A Thesis Presented to

The Faculty of Alfred University

# MOBILITY OF HEAVY METALS FROM ILLEGAL GARBAGE BURN PILES IN WEST HAVEN,

# VERMONT

By

Roxanne Baker

In Partial Fulfillment of

the Requirements for

the Alfred University Honors Program

May 6, 2015

Under the Supervision of:

Chair: Michele Hluchy

Committee Members:

Frederic Beaudry

Justin Grigg

## ACKNOWLEDGMENTS

This thesis would have not been possible without the generous help of Michele Hluchy. Michele has been consistently patient and understanding in the face of all my questions and worries. I am grateful every day that I chose to attend Alfred University because I do not know of the existence of a better advisor or friend.

Fred Beaudry, Justin Grigg, and Nicole Munkwitz also offered copious amounts of help with this thesis and I am proud to be their student and friend.

I would like to acknowledge Catherine Tuxbury. Giving birth to me is already something to be grateful for, but she has always been available to me when this thesis became a weight I thought I could not carry. Always willing to read over my thesis drafts (though she has no understanding of the scientific practices I completed) and provided needed motivation. I have been, and will always be, grateful to be her daughter.

Finally, I would like to express my gratitude towards Kristen Tuxbury. Kristen always succeeds academically and by challenging herself she pushed me to challenge myself. What can I say, my family is competitive.

# TABLE OF CONTENTS

|                               | Page    |
|-------------------------------|---------|
| Acknowledgements              | 2       |
| List of Tables                | 4       |
| List of Figures               | 5       |
| Summary                       | 6 – 9   |
| Abstract                      | 10 - 11 |
| I. Introduction               | 12 - 14 |
| II. Methods                   | 15 - 18 |
| III. Results                  | 19 - 22 |
| IV. Discussion and Conclusion | 23 - 27 |
| V. Literature Cited           | 28 - 29 |
| Appendix I                    | 30 - 31 |
| Appendix II                   | 31 - 32 |
| Appendix III                  | 32      |
| Appendix IV                   | 33      |
| Appendix V                    | 33 - 34 |

# LIST OF TABLES

Table 1. Mango surface soil samples with initial bulk chemistry concentrations of lead, zinc, andbarium. Page 6.

Table 2. Soil sample locations, soil types, and sample collection dates (Mango, 2013). Page 16.

Table 3. Reagent blank for each of the four PBASE phases. Page 17.

Table 4. Soil characteristics for each soil type in West Haven, VT. Page 23.

## LIST OF FIGURES

Figure 1. ArcGIS map of West Haven, VT burn pile locations, land type of that location, and soil classifications beneath the burn piles. Page 7.

Figure 2. Leaching method Potentially BioAvailable Sequential Extraction (PBASE). Page 15.

Figure 3. Diagram of inductively coupled plasma – optical emission spectrometry (ICP-OES). Page 18.

Figure 4. XRD results for surface soil sample WH-11-13-1. Page 20.

Figure 5. XRD results for surface soil sample WH-11-13-6. Page 20.

Figure 6. Average concentrations of barium in extractant from six surface soil samples for each of the PBASE leaching phases (mg/kg). Page 21.

Figure 7. Average concentrations of zinc in extractant from six surface soil samples for each of the PBASE leaching phases (mg/kg). Page 21.

Figure 8. Average concentrations of lead in extractant from six surface soil samples for each of the PBASE leaching phases (mg/kg). Page 22.

#### SUMMARY

The purpose of this study is to evaluate the threat of three toxic heavy metals to the environment based on their estimated bioavailability and mobility. Since 2013 Helen Mango, Department of Natural Sciences at Castleton State College, has been collecting data from illegal garbage burn piles in the West Haven, Vermont area. Six samples were chosen from Mango's study to determine concentrations of lead, zinc, and barium. Mango's bulk chemical analysis was used to obtain an estimation of the concentrations of these metals in the six surface soil samples chosen for this study (Table 1). Mango's (2013) study showed that ash and soil at the burn pile sites contain elevated concentrations of several metals, indicating that metals in the burned garbage are contaminating surface and some subsurface soils.

Table 1. Mango surface soil samples with initial bulk chemistry concentrations of lead, zinc, and barium (Mango, 2013).

| Analyte Symbol<br>Unit Symbol<br>Detection Limit<br>Analysis<br>Method | Sample                                     | Pb<br>ppm<br>3<br>TD-<br>ICP | Zn<br>ppm<br>1<br>MULT INAA / TD-<br>ICP | Ba<br>ppm<br>50<br>INAA |
|--|--|------------------------------|--|-------------------------|
| WH-11-13-1   | Burn Pile 1 solid surface material         | > 5000                       | 12500                                    | 7480                    |
| WH-11-13-3   | Burn Pile 1 ash from surface               | 1300                         | 10700                                    | 1970                    |
| WH-11-13-6   | Surface soil between Burn Pile 1 and river | 167                          | 408                                      | 450                     |
| WH-11-13-11C   | Burn Pile 2, surface                       | 196                          | 494                                      | 530                     |
| WH-11-13-15  | Burn Pile 3, surface                       | 122                          | 467                                      | 520                     |
| WH-3-14  | Burn Pile 4                                | 628                          | 4660                                     | 780                     |

Soil samples, bulk chemistry data, and the related study of the appearance of heavy metals from trash burning sites were used in this study (Mango 2013). A map was constructed of the area of interest and the four burn pile sites using location data provided by Mango. A shapefile from Web Soil Survey



West Haven, Vermont Garbage Burning Locations

Figure 1. ArcGIS map of West Haven, VT burn pile locations, land type of that location, and soil classifications beneath the burn piles.

containing information about soil types and soil characteristics for the region was added to the map (Figure 1). The resulting map identifies where each burn pile is located and also shows what soil type is present beneath each burn pile. Soil type and characteristics provide information that can be useful when determining the possible extent of leaching and erosion in this area. A Scanning Electron Microscope and X-ray Diffractometer were used in an attempt to determine what metals were present and to estimate the concentrations of those metals. However, the results from both procedures were inconclusive, possibly because of high organic matter content that interfered with the results.

A soil leaching procedure was performed in triplicate after choosing six samples from Mango's study, all of which are surface soil samples with at least one sample from each of the four burn piles discovered during the duration of Mango's study. This leaching method, described in a paper by Basta (2000), is referred to as Potentially BioAvailable Sequential Extraction (PBASE).

PBASE involves four extraction phases. In phase 1 the most readily available heavy metals are exchanged off the surfaces of the soil. Phase 2 extracts acid-soluble metals that may be present in weaker complexes. Phase 3 extracts surface complex metals and precipitates. Phase 4 extracts the very insoluble metals from each soil sample (Figure 2). Each phase is sequential in the leachable extraction of heavy metal; thus, estimation of metal mobility can be inferred for each of the six samples.

Mango analyzed bulk chemistry for each soil sample to determine concentrations of gold, copper, lead, nickel, zinc, arsenic, barium, bromine, calcium, chromium, iron, manganese, and antimony. This study is focused on determining concentrations of lead, zinc, and barium for each of the six samples in sequential phases of leaching.

An Inductively Coupled Plasma Atomic Emission-Optical Emission Spectrometry (ICP-OES) was used to determine the concentrations of lead, zinc, and barium for each of the four PBASE phases after PBASE leaching was completed for each sample. A set of standards for each metal was used to create a calibration curve for the ICP.

Results of the replicate ICP analysis were averaged and graphs of these data can be found in Figures 6, 7, and 8. The bioavailability of each metal was compared to the four sequential PBASE phases and it is apparent that some of the samples show higher concentrations of bioavailable metals with extended leaching. The more bioavailable metals that are leached from the soil contribute to an increase in the movement of these metals through the subsurface, i.e. mobility.

The extent of heavy metal mobility in West Haven, VT can be estimated by comparing the apparent PBASE bioavailability of these metals to the soil characteristics obtained from Web Soil Survey. The results indicate that Burn Pile 1 does not promote high mobility, as the soil beneath is poorly drained and has a low runoff potential. Thus, the immediate danger of heavy metal pollution to the surrounding area of Burn Pile 1 is low. However, contamination from Burn Pile 4 will most likely be a danger to the surrounding environment because of its high runoff potential.

There is a danger of contamination and pollution of the West Haven area without remediation. In time these heavy metals will probably be able to infiltrate the soil and move into the surrounding surface and groundwater environments even in poorly drained soils.

#### ABSTRACT

The soils from illegal garbage burning sites in West Haven, Vermont were sampled and it was determined that heavy metals, presumably from the garbage, migrated downward into the soil. Soil samples, bulk chemistry data, and the related study of the appearance of heavy metals from trash burning sites were used in this study (Mango 2013).

A map was constructed of the area of interest and the four burn piles using location data provided by Mango. A shapefile from Web Soil Survey containing information about soil types and soil characteristics for the region was added to the map (Figure 1). The resulting map identifies where each burn pile is located and also shows what soil type is present beneath each burn pile. Soil type and characteristics provide information that can be useful when determining the possible extent of leaching and erosion in this area.

A Scanning Electron Microscope and X-ray Diffractometer were used in an attempt to determine what metals were present and to estimate the concentrations of those metals. However, the results from both procedures were inconclusive, possibly because of high organic matter content that interfered with the machines.

A soil leaching procedure was performed in triplicate after choosing six samples from Mango's study, all of which are surface soil samples, with at least one sample from each of the four burn piles discovered during the duration of Mango's study. This leaching method, described in a paper by Basta (2000), is referred to as Potentially BioAvailable Sequential Extraction (PBASE).

An Inductively Coupled Plasma Atomic Emission-Optical Emission Spectrometer (ICP-OES) was used to determine the concentrations of lead, zinc, and barium for each of the four PBASE phases after PBASE leaching was completed for each sample. Sample WH-11-13-1 from Burn Pile 1 contained significant concentrations of all three metals, although sample WH-3-14 from Burn Pile 4 displayed the highest concentrations of zinc.

The characteristics of the soil beneath Burn Pile 1 would not promote movement of metals because the soil is poorly drained and has a low runoff potential. Thus, the immediate danger of heavy metal pollution to the surrounding area of Burn Pile 1 is low. However, contamination from Burn Pile 4 will most likely be a danger to the surrounding environment because the soil has a high runoff potential.

## I. INTRODUCTION

Illegal garbage dumping and burning is not uncommon in the United States. People dump and burn their garbage in various locations as a means to avoid the costs of proper garbage disposal (White, 2015). The burning of dumped garbage may be an attempt to further disguise the illegal dumping, or to avoid harsher punishment if caught because it is hard to decipher what the contents of the pile were before burning. Legal repercussions for illegal garbage dumping vary by state. Misdemeanors are most common for people caught dumping, but conviction of a felony is possible with repeated dumping (White, 2015).

Many heavy metals can be toxic and are also capable of contaminating soils, groundwater sources, and vegetation. Elevated concentrations of bioavailable heavy metals introduce a severe health risk to surrounding ecosystems. Bioavailable heavy metals are an environmental danger because they can affect humans and other biota through multiple exposure pathways. Two of the exposure pathways that are most relevant to this study are: 1) exposure to food webs via plant uptake, and 2) exposure to ingestion of heavy metals in contaminated soils through hand-to-mouth contact (Basta, 2000).

Exposure to high concentrations of heavy metals can result in severe health problems. Heavy metal exposure can damage the central nervous system, the cardiovascular system, the respiratory system, and the skeletal system. This damage can hinder mental and physical development. For example, lead poisoning damages the central nervous system and interferes with mental development in children that are exposed to available lead at a young age. Contact with toxic heavy metals also leads to an increase in cancer risk as the body is damaged or weakened from initial exposure (Heavy Metal Detoxification, 2015).

Heavy metals in soils are usually in molecular form and bound to other elements or molecules in the soil. Any accessible metals would exist within pore spaces and move with the transfer of water (Soil Quality Indicators, 1998). pH is one of many factors that can affect the bioavailability and

12

mobility of heavy metals. Free hydrogen ions in low pH soils can exchange for heavy metals on the surfaces of soil particles, releasing them to the liquid portion of the soil, which allows them to migrate or be taken up by vegetation. Garbage burning releases significant quantities of particles and trace gases into the atmosphere due to the physical and chemical reactions that occur when burning different materials. Burning trash may also be a major source of hydrochloric acid formed by the chemical decomposition of plastics and coated metals (Christian et al., 2010). The release of hydrochloric acid when burning garbage will acidify adjacent soils and increase the mobility of metals in the soil.

pH has a large impact on the bioavailability and mobility of heavy metals, but other anthropogenic processes can also affect metal mobility in soils. An example of an anthropogenic process that affects mobility is leaking from underground gasoline tanks that can introduce many toxic chemicals, including heavy metals, to surrounding soils and groundwater systems. Some of the leaked material may bind to soil particles or undergo ion exchange to become incorporated into the molecular structure of the soil. However, if it is a large spill most of the contaminant will most likely move with the flow of water through the pore spaces in the soil (Schalscha, 1982).

The working definition of bioavailable in this study is the ability to be absorbed by an organism when available in the immediate environment (Semple et al., 2004). High concentrations of bioavailable metals can be dangerous. Introduction of these metals from either of the exposure pathways previously listed is a major health risk to biota due to the metals' toxicity. The contents of burn piles before their incineration is often unknown. The action of burning these unknown items may have released toxic metals into the environment. The most common source of available lead is lead-based paint. High concentrations of barium and zinc can also be found in paints. Lead based paint is no longer used today, but disposal of old window frames, walls, and wood that were painted previously with lead based paint can be difficult and expensive. Large quantities of Ba and Zn are also found within other commonly dumped items such as rubber, nails, plastics, batteries, tiles, vacuum tubes, and

13

spark plugs (Lenntech, Thomas Jefferson National Accelerator Facility, 2015).

The effect of bioavailability and mobility of these heavy metals from illegal garbage burn piles has yet to be determined. The purpose of this study is to evaluate the threat of heavy metals to the environment based on their estimated bioavailability and mobility.

Over the past two years Helen Mango, Department of Natural Sciences at Castleton State College, has been identifying and collecting soil samples from illegal garbage burn piles in the West Haven, VT area. A preliminary study has provided bulk chemical compositions for each soil sample collected. This study is focused on determining the bioavailability and mobility of only three heavy metals (Pb, Ba, Zn) in surface soils collected at Mango's sites. Six samples of the surface soil were chosen for this study with at least one sample from each of the four burn piles. This research concentrates on Pb, Ba, and Zn because in the initial chemical analysis performed by Mango (2013) these three metals displayed the highest concentrations in the six samples chosen to be analyzed. Thus, these samples represented a "worst case scenario" for the site.

All of Mango's sites are less than a half mile from the New York State border in Rutland County Vermont. The Poultney River borders the private conservation land where the sites are located and the river is also down slope of all four burn piles as seen in Figure 1. All samples used in this study, except one (WH-11-13-6), were taken directly from burn piles. Sample WH-11-13-6 was collected between Burn Pile 1 and the adjacent Poultney River. This surface sample was included in the study in the hopes of determining the rate of mobility of bioavailable heavy metals over the ground surface. The results may help to determine if the river is being contaminated from heavy metal runoff.

## **II. METHODS**

Metal bioavailability was determined using a procedure published by Basta (2000) which involves four sequential leaching phases called Potentially BioAvailable Sequential Extraction (PBASE), see Figure 2. Metals removed during phase 1 come from exchange sites and are the most readily available heavy metals. Phase 2 extracts acid-soluble metals that may be present in weaker complexes. Phase 3 extracts surface complex metals and precipitates. Phase 4 extracts the very insoluble metals from each soil sample. Mobility and bioavailability was estimated using the results of the extractions and the soil characteristics of the soils found beneath each burn pile.



# PBASE Procedure

Figure 2. Leaching method Potentially BioAvailable Sequential Extraction (PBASE) from Basta (2000), p. 153.

All four identified trash burn piles were found on private conservation land in West Haven, VT (Rutland County), as depicted in Figure 1. Burn Piles 1 and 2 are located on Aquents soils in the Histosol soil order, Burn Pile 3 is located on Vergennes clay, and Burn Pile 4 is located on Kingsbury silty clay loam soil (Table 2). The characteristics of these soils are described in Appendix 1.

| Sample ID    | Sample   | Soil Type                       | Sample Date |
|--------------|--|---------------------------------|-------------|
| WH-11-13-1   | Burn Pile 1 solid surface material                                   | Aquents                         | Nov. 2013   |
| WH-11-13-3   | Burn Pile 1 ash from surface<br>Surface soil between Burn Pile 1 and | Aquents                         | Nov. 2013   |
| WH-11-13-6   | river  | Aquents                         | Nov. 2013   |
| WH-11-13-11C | Burn Pile 2, surface   | Aquents                         | Nov. 2013   |
| WH-11-13-15  | Burn Pile 3, surface   | Vergennes<br>Clay               | Nov. 2013   |
| WH-3-14      | Burn Pile 4 surface  | Kingsbury<br>Silty Clay<br>Loam | March 2014  |
|              |  |                                 |             |

Table 2. Soil sample locations, soil types, and sample collection dates (Mango, 2013).

The dates of these trash burnings are unknown, but based on the limited erosion that has occurred on the surface of each pile, burning has been fairly recent (probably a maximum of 3 years old). Burn Pile 1 is noticeably the most recent as ash was still able to be collected for sampling. Five of the six samples analyzed in this study were collected in November of 2013. WH-3-14 was collected in March of 2014 after its discovery by Mango. No controls were available for this study because it is not known how far or fast these metals have migrated into the surrounding soil before samples were taken. For future study it may prove beneficial to collect soil sample up slope from each pile in an attempt to analyze how much Pb, Ba, or Zn are naturally occurring in the soils upon which each burn pile resides.

The PBASE four phase leaching method was performed on the six samples. The step by step procedure can be found in Appendix II and lab observations made throughout the procedure are in Appendix III. The procedure was run in triplicate for each of the six samples. All samples were collected by Mango using a trowel and stored in whirl-pack sterile bags. Initial results received from the Atomic Absorption Spectrometer were inconclusive so an Inductively Coupled Plasma Atomic Emission – Optical Emission Spectrometer (Perkin Elmer Optima 8000 ICP-OES) was used to determine the heavy metal concentrations in each extractant. Every sample and reagent blank was diluted by a 1:10 ratio so that high element concentrations would not damage the machine. Reagent blanks consisting of the solution used for each phase of leaching (Phase 1 and 2 included an addition of 0.5ml of 12.1 N HCl, Table 3) were analyzed along with samples and standards. The concentration of lead, zinc, and barium in each reagent blank was subtracted from the concentration found in each sample.

Several samples were observed under an Environmental Scanning Electron Microscope (Quanta 200F manufactured by FEI Co., INC.) in an attempt to locate high concentrations of barium, zinc, and/or lead in the soils. This analysis was not successful because there were too many variables that could be affiliated with preferred metal bonding sites. For example, lead was found present on wood particles in a sample, but it could not be determined if the lead prefers bonding to wood over other soil particles or if the lead was present on this wood as a remnant of lead based paint. Some samples were also powdered and analyzed by an X-ray Diffractometer (Bruker D2 Phaser) to determine bulk mineralogy. However, large organic matter concentrations present caused high background noise that interfered with analysis.

ICP-OES uses light emitted from an element to determine concentration (Figure 3). Analyte within the sample are first excited, and absorb energy, moving their electrons into higher orbital shells which then return to ground state, emitting light energy. The wavelength emitted is specific to an element. The ICP-OES detects the visible and ultra-violet light emitted by metals and uses that to determine the concentration of that analyte in a sample. Plasma, created when ionized gas is at extremely high temperature, is used to excite electrons in an ICP-OES. Argon gas is usually used as a support gas to create the plasma at common temperatures of around 9000 Kelvin (Zhang, 2007). Table 3. Reagent blank for each of the four PBASE phases.

```
Phase 1:Reagent Blank 1:0.5 M Ca(NO3)2 solution with 0.5 mL 12.1 N HClPhase 2:Reagent Blank 2:1 M NaOAc solution, adjusted to pH 4.96 with 0.5 mL 12.1 N HClPhase 3:Reagent Blank 3:0.1 M Na2EDTA solution adjusted to pH 7.07 with 1M NaOHPhase 4:Reagent Blank 4:4 M HNO3 solution
```

```
Phase 1: Reagent Blank 1: 0.5 M Ca(NO3)2 solution with 0.5 mL 12.1 N HCl
Phase 2: Reagent Blank 2: 1 M NaOAc solution, adjusted to pH 4.96, with 0.5 mL 12.1 N HCl
Phase 3: Reagent Blank 3: 0.1 M Na2EDTA solution adjusted to pH 7.07
Phase 4: Reagent Blank 4: 4 M HNO3 solution
```



223.

Figure 3. Diagram of inductively coupled plasma – optical emission spectrometry (ICP-OES) from Zhang, 2007, p.

An advantage of using an ICP-OES, axial view, over an Atomic Absorption Spectrometer (AAS) was that an ICP-OES has a lower detection limit than the AAS. This provides more accurate concentration readings for samples with lower quantities of heavy metals. Another advantage of an ICP-OES is its ability to analyze multiple elements at the same time, where an AAS requires the changing of hollow cathode lamps for the analysis of multiple elements; this reduces the amount of time needed in the lab to determine results.

Careful lab procedures were followed to decrease possible sources of error in the PBASE leaching procedure. For example, deionized water to rinse and clean all equipment in the lab helped to diminish sample contamination during each phase of leaching. However, some error in sample heavy metal concentrations may have been caused by accidental dilution of the samples (a few drops of deionized water may have been present in equipment that caused unintentional dilution). There may also have been cross contamination between samples in an effort to minimize particle loss between phases when the dried filters of the last phase of solution were dipped into the centrifuge tubes containing the next phase solution. Minute traces of the reagent from the previous sample may have transferred into the next phase solution when dipping these filters.

### **III. RESULTS**

Two of the six soil samples were analyzed using the XRD (WH-11-13-1, WH-11-13-6). The resulting data did not show the presence of any crystalline materials containing heavy metals (figures 5 and 6). Only these two samples were analyzed because they showed the highest concentrations of all three heavy metals in Mango's bulk chemical analysis, but quantities high enough to be detected by XRD were not found; thus, the remaining samples were not analyzed for crystalline materials containing heavy metals. Minerals found in the samples included typical soil minerals such as quartz and feldspar. The uncertainty of there being any detectable quantities of crystalline material containing heavy metals may have been due to high organic matter content, as the samples were surface soils, causing elevated background in some of the results.

Results obtained from the Environmental Scanning Electron Microscope did not signify that there were large concentrations of lead, zinc, or barium present, but every particle of soil was not analyzed. Figures 6, 7 and 8 show the concentrations of Ba, Zn, and Pb in the extractants from the PBASE procedure.

Surface soil sample WH-11-13-1 had the highest overall Ba concentration and most of that Ba is in the occluded fraction (metals retained by substances in the soil). Ba concentrations in the other samples were relatively low (< 580 mg/kg soil)

All samples, with the exception of WH-3-14, showed concentrations of zinc less than the EPA standard limit of 3500 mg/kg soil. Sample WH-3-14 had extremely high concentrations of zinc in the last three phases of the PBASE leaching method. Since these zinc concentrations appeared high in all but the first phase of PBASE, it is apparent that the zinc is not present in easily soluble or exchangeable

forms in any of the burn piles. However, with a little acidification the zinc could become easily mobile.

Finally, with the exception of sample WH-11-13-1, the lead concentrations are low within all the samples. Lead concentrations in WH-11-13-1 are high for phases 2, 3, and 4, but almost non-existent in phase 1.



Figure 4. XRD results for surface soil sample WH-11-13-1.

b/w burnpile 1 and river surface (Coupled TwoTheta/Theta)



Figure 5. XRD results for surface soil sample WH-11-13-6.



Figure 6. Average concentrations of barium in extractant from six surface soil samples for each of the PBASE leaching phases (mg/kg).



Figure 7. Average concentrations of zinc in extractant from six surface soil samples for each of the PBASE leaching phases

(mg/kg).



Figure 8. Average concentrations of lead in extractant from six surface soil samples for each of the PBASE leaching phases (mg/kg).

#### IV. DISCUSSION AND CONCLUSION

The three heavy metals tested have a low initial bioavailability. However, we can infer from the PBASE results that any long term weathering that may occur can increase the amount of bioavailable lead, zinc, and barium in soils. Overall, the samples from Burn Pile 1 are the most concerning since they have elevated concentrations of all three heavy metals analyzed. Although the soil below Burn Pile 1 has low drainage potential the soil is still slightly porous and permeable, so if chemical conditions are such that metals are released, they will mobilize and possibly move downward through the soil. Bioavailability and mobility of metals has been shown to be directly proportional and metals tend to follow the flow of water in soil once in bioavailable form (Violante et al., 2010). Thus, immediate remediation of this site would decrease any metal bioavailability and mobility that may lead to further environmental harm.

Soil properties are of extreme importance since they can help estimate how heavy metals from each of these burn piles will move through the soils by leaching and erosion (Table 4). A.T. de Matos et al. (2001) study concluded that soil types and soil horizons influenced the mobility of metals. The heavy metals located in Burn Piles 1 and 2 will most likely have limited mobility in the short term because Aquent soils in the Histosol order have poor natural drainage and little runoff. However, long-term leaching in this area may eventually carry heavy metals to lower soil horizons or even to the groundwater zone.

| Burn Piles  | Soil Type                              | Drainage Potential | <b>Runoff Potential</b> |  |
|-------------|--|--------------------|-------------------------|--|
| Burn Pile 1 | Aquents                                | Almost None        | Very Low                |  |
| Burn Pile 2 | Aquents                                | Almost None        | Very Low                |  |
| Burn Pile 3 | Vergennes Clay<br>Kingsbury Silty Clay | Moderate           | High                    |  |
| Burn Pile 4 | Loam                                   | Low                | High                    |  |

Table 4. Soil characteristics for each soil type in West Haven, VT.

The heavy metals from Burn Pile 3 are more likely to be washed off the surface of the soil and travel laterally than to be transported vertically in the subsurface because the Vergennes clay upon which Burn Pile 3 is located has low permeability and therefore high runoff potential.

The Kingsbury silty clay loam soil upon which Burn Pile 4 is located has high runoff potential, but very poor drainage and ability to transmit water. These characteristics suggest that leached heavy metals will be more likely to be transferred through runoff to the nearby stream. This can be highly dangerous because runoff can transfer these toxic metals to a larger area by being introduced to the stream.

Almost all samples show moderate bioavailability of barium in the first PBASE phase, which suggests that these samples all have some easily soluble or exchangable forms of barium. WH-11-13-1 shows a greater barium concentration in the fourth PBASE phase. This higher concentration indicates that barium is in the soil in an occluded form. Barium results from all four burn piles suggest only a mild risk of environmental contamination as none of the samples contain concentrations that exceed Environmental Protection Agency limits (15000 mg/kg of soil); (EPA, 2015).

Burn Pile 4 is at risk of contaminating surrounding environments due to the presence of elevated zinc concentrations. The soil characteristics of Kingsbury silty clay loam soil do not promote the mobility of metals in the soil because it has poor drainage and water transmitting abilities. However, this soil type promotes high runoff quantities. Hence, the large concentrations of bioavailable zinc will be transported with runoff into the adjacent stream and environments downstream of Burn Pile 4.

The highest concentrations of zinc were leached from occluded forms. Occluded metals are very insoluble because they are retained within the soil as a complex molecule. High concentrations of zinc available from leached occluded structures imply that most of the zinc present is strongly retained by substances in the soil. High zinc concentrations from Burn Pile 4 will move through runoff to contaminate adjacent environments and the local stream system if remediation is ignored. However, none of the burn piles contained enough zinc to violate the 23,000 mg/kg limit set by the EPA.

The last three PBASE leaching phases of sample WH-11-13-1 showed highly elevated concentrations of lead. This is the only sample that contained heavy metal concentrations that exceeded EPA limits. Burn Pile 1's lead concentrations surpassed the 800 mg/kg limit set by the EPA (2015). The high concentrations of lead from extraction phases 2, 3, and 4 indicate that lead within this sample exists in acid-soluble, surface complex, and occluded forms. Soils in the West Haven region are likely already acidic due to acidic precipitation. Thus, the easily soluble and exchangeable bioavailable forms and the acid soluble bioavailable forms of lead in this soil are an environmental risk.

Sample WH-11-13-6 had very low concentrations of Pb, Ba, and Zn in all PBASE phases. Since this sample was collected between Burn Pile 1 and the river it is possible that none of the high concentrations of Pb, Zn, or Ba is moving over the ground surface into the river. However, it is still unknown if contaminants may be moving from Burn Pile 1 to the river through the subsurface, or if

25

they were transported over the ground surface previously. In future research it may be helpful to take samples at increasing distances from Burn Pile 1 towards the river. The concentrations of heavy metals at varying distances from the pile may help determine how fast these contaminants are moving or if they are moving over the ground surface at all.

ICP analysis offers total concentration results for metals, but it cannot identify what form these metals take in a sample. The PBASE procedure separates the leaching process into sequential phases so that inferences can be made about where and how these metals are present in the soil. Each heavy metal displayed high concentrations during the fourth phase of PBASE. This signifies that there is a high concentration of these metals in occluded form in the soils. There is less of an environmental risk of these occluded metals contaminating the environment compared to the bioavailable metals present in the other three phases because extensive chemical weathering would have to occur in nature to duplicate phase 4 leaching in PBASE. The concentrations of bioavailable lead, zinc, and barium in the first two phases poses the highest environmental risk because phase 1 represents easily soluble forms of metal and phase 2 represents acid-soluble forms of metal. Precipitation in the West Haven area is already slightly acidic due to acid rain; hence, the most likely form of leaching in nature will be similar to phases one and two of PBASE.

Remediation of these burn piles should not be ignored because any long term leaching of these sites will lead to increased bioavailability and mobility of barium, lead, and zinc. The cleanup of these heavy metals, remediation, depends on the level of contamination. The higher concentrations of these metals in the soil may require more extensive remediation methods such as soil washing and excavation. Excavation of the dangerously contaminated sites may be necessary, followed by treatment to immobilize bioavailability of these metals. An increase in bioavailability and mobility of these metals raises the risk of toxic contamination. Given enough time, these metals will move through the soil or over the ground surface to contaminate nearby areas. However, the response of these metals may

26

vary from those obtained in this study due to differences between lab and field conditions. While the PBASE procedure can give an indication of the likelihood of metals mobilizing under different conditions, there are too many variables in nature to perfectly predict how metals will act in soils (Johnson et al., 1996).

There are many suggested methods for preventing illegal garbage dumping, including site maintenance and controls, community outreach and involvement, targeted enforcement, and program measurement (Illegal Dumping Prevention Guidebook, 1998). Of these methods, I believe that community outreach and involvement would be best strategy to use to prevent future dumping. Since these piles were anonymously dumped and burned, these unidentified perpetrators will probably not feel legal repercussions of their actions. Community outreach and involvement will expose more people to what is happening and the negative environmental and health risks associated with burning garbage. The chance of someone witnessing future dumping and reporting it to the police increases as more people become aware the situation. The landowner of this West Haven private land may have to pay for the remediation of these sites because the perpetrators of this illegal garbage burning are still unknown. However, the West Haven community may choose to contribute to remediation of these local sites because contamination of the river can affect anyone living downstream.

### **VI.LITERATURE CITED**

- Basta, N. (2000). Estimation of Cd, Pb, and Zn Bioavailability in Smelter-contaminated Soils by a Sequential Extraction Procedure: *Journal of Soil Contamination*, *9*.2, 149-64.
- Christian, T. J. and Yokelson, R. J. and C\'ardenas, B. and Molina, L. T. and Engling, G. and Hsu, S.-C. (2010). Trace gas and particle emissions from domestic and industrial biofuel use and garbage burning in central Mexico. *Atmos. Chem. Phys.*, *10.2*, 565-584. Retrieved April, 2015, from http://www.atmos-chem-phys.net/10/565/2010/
- de Matos, A.T. and Fontes, M.P.F. and da Costa, L.M. and Martinez, M.A. (2001). Mobility of heavy metals as related to soil chemical and mineralogical characteristics of Brazilian soils:
   *Environmental Pollution*, 111.3, 429-435, ISSN 0269-7491, http://dx.doi.org/10.1016/S0269-7491(00)000889.

(http://www.sciencedirect.com/science/article/pii/S0269749100000889)

- Environmental Guidelines and Standards (2015). Retrieved April, 2015, from http://www.esdat.com.au/Environmental\_Standards.aspx
- Heavy Metal Detoxification. (n.d.). Retrieved April, 2015, from http://www.lef.org/protocols/healthconcerns/heavy-metal-detoxification/page-01?checked=1
- Illegal Dumping Prevention Guidebook EPA Region 5 (1998). Retrieved April, 2015, from http://www.epa.gov/region5/waste/illegal\_dumping/downloads/il-dmpng.pdf

Johnson, C.A. and Kersten, M. and Ziegler, F. and Moor, H.C. (1996). Leaching behaviour and solubility — Controlling solid phases of heavy metals in municipal solid waste incinerator ash: *Waste Management*, *16*.1–3, 129-134, ISSN 0956-053X, http://dx.doi.org/10.1016/S0956-053X(96)000360.(http://www.sciencedirect.com/science/article/pii/S0956053X96000360)

Lenntech, B.V. Barium - Ba. (1998-2015). Retrieved April, 2015, from http://www.lenntech.com/periodic/elements/ba.htm

- Mango, H. (2013). Soil contamination associated with illegal burn piles in West Haven Vermont: NEGSA, Unpublished study.
- Schalscha, E. B. (1982). Chemical Fractionation of Heavy Metals in Wastewater-Affected Soils. Journal (Water Pollution Control Federation), 54.2, 175-180. Retrieved April, 2015, from http://www.epa.gov/superfund/remedytech/tsp/download/issue14.pdf
- Semple, K. T. and Doick, K. and Jones, K. and Burauel, P. and Craven, A. and Harmsufz, H. (2004). Defining Bioavailability and Bioaccessibility of Contaminated Soil and Sediment is Complicated: *Environmental Science & Technology*. 229A-231A. Retrieved April, 2015, from http://lqma.ifas.ufl.edu/sws6262/handout/semple-04.pdf
- Soil Quality Indicators: PH. Indicators PH (1998). Retrieved April, 2015, from http://urbanext.illinois.edu/soil/sq\_info/ph.pdf
- Thomas Jefferson National Accelerator Facility Office of Science Education. The Element Zinc. Retrieved April, 2015, from http://education.jlab.org/itselemental/ele030.html
- Violante, A. and Cozzolino, V. and Perelomov, L. and Caporale, A.G. and Pigna, M. (2010).
  Mobility and Bioavailability of Heavy Metals and Metalloids in Soil Environments: *J. Soil. Sci. Plant Nutr, 10.3, 268 – 292.* Retrieved April, 2015, from http://www.scielo.cl/pdf/jsspn/v10n3/art05.pdf
- Web Soil Survey: Retrieved April, 2015, from www.websoilsurvey.sc.egov.usda.gov.
- White, C. (n.d.). Illegal Dumping: Laws, Penalties, & Defenses | Criminal Law. Retrieved April, 2015, from http://www.criminaldefenselawyer.com/crime-penalties/federal/Illegal-Dumping.htm
- Zhang, C. (2007). Fundamentals of Environmental Sampling and Analysis: John Wiley & Sons Inc. 220-243.

## **APPENDIX 1**

## Vergennes clay

#### **Properties and qualities**

Slope: 8 to 15 percent Depth to restrictive feature: More than 80 inches Natural drainage class: Moderately well drained Runoff class: Very high Capacity of the most limiting layer to transmit water (Ksat): Very low to moderately low (0.00 to 0.06 in/hr) Depth to water table: About 12 to 36 inches Frequency of flooding: None Frequency of ponding: None Available water storage in profile: Moderate (about 6.0 inches)

#### Kingsbury silty clay loam

#### **Properties and qualities**

Slope: 0 to 3 percent Depth to restrictive feature: More than 80 inches Natural drainage class: Somewhat poorly drained Runoff class: Very high Capacity of the most limiting layer to transmit water (Ksat): Very low to moderately low (0.00 to 0.06 in/hr) Depth to water table: About 6 to 18 inches Frequency of flooding: None Frequency of ponding: None Calcium carbonate, maximum in profile: 10 percent

## **Histosols and Aquents**

#### **Description of Aquents**

#### **Properties and qualities**

Depth to restrictive feature: More than 80 inches Natural drainage class: Very poorly drained Runoff class: Very low Capacity of the most limiting layer to transmit water (Ksat): Moderately high to high (0.20 to 2.00 in/hr) Depth to water table: About 0 to 12 inches Frequency of flooding: None Frequency of ponding: Frequent Calcium carbonate, maximum in profile: 5 percent Available water storage in profile: High (about 11.7 inches)

#### **Description of Histosols, Undrained**

Properties and qualities Depth to restrictive feature: More than 80 inches Natural drainage class: Very poorly drained Runoff class: Very low Capacity of the most limiting layer to transmit water (Ksat): Moderately high to high (0.20 to 2.00 in/hr)

## Depth to water table: About 0 to 12 inches Frequency of flooding: None Frequency of ponding: Frequent Available water storage in profile: Very high (about 13.4 inches)

Web Soil Survey soil characteristics for identified soil types beneath the four burn piles identified in West Haven, VT (Web Soil Survey, 2015).

# **APPENDIX II**

# Procedure:

- Place 1 gram of soil into 50 ml polypropylene centrifuge tube and treat with 20 ml of 0.5 M calcium nitrate solution (E1 solution).
- 2. Shake the tubes horizontally for 16 hours on a shake table.
- 3. After shaking, place samples in a centrifuge for 15 minutes (3000 rpm).
- Decant the supernatant and filter through 0.45 micrometer membrane filter using syringe filters (2 oz. syringes).
- Acidify with 0.5 ml 12.1 N hydrochloric acid and store in refrigerator kept at a constant 5 degrees Celsius until ICP metal analysis.
- Treat residue in centrifuge tubes with 20 ml of 1 M Sodium Acetate solution adjusted to pH 5 (E2 solution). Take dried filters from decanting supernatant in E1 and dip into centrifuge tubes now containing E2 solution so as to minimize the loss of particulates between phases.
- 7. Shake tubes horizontally on shaker table for 5 hours.
- 8. Repeat steps 3, 4, and 5.
- 9. Treat residue in tubes with 20 ml of 0.1 M Sodium EDTA solution adjusted to pH 7 (E3 solution). Take dried filters from decanting supernatant in E2 and dip into centrifuge tubes now containing E3 solution so as to minimize the loss of particulates between phases.
- 10. Shake horizontally for 6 hours on shaker table.

- 11. Repeat steps 3 and 4.
- 12. Treat residue in tubes with 20 ml of 4 M nitric acid solution (E4 solution). Take dried filters from decanting supernatant in E3 and dip into centrifuge tubes now containing E4 solution so as to minimize the loss of particulates between phases.
- 13. Place centrifuge tubes, containing E4 solution, into a hot water bath for 16 hours at a temperature of 80 degrees Celsius.
- 14. Repeat steps 3 and 4.
- 15. Preform 1:10 ratio dilution for all samples for ICP analysis. Place dilutions in 15 mL centrifuge tubes.

# **APPENDIX III**

# **Observations:**

- Soil sample 1 gram samples varied by +/- 0.01 grams
- Sample WH-13-11C appeared statically charged
- Phase E1 leaching supernatant contained noticeable suspended particles even after centrifuge, was captured by filter.
- Alternated between three different 2 oz. syringes for filtering process. After each sample the syringes were rinsed with deionized water and dried with chem wipes.
- 211 drops of 12.1 N hydrochloric acid was added to Sodium Acetate solution to adjust pH 8.6 to pH 4.96.
- 760 drops of 1 N Sodium Hydroxide was added to Sodium EDTA solution to adjust pH 4.68 to pH 7.07.

# **APPENDIX IV**

Calculations:

- Given Calcium Nitrate crystals (FW=236.15 grams). To make 500 ml of 0.5 M calcium nitrate I need 118.075 g of solid calcium nitrate (diluted with deionized water).
- Given Sodium Acetate crystals (FW=136.08 grams). To make 500 ml of 1 M sodium acetate I need 68.04 grams of solid sodium acetate (diluted with deionized water).
- Given Sodium EDTA crystals (FW=372.24 grams). To make 500 ml of 0.1 M sodium EDTA I need 18.612 grams of solid sodium EDTA (diluted with deionized water).
- Given Nitric acid 15.8 N. To make 500 ml of 4 M nitric acid I need 126.58 ml of 15.8 N of nitric acid diluted with 373.42 ml of deionized water.

# **APPENDIX V**

## **Standard Calculations:**

- Given Zinc 100 mg/L.
  - <sup>o</sup> Standard 1- 1 mg/L- 0.5 ml of stock, 49.5 ml of 1 M nitric acid.
  - <sup>o</sup> Standard 2- 3 mg/L- 1.5 ml of stock, 48.5 ml of 1 M nitric acid.
  - <sup>o</sup> Standard 3- 6 mg/L- 3 ml of stock, 47 ml of 1 M nitric acid.
- Given Lead 100 mg/L (S1, S2), 500 mg/L (S3)
  - <sup>o</sup> Standard 1- 20 mg/L- 10 mL of stock, 40 mL of 1 M nitric acid.
  - Standard 2- 60 mg/L- 30 mL of stock, 20 mL of 1 M nitric acid.
  - Standard 3- 120 mg/L- 12 mL of stock, 38 mL of 1 M nitric acid.
- Given Barium 100 mg/L (S1, S2), 500 mg/L (S3)

- $^\circ$  Standard 1- 20 mg/L- 10 mL of stock, 40 mL of 1 M nitric acid.
- Standard 2- 60 mg/L- 30 mL of stock, 20 mL of 1 M nitric acid.
- Standard 3- 120 mg/L- 12 mL of stock, 28 mL of 1 M nitric acid.