9	10.2	16.5		4.69	0.52	1.61	0.97	2.64	18.7		43.3	100
Spectrum 2	Yes	0.63	9.14	14.1		1.97		1.55	0.88	2.87	20	12.1	36.8	100
Spectrum 3	Yes	0.69	9.97	15.7	0.68	3.79		1.62	1.16	3.1	20.7		42.6	100

All results in weight%

Table 2: This table shows the three spectrums that were taken of the particle that was the first particle positively identified in the image above labeled as figure 3. After EDS was completed using INCA software, a table of the results of the elements by weight percentage was generated. The three spectrums were all measured on the brightest particle on the image on figure 3, and spectrum 2 reported positive for peaks for lead. 12% of the total weight was lead on that particle.

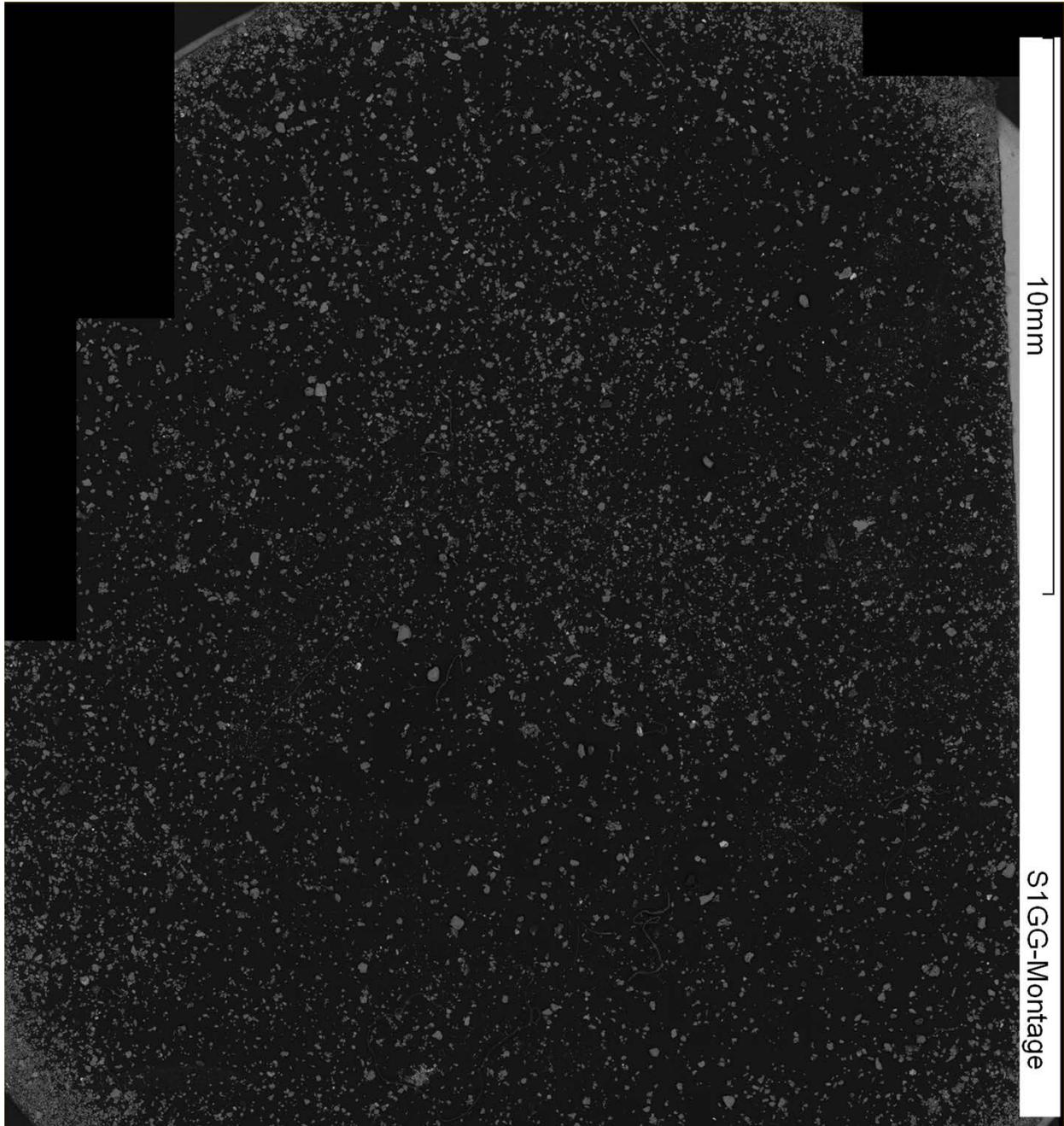


Figure 4: Shows an image montage of the S1GG 32µm sample for Sample 1. The INCA software breaks up the entire sample area into square fields that are captured as images. The images are stitched together to show the overall area of the sample pin stub that was recorded during the feature survey.

Measure	Count	Min	Max	Mean	St Dev
Fe (Wt%)	3	1.58	4.38	2.77	1.45
Ti (Wt%)	1	2.11	2.11	2.11	0
Ba (Wt%)	11	9.08	16.12	12.42	2.08
Sb (Wt%)	12	9.73	33.94	15.34	6.51
Pb (Wt%)	14	7.38	41.27	28.72	8.36
Area (sq. μm)	14	0.92	199.94	61.21	66.2
ECD (μm)	14	1.08	15.96	7.6	4.66
Length (μm)	14	1.51	22.48	10.29	6.67
Perimeter (μm)	14	3.1	55.42	26.17	16.72
O (Wt%)	14	4.83	54.03	14.85	14.91
Si (Wt%)	14	5.61	46.74	29.04	14.42
Cl (Wt%)	8	1.18	1.88	1.5	0.23
As (Wt%)	7	0	0.73	0.22	0.32
Kr (Wt%)	1	1.3	1.3	1.3	0
F (Wt%)	1	3.43	3.43	3.43	0
Al (Wt%)	3	3.1	6.84	4.64	1.95
K (Wt%)	1	1.21	1.21	1.21	0
Ca (Wt%)	2	2.18	6.14	4.16	2.8
P (Wt%)	2	4.58	5.94	5.26	0.96

Table 3: Shows the feature survey results from Sample 1 from the S1GG 32 μm soil fraction. The number of particles that were measured for lead is in the count column, the minimum and maximum size of the particle are in the next two columns followed by the mean size and standard deviation. The lengths and perimeters were also recorded for each particle that was detected.

Discussion/Conclusions:

One of the major problems that occurred when attempting to identify and measure lead particles in the soil samples is the distribution and spacing of the particles. Also, some of the particles are very small in size ($\sim 1\mu\text{m}$) which can make it difficult to locate them at low magnification. This made running a survey of the samples very difficult without using a high magnification which would greatly increase the run time of a survey and very quickly burn out filaments. Also, before spreading out the soil

particles on the large sample stubs, the particles were too close in proximity to each other. This may have caused an obstruction of the electron beam or the X-rays that are emitted from the energy transfer of an electron moving from an outer valence electron shell down to a lower energy shell. This is especially true in the larger soil fractions such as the 500 μm and 250 μm samples. This is due to the fact that they have greater topography due to the larger aggregates of soil packed together. The larger soil fractions (500 μm) contained concentrations of lead in ppm that were similar in concentrations to the smaller soil fraction size (<32 μm) which was confirmed by the XRF results (Pyle 1996). It was very difficult to locate the small lead particles on the surface of the large soil fraction particles because as the surface area of the particles increases, the volume under the subsurface of the particles also increases. This means that if there were lead particles present in the larger soil fractions, they are not visible using imaging on the SEM and random point and ID analysis would have been as efficient as finding a needle in a haystack. Due to these issues, the spread out method of the smallest soil fraction (32 μm) as described above in the Materials & Methods section was developed. The smaller particles contain a greater surface to volume ratio, which means that the probability that a lead particle is present on surface is much higher. Lead particle sizes in these samples ranged from smaller than 1 μm to up to 20 μm , so in order to find those very small particles the smaller soil fraction is more desirable than the larger fractions. The larger size pin stubs were used instead of the smaller size pin stubs, because the larger pin stubs allow more soil to be loaded over a larger area. This increased the potential number of lead particles and made them easier to find at a lower magnification. Also, the spacing between the particles on the spread

out method allowed for the X-rays to reach the back scatter electron detector much easier without obstruction from other soil particles.

Since lead is a much heavier element than the primary comprising elements normally present in soil, they tend to be much brighter in comparison which is an advantage. The contrast setting was increased to a value around 80 and the brightness was turned down to a value around 15. This gave the heavy elements higher contrast so that when the brightness was turned down, the heavy elements such as lead were the only particles that were still showing up on the microscope. This helped to locate the lead particles in a shorter amount of time. Also the contrast settings could be used to calibrate the SEM to find only heavy elements so that there were less particles to be analyzed during a survey run; this reduced the survey run times.

Using the smallest soil fraction size of $<32\ \mu\text{m}$ is potentially a very important soil fraction when it comes to how humans, especially children, may become exposed to lead contaminated soils. Soil samples that are less than $32\ \mu\text{m}$ are more readily available to become airborne and end up in our lungs and ultimately enter the bloodstream. The lead particles that are only $1\ \mu\text{m}$ in length are of primary concern since these smaller particles can enter the respiratory or digestive systems more easily and can be absorbed into the blood which can affect the nervous system (Clarkson 1987). Lead particles that are $10\ \mu\text{m}$ or less in size are very susceptible to entering our bloodstream once those soil particles enter the airways and lungs (Boisa 2014). The movement of lead from a source to soil, soil which is crushed to dust, dust which can become airborne and absorb into the bloodstream via the lungs is caused by industrial sources, leaded gasoline exhaust and pulverized lead particles in soil (Mamane 1995).

There are many factors that can affect the amount of exposure in children which include: season of the year, weather which includes wind, age, socioeconomic status, and time spent outside (Mielke 1998). Children who live in old industrial cities and do not have much wealth cannot afford to move to a new home that has better soil quality without lead contamination. This can cause many exposures throughout their childhood either via digestion or inhalation during their critical neurological development stages (Garcia-Rico 2015).

Lead can enter the bloodstream via digestion from contaminated soils when hands are not adequately washed after exposure. This is especially true in young children who are not concerned with washing their hands before eating or putting their hands in their mouths especially after playing in the dirt and soil. Children play in the dirt which is normally seen as harmless in areas where lead concentrations are below 400 ppm, but this can be extremely hazardous to neurological development even after a one time small exposure (Mendelsohn 1998). The standard set by the World Health Organization (WHO) for the action level of lead in children's blood is 10 $\mu\text{g}/\text{dl}$, but studies have shown that in children that have had blood lead levels below 10 $\mu\text{g}/\text{dl}$ for a lifetime still have neurological damage (Koller 2004). In a simulated stomach digestion study in Glasgow Scotland, which used a pH of 1.5 to simulate the conditions in our stomach, the study determined that a range of 23-77% of the lead in contaminated soils could be bioaccessible to humans (Farmer 2011).

Locating areas in cities where children may become exposed to elevated lead levels in soil is important in order to reduce the possibility of exposure of any concentration of lead to children. Figure 5 below shows an example in Philadelphia

where soil studies should be completed in order to determine the lead concentrations of an industrial reclaimed plot of land which is now a public space. Figure 5 shows a Google Earth satellite image of Chew Park which is located along Washington Avenue between South 18th and 19th streets. This area has been reclaimed and converted into a public park which contains playgrounds for children, a baseball diamond and other play areas which from this aerial image appears that much of the surface of the park is exposed soil. This location also is one of the former suspected lead smelting sites in the city of Philadelphia that can be found on Figure 1 much like Greensgrow Farms in northeast Philadelphia. This should raise an alarm to residents who use this park that there could be elevated lead levels in the soil. Since this is a potential source of exposure to young children, samples should be taken here by the city or state and remediation steps should be taken if the concentrations are above the WHO's standards in order to reduce lead blood levels of children in Philadelphia. Further research should be completed of all parks, playground areas, schools and anywhere else children are regularly exposed to dirt. This should especially be done in areas where former industries may have been used in lead production (Eckel 2001).



Figure 5: Shows a satellite image of Chew Playground along Washington Avenue and between South 18th street and South 19th Street in south Philadelphia. This is another location of a former suspected lead smelting plant. Currently a park has been constructed here with a playground, baseball field and other areas of exposed soil. There are many parks and playgrounds like Chew Park throughout cities in the United States that could be sources of lead exposure for neurologically developing children (Google Earth).

Determining who is at fault for lead contamination of soils is difficult since many of the business that once smelted lead no longer exist, or the properties have been purchased and the new owners have no idea that the property they have purchased is

heavily contaminated with lead. Also expecting the city or state to pay for soil remediation is not possible since many cities and states have budget issues and simply cannot afford to hire remediation companies. Finding other, cheaper methods of remediation is very important in order to start the remediation process right away without generating a large remediation cost. This is why phytoremediation could be an effective method of treatment of contaminated soil since it is a cheap and easy to grow heavy metal absorbing plants, cut them down and treat the plants as hazardous waste instead of removing and treating enormous amounts of contaminated soil.

Phytoremediation is an easy and cost effective method for remediating lead contaminated soil. Plants that absorb lead usually only absorb about 1% of lead in their biomass, but with the addition of chelating agents such as Ethylenediaminetetraacetic acid (EDTA) lead absorption can be increased from the roots of the plants to the shoots by up to 120 fold (Huang 1997). While lead is not an essential element for the functionality of plant systems it can be absorbed into the root systems, which makes certain vegetable skins such as carrots or potatoes more susceptible to being contaminated with lead (Pourrut 2011). Lead is not considered to generally be a phytotoxic compound to plants which is beneficial for plant use to absorb and collect lead for soil remediation (Stevens 2003).

Continuing to locate urban soils that are contaminated with lead throughout the United States as well as the world is very important in order to protect the neurological development of the children who come into contact with these soils on a semi-daily basis. Ongoing sample collection and analysis must be done in areas that are near highways or used to house lead smelting industries in order to keep lead sensitive

children away and healthy (Motto 1970). Profiling of where lead is located in soil and finding the other elements that are associated with lead can help to identify the sources of lead contamination as well as give in sight towards the bioaccessibility to humans. Cheap and effective lead remediation methods for soil must be invented in order to clean up our post-industrial revolution world that we live in.

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Appendix A:

Soil Preparation Protocol for Scanning Electron Microscope

Materials:

- Handheld X-Ray Fluorescence (XRF) Detector
- Collected soil samples in plastic bags
- Analytical scale
- Weighing spatula
- Weighing paper
- PVC pipe
- Petroleum Jelly
- Rubber Sheet
- Double sided clear tape
- Large Sample Pin Stubs
- Scalpel
- Fine point lab marker

Protocol:

1. Use the handheld X-Ray Fluorescence detector on the plastic bagged sample of soil in order to get the concentration of the metals in the soil sample.
2. Sieve the soil samples into the desired fractions sizes (ex: 2 mm, 500 μm , 250 μm , and 32 μm) and place the fractions into separate plastic ziploc bags.
3. Use the handheld X-Ray Fluorescence detector on the bagged samples of soil for each fraction and record the results to detect if the concentrations of the metals vary by fraction size.
4. Use the smallest sized fraction of soil (ie: 32 μm) and weight out 0.2 grams of the soil on a weighing paper.
5. Transfer the soil from the weighing paper onto the middle of the thin rubber sheet.
6. Apply some petroleum jelly around the sanded top edge of the PVC pipe in order to reduce friction.
7. Cut off a piece of double sided tape so that the majority of a large sample pin stub has tape on it (you do not have the cover the whole stub).
8. Use the scalpel to cut off the excess tape so that the tape has rounded edges and weigh the pin stub on the scale.
9. Place the rubber sheet on top of the PVC pipe and spread it out into a thin, uniform surface coating on the rubber sheet.

10. Stretch the rubber sheet with the soil on it outward in all directions over the PVC pipe in order to spread out the soil particles so that they are barely touching one another.
11. Once the soil particles are thoroughly spread out, hold the stretched out rubber with one hand around the sides of the pipe and pick up the sample stub with your other hand and press the prepared sample stub on to the spread out soil particles on the rubber. (you are aiming to have a thinly coated piece of tape with soil particles so that it is fairly hard to see them with the naked eye)
12. Weigh the pin stub again on the scale to see how much soil by weight was applied to the pin stub.
13. Use the handheld XRF detector on the pin stub with the soil on it to ensure that the sample is still reading about the same concentration of lead as the full bag of soil fraction size that you are working with (ie: 32 μm).
14. The sample is now ready for analysis using the Scanning Electron Microscope. A carbon coating can be applied to the sample to prevent charging on the SEM if you are having this issue.
15. Store the prepared sample pin stub in a covered container so that dust does not contaminate the sample by sticking on the double sided tape.

Appendix B:

Energy Dispersive Spectrometry Analysis (EDS) Using Point & ID on the Scanning Electron Microscope

Materials:

- Prepared Large Sample Pin Stubs
- Scanning Electron Microscope
- INCA Software
- Microsoft Word

Protocol:

1. Load the prepared soil sample on the single stage holder in the chamber of the Scanning Electron Microscope.
2. Click on the low vacuum radial button on the right computer monitor with the microscope controls.
3. The computer will prompt you to flip the lever to the low vacuum setting if it is not already in the correct position (the lever is located above the square sample chamber of the microscope to the left)
4. Wait until the vacuum has pumped down to the operating pressure and the vacuum square in the bottom right of the screen will turn green showing that the chamber is at the operational level.
5. Use the mouse to raise the stage to the 10mm line by clicking and holding in the mouse scroll wheel and dragging the mouse upwards. Once you are in position let go of the mouse wheel and the stage will stop moving.
6. Change the detector of the upper left hand quadrant to the Solid State detector which is the Back Scatter Detector for low vacuum analysis.
7. Click on the HV button on the right side of the microscope controls in order to turn the high voltage on to the filament which turns on the electron beam. Make sure that the beam current is operating at 100 μA if not change it by increasing/decreasing the bias by un-checking the auto bias button.
8. Move around the sample in order to find an area of interest by double left clicking on the screen. If you are looking for a heavy element such as lead then adjust the contrast to around 75 and a brightness setting of around 20. This will allow the heaviest elements to still show up on the microscope while other elements will disappear.
9. Open the INCA software on the left computer and make sure that the drop down menu in the bottom left has "Point & ID" selected.

10. Use the flow chart on the left hand side of the software in order to name the project file and then the sample name on the next point downwards of the flow chart.
11. Move left on the flow chart to microscope setup. Click the green circle with the red arrows going around it to start cyclic acquisition and determine which element has the strongest peak.
12. Click the next square down to Quant Optimization and use the element from microscope setup in the drop down menu and click the green circle in the upper right hand side of the screen to optimize your measurements. Once it is finished click the measure button and make sure that it says OK.
13. Next move to the right to the area of interest button on the INCA software and make sure that the back scatter detector box is clicked on in the upper center of the selection buttons. Click the green capture button when you have your image that you want to analyze on the right computer monitor with the microscope controls.
14. Once the image is captured, then move down to the next flow chart button which is Acquire Spectra. Click the left mouse button to select areas on the image that you want to run Energy Dispersive Spectrometry (EDS) on and once you have all the areas selected, wait for the software to finish all the sample locations.
15. Move down to the Confirm Elements button which is where you can add or remove elements that do not typically appear in your samples if they share a similar peak with another element.
16. Move down to Quant on the flow chart which is where a chart for the elements present in the EDS are listed by atomic and weight percentage.
17. Finally click on Report below Quant and you can export a Word document so you can access your data on another computer. Put the files on a flash drive so you can take them away from the computer.

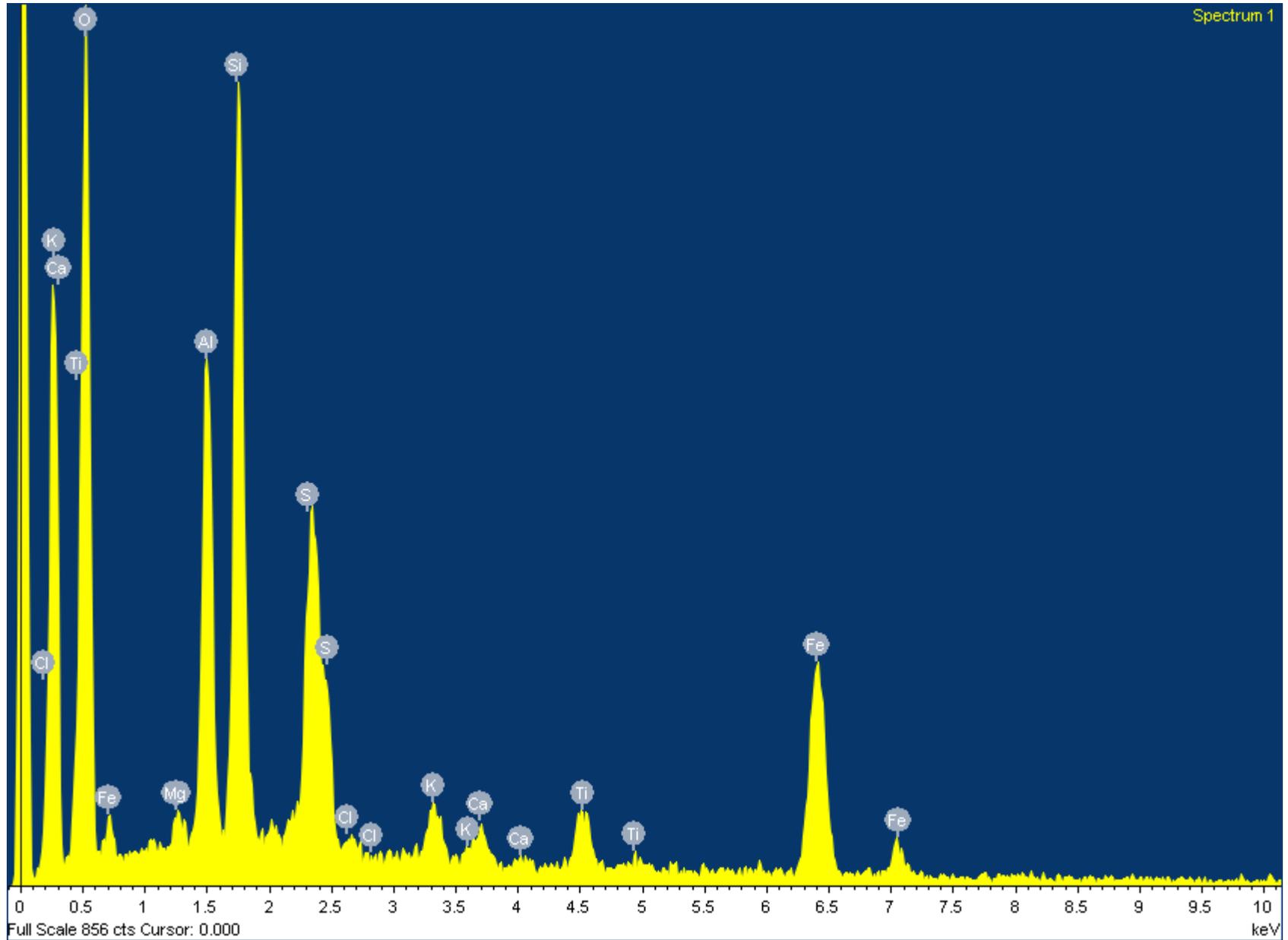
Appendix C:

S1GG Sample 1 32 μ m



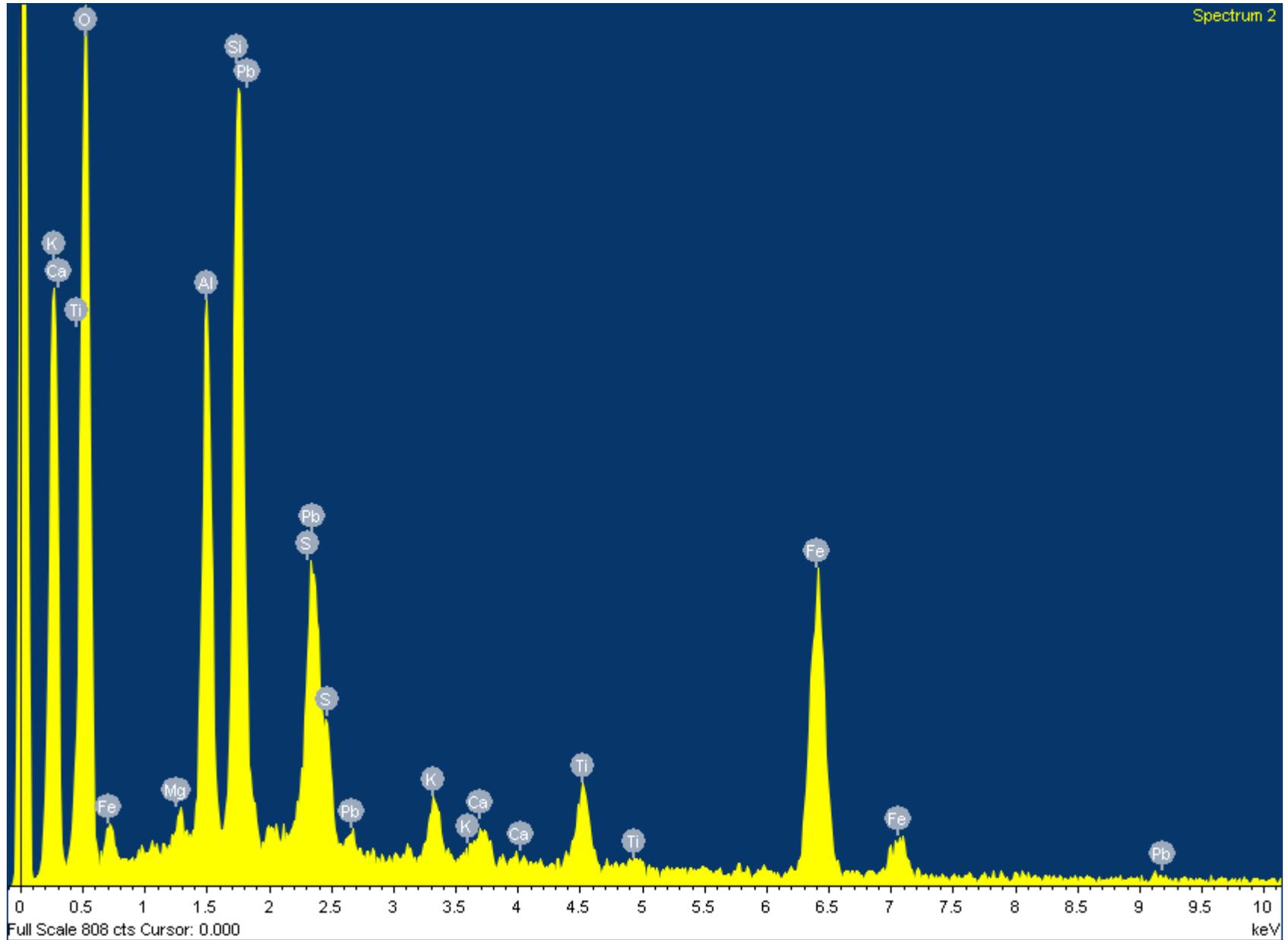
10 μ m

S1GG 32um Spread Out



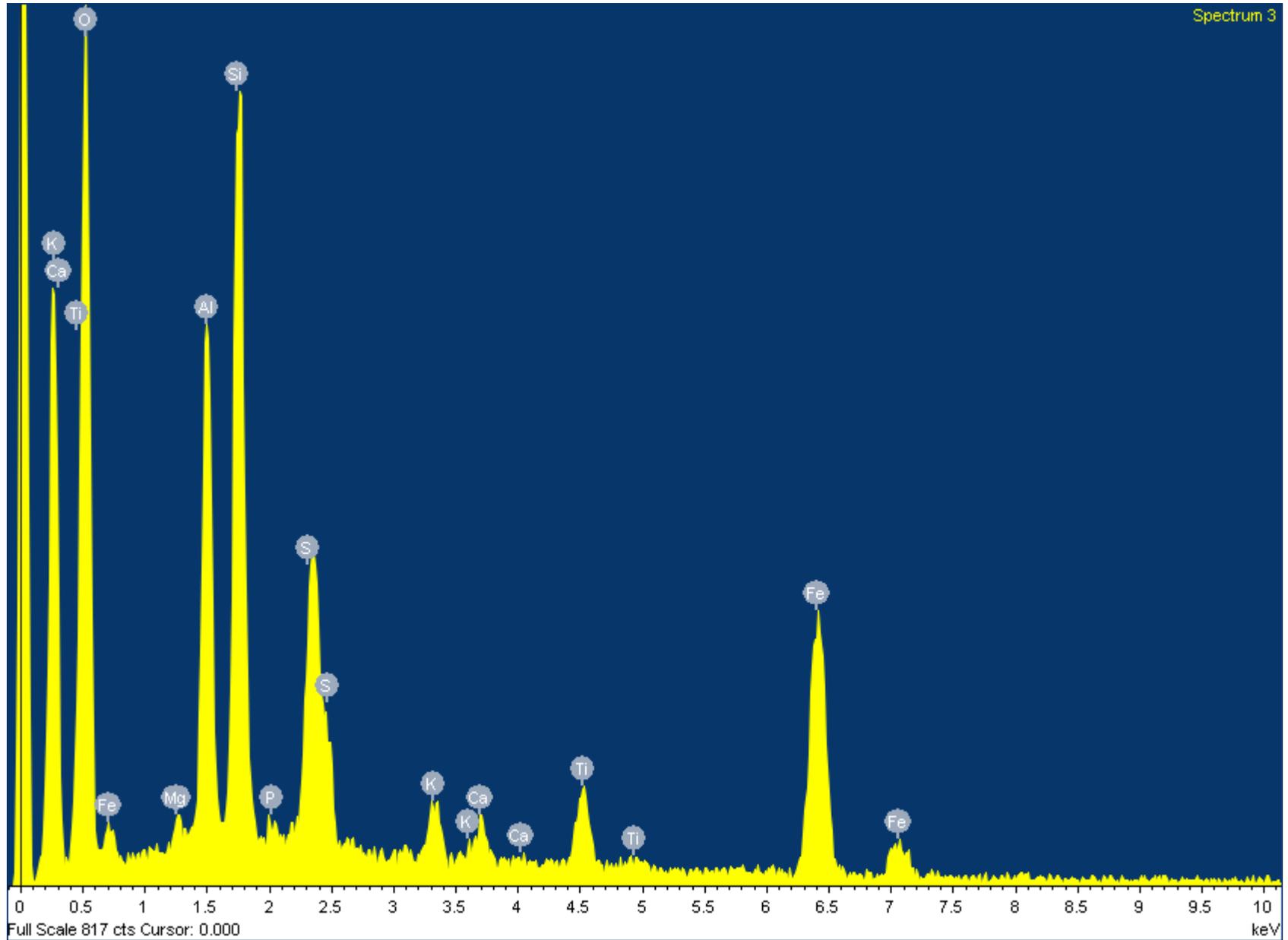
Comment:





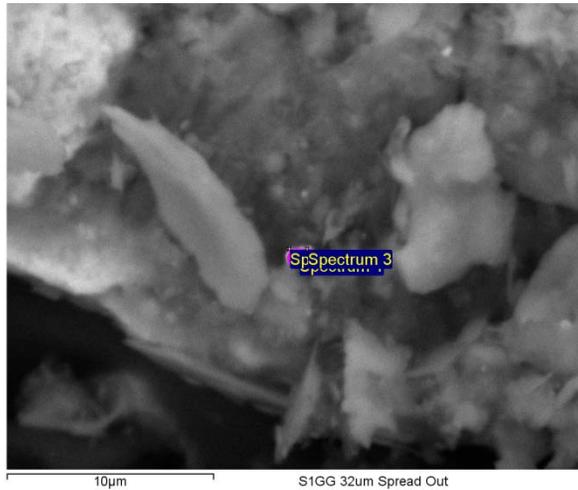
Comment:





Comment:





Spectrum processing:

No peaks omitted

Processing option: Oxygen by stoichiometry (Normalised)

Number of iterations = 3

Standard:

Mg MgO 1-Jun-1999 12:00 AM

Al Al2O3 1-Jun-1999 12:00 AM

Si SiO2 1-Jun-1999 12:00 AM

P GaP 1-Jun-1999 12:00 AM

S FeS2 1-Jun-1999 12:00 AM

K MAD-10 Feldspar 1-Jun-1999 12:00 AM

Ca Wollastonite 1-Jun-1999 12:00 AM

Ti 1-Jun-1999 12:00 AM

Fe 1-Jun-1999 12:00 AM

Processing option: Oxygen by stoichiometry (Normalised)

Element	Weight%	Atomic%	Compd%	Formula
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Spectrum	In stats.	Mg	Al	Si	P	S	Cl	K	Ca	Ti	Fe	Pb	O	Total
Spectrum 1	Yes	0.90	10.17	16.48		4.69	0.52	1.61	0.97	2.64	18.73		43.28	100.00
Spectrum 2	Yes	0.63	9.14	14.06		1.97		1.55	0.88	2.87	20.03	12.11	36.76	100.00
Spectrum 3	Yes	0.69	9.97	15.70	0.68	3.79		1.62	1.16	3.10	20.74		42.56	100.00

Comment:

