ASSESSMENT OF TRUE IMPACTS OF E-WASTE DISPOSAL IN FLORIDA

ANNUAL REPORT

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EXECUTIVE SUMMARY

PROJECT TITLE: Assessment of True Impacts of E-Waste Disposal in Florida

PRINCIPAL INVESTIGATOR: Timothy G. Townsend

AFFILIATION: Department of Environmental Engineering Sciences, University of Florida

COMPLETION DATE: December 2003

This is an annual report of activities on a two-year study and presents preliminary results. The final project report will present the complete set of results and interpretation.

OBJECTIVES

The objective of the research is to provide data pertaining to the impact of electronic waste (E-Waste) disposal on landfills and WTE facilities in Florida that can be used by decision-makers involved with this issue. The specific objectives include:

1. Measure the concentration of heavy metals in leachate from simulated landfills that contain known amounts of E-waste.
2. Determine the presence and measure the concentrations of brominated flame retardants (BFRs) and metals in Florida landfill leachate (Class I and Class III where available).
3. Measure the leachability of heavy metals from several common E-waste components in landfill leachate and compare to the leachability via the TCLP.
4. Use the results from objectives 1-3 to assess the true impact of E-waste disposal in landfills in Florida.
5. Assess the impact of E-waste heavy metals on Waste-to-Energy systems by performing a mass balance of these metals and their final concentrations in the WTE residuals.

METHODOLOGY

A series of landfill columns (lysimeters) will be built and filled with municipal solid waste containing known amounts of E-waste. Florida landfill leachate samples will be collected and analyzed for the presence and concentration of metals and BFRs. E-waste samples will be leached using MSW leachate and the concentrations compared to results from the TCLP. Using this information, the potential impact of E-waste on Florida landfills will be assessed. Existing ash data will be compiled. The impact of E-waste on WTE in Florida will be assessed by performing a mass balance of heavy metals from E-waste to estimate the resulting concentrations in WTE ash. In addition to the investigator, Dr. Yong-Chul Jang will work as a Post-Doctoral Associate on the project and a graduate research assistant will be hired.

1.0 INTRODUCTION

The management of discarded electronics or "E-waste" presents solid waste professionals and regulators with several challenges. One reason for the concern is the presence of heavy metals and organic pollutants in E-waste. Landfill operators and policy makers have cited potential contamination of leachate and groundwater as reasons to restrict the flow of E-waste into MSW landfills. Heavy metals from E-waste are also a concern for ash quality at Waste to Energy (WTE) facilities. The long-term impacts of E-waste disposal on landfills may include increased operating costs and potential environmental impacts. This project will help provide data to policy makers who must decide how to manage E-waste in the waste stream or to what extent to invest resources to divert E-waste from disposal. This annual report presents the preliminary results from the first year of this two-year project. The final project report will present the complete set of results and interpretation for use by decision-makers involved with this issue.

Previous research has used batch leaching tests to characterize E-wastes. The Toxicity Characteristic Leaching Procedure (TCLP) is used by the USEPA to determine if a solid waste is classified as a Toxicity Characteristic (TC) hazardous waste. TCLP results for many common E-wastes show that the amount of lead leached is sufficient to classify the wastes as TC hazardous wastes (Musson et al., 2000, Townsend et al., 1999). One criticism of the TCLP is that the conditions in the test are not representative of conditions inside most landfills. The behavior of specific E-wastes in landfills is unknown, but concerns about these materials have resulted in precautionary measures.

1.1 Objectives

The overall objective of this research is to provide data pertaining to the impact of electronic waste (E-Waste) disposal on landfills and WTE facilities in Florida that can be used by decision-makers involved with this issue. The specific objectives include:

1. Measure the concentration of heavy metals in leachate from simulated landfills that contain known amounts of E-waste.
2. Determine the presence and measure the concentrations of brominated flame retardants (BFRs) and metals in Florida landfill leachate (Class I and Class III where available).
3. Measure the leachability of heavy metals from several common E-waste components in landfill leachate and compare to the leachability via the TCLP.
4. Use the results from objectives 1-3 to assess the true impact of E-waste disposal in landfills in Florida.
5. Assess the impact of E-waste heavy metals on Waste-to-Energy systems by performing a mass balance of these metals and their final concentrations in the WTE residuals.

1.2 Organization of Report

This report is organized according to the objectives. Chapter 1 presents the introduction, organization, and some background on E-waste. Chapter 2 deals with Objective 1, the simulated landfill leaching experiment, which will begin in January 2004. Objective 2, the measurement of

BFRs and metals in landfill leachate is addressed in chapter 3 (BFRs) and 4 (metals). Objective 3, the leaching behavior of common E-wastes was carried out in two phases, PWBs and CRTs were evaluated first, followed by the evaluation of cellular phones, mercury lamps, and nickel cadmium batteries. Chapter 5 compares the leaching behavior of PWBs and CRTs using leachate samples collected from full-scale landfills in 2001 and 2002. Chapter 6 compares the leaching behavior of cellular phones, mercury lamps, and nickel cadmium batteries using leachate samples collected in 2003. Once the first three objectives are completed, a chapter in the final report will assess the true impact of E-waste disposal in landfills in Florida (Objective 4). Chapter 7 describes the approach for Objective 5, to assess the impact of E-waste heavy metals on Waste-to-Energy systems. Chapter 8 summarizes preliminary observations from the first year of research and presents plans for year two of the project.

1.3 Background

E-waste represents a growing segment of the solid waste stream. According to a study prepared for the US EPA, discarded electronic devices have been estimated to comprise approximately 2% to 5% of the US municipal solid waste (MSW) stream (Global Futures Foundation, 2001). Industry experts have projected that more than 20 million personal computers became obsolete in 1998, and more than 60 million personal computers will be retired in 2005 (National Safety Council, 1999). Approximately 3 million tons of E-waste were estimated to be disposed in US landfills in 1997 (Global Futures Foundation, 2001).

Concerns have been raised that toxic chemicals will leach from these devices when disposed (Yang, 1993; Lee et al., 2000; White et al., 2003). The toxic chemicals commonly used in electronic devices include metals and metalloids (e.g., arsenic, cadmium, chromium, copper, lead, and mercury) and organic chemicals such as brominated flame retardants (BFRs). The printed wire boards (PWBs, also referred to as circuit boards) found in most E-waste, for example, may contain arsenic, cadmium, chromium, lead, and mercury (Nordic Council of Ministers, 1995; Five winds International, 2001). Cathode ray tubes (CRTs) in computer monitors and televisions may contain barium, cadmium, copper, lead, zinc, and several rare earth metals (Five Winds International, 2001). Lead is one heavy metal with known toxic properties that is found in large amounts in many electronic devices (Nordic Council of Ministers, 1995). Electronic devices, along with lead-acid batteries, are the major contributors of lead in the municipal solid waste stream (US EPA, 1989). Lead-based solder (typically a 60:40 ratio of tin to lead), which is used to attach electrical components to PWBs, represents the major solder type used in most PWB applications (Nordic Council of Ministers, 1995; Five winds International, 2001). Typical PWBs have been reported to contain approximately 50 g of tin-lead solder per m^2 of PWB (Five winds International, 2001), and approximately 0.7% of the total weight of a PWB (Electronic Industry Alliance, 2000). In CRTs, leaded glass provides shielding from X-rays generated during the picture projection process. Color CRTs contain 1.6 kg to 3.2 kg of lead on average (Microelectronics and Computer Technology Corporation, 1996). The possible effects of lead on human health and the environment are well documented (Waldron, 1980; Gosselin et al., 1984; Sitting, 1996).

In the US, under regulations promulgated as part of the Resource Conservation and Recovery Act (RCRA), solid wastes containing large amounts of leachable lead are regulated as hazardous wastes unless otherwise exempted. Lead leaching is measured using a batch extraction test known as the Toxicity Characteristic Leaching Procedure (TCLP, US EPA Method 1311) (Federal Register, 1986; US EPA, 1996). In a previous study, color CRTs from televisions and computer monitors were found to leach enough lead using the TCLP to be toxicity characteristic (TC) hazardous wastes in most cases (Musson et al., 2000). The majority of samples tested exceeded the TC limit of 5 mg/L for lead. Discarded color CRTs are thus considered TC hazardous wastes unless test results show otherwise (Federal Register, 2002).

Generators other than households who dispose of more than 100 kg of color CRTs per month must manage them via a permitted hazardous waste facility. Generators who produce less than 100 kg per month (conditionally exempt small quantity generators [CESQGs]) may under RCRA dispose of these wastes in a state-permitted solid waste management facility (e.g., MSW landfill). Many states, however, ban CESQG hazardous waste from landfills. RCRA regulations exclude solid waste produced by households from the definition of hazardous waste; a color television or computer monitor that is disposed by a household is not a hazardous waste. At least one state, California, has not adopted the household waste exclusion. Because many CRTs can still be legally disposed in MSW landfills, state environmental regulators and local communities must determine what additional initiatives, if any, should be enacted to address CRT disposal. One possible action is to provide funding so CRTs can be collected at household hazardous collection facilities, by curbside collection or through special collection events. The estimated cost to recycle one CRT has been reported to range from \$9 (computer monitors, small TVs) to \$ 35 (console TVs) (Price, 1999). States also have the option of banning the disposal of these devices in landfills. In the US, both California and Massachusetts have banned CRT disposal in landfills (Federal Register, 2002). With recent research indicating that other discarded electronic devices (those that contain PWBs with lead solder) will in many cases fail the TCLP for lead (Townsend et al., 1999), similar questions will be raised for E-waste as a whole.

It is important to note that the TCLP was designed to be a conservative regulatory test to rapidly screen which solid wastes warrant more stringent management as hazardous wastes. The TCLP leaching solution uses acetic acid to represent the types of acids produced during the biological decomposition of waste in a landfill; the concentrations prescribed, however, were selected to represent worse-case acid forming conditions (Francis et al., 1984). The TCLP extraction fluid pH is 4.93 (2.88 for alkaline wastes), while the pH of typical landfill leachates are much closer to neutral (Tchobanoglous et al., 1993; Farquhar, 1989). The TCLP was not intended, per se, to be a method for predicting pollutant leachate concentrations from a typical landfill where a potential hazardous waste is disposed. The question “what will the concentration of lead be in a landfill’s leachate as result of disposing of lead-containing E-waste?” is a separate question from “is lead-containing E-waste a TC hazardous waste?” This research will help determine how the disposal of E-waste in landfills impacts leachate quality. As previously explained, even if a waste is determined to be hazardous by the TC, there will still be times when it is disposed in a landfill (from household waste, CESQG waste). In addition, wastes that do not exceed TC limits using TCLP might still leach sufficient concentrations of pollutants to elevate concentrations in the landfill’s leachate. While modern MSW landfills are lined to intercept and collect the leachate, elevated pollutant concentrations in a landfill’s leachate can pose problems for leachate treatment and disposal and perhaps impact the long term management of leachate after the landfill is closed. Thus, an understanding of how E-waste might leach in a landfill is beneficial to landfill operators who must decide which wastes they are willing to accept and to policy makers and regulators when weighing the costs and benefits of measures such as landfill bans or funding for household hazardous waste collection of E-waste.

In addition to heavy metals, organic compounds contained in E-waste can be leached into landfill leachate. Brominated flame retardants (BFRs) are bromine containing organic compounds that are widely used in electronics and other products to reduce the risk of fire. BFRs have become a concern because they are persistent in the environment, bioaccumulative and potentially toxic. BFRs have been found in human breast milk, human blood serum, animal tissue, air, water, sediments and sewage sludge (de Boer et al., 2003; de Wit, 2002; Watanabe and Sakai, 2003). Studies have found increased levels of BFRs in electronics disassembly workers (Sjodin et al., 2001) and in individuals who consume large amounts of fish (Sjodin et al., 2000). Potential locations at which BFRs may enter the environment include the plants where they are manufactured, the plants where they are added to products, the locations where the products are used and the locations where the products are disposed. Because landfills serve to concentrate many products that contain BFRs (E-waste as well as textiles, furniture and construction products), they represent a possible source of BFRs to the environment Since BFRs are not routinely measured in landfill leachate, the potential movement of BFRs out of landfills through landfills is unknown.

2.0 SIMULATED LANDFILLS FOR ASSESSING IMPACT OF E-WASTE DISPOSAL ON LANDFILL LEACHATE

2.1 Overview of Experiment

This research will involve placing 12 high density polyethylene (HDPE) leaching columns or *lysimeters* inside the Polk County North Central Landfill. The lysimeters will be filled with synthetic waste mixtures containing known amounts of E-waste. Heavy metals will be monitored in the leachate. One of the challenges with previous lysimeter studies, which this experiment will address, is temperature moderation. A lysimeter in a laboratory or outside will not maintain the temperature of a landfill, which is approximately 50°C. Temperature influences both the microbiology and chemistry of the waste. This issue will be addressed by placing the entire lysimeter inside the landfill where the surrounding waste will moderate the temperature. The construction of the lysimeters began in early January 2004 and the installation should occur in middle to late January, 2004.

2.2 Methods and Materials

Lysimeters for this study will be constructed of 24-inch diameter HDPE approximately 16.5-feet long. A 3-inch diameter HDPE pipe will be attached to the lysimeter and connected at the bottom to allow leachate to be sampled using a pump or bailer. A schematic of the lysimeters is included as Figure 1. Waste will be packed into the columns to a similar waste density as that of a landfill. The columns will be buried upright in 36-inch diameter bucket auger borings. The section of the landfill that has been set aside for the lysimeters is not planned for active fill for another 2-3 years, at which time lysimeter studies will cease. Upon completion, the lysimeters will remain part of the landfill unless research interests warrant extracting the lysimeters. Current waste elevation at the proposed lysimeter site is approximately 180’ above mean sea level (MSL). The liner is located at an elevation of 110’ MSL. Therefore, a boring depth of 15-18 feet will not threaten to compromise the liner.

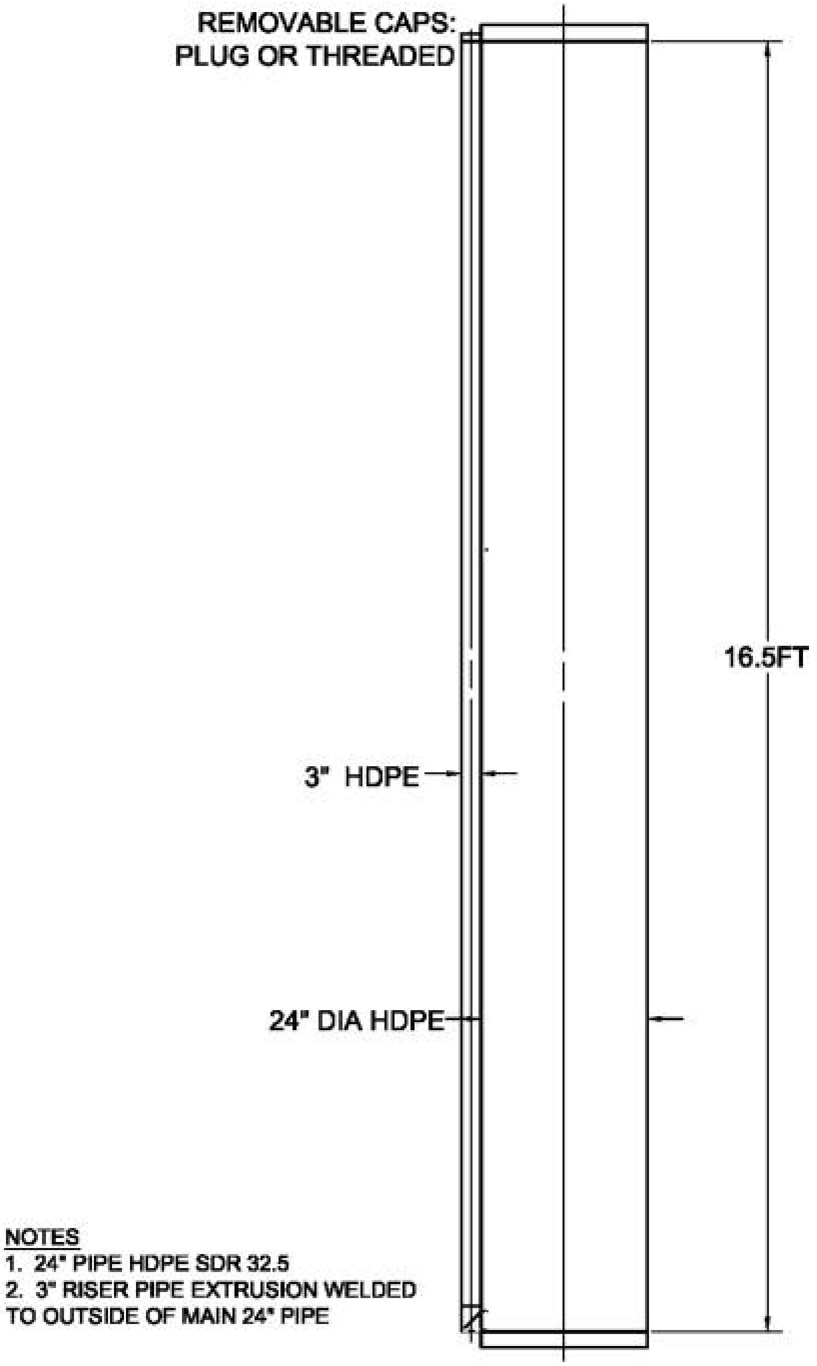

FIGURE 1. Schematic of lysimeter.

Once the lysimeters are placed inside the landfill, each will be filled with a unique waste mixture. Different waste mixtures have been selected to address a variety of waste materials such as cathode ray tubes, cell phones, mercury bulbs, pressure treated wood, lead based paint and wood and tire ash. Seven lysimeters will simulate MSW landfills, two will simulate C&D landfills and one will simulate Class III landfills. Two lysimeters are available for wastes yet to be determined. The types of landfill simulated and the waste of interest for each column are shown in Table 1. The waste mixtures will be determined by referring to the literature and waste composition studies conducted in Polk County. Additional wastes of interest will be included in the columns if they can complement the materials included without interfering with the detection of any important parameters.

The sampling schedule has not been determined. Parameters selected for monitoring will include water quality parameters, gas production, gas composition and settlement. The goal of the sampling is to track the conditions inside the lysimeters and evaluate the impact of the wastes on the leachate quality.

Table 1. Landfill type and wastes for lysimeter study

Landfill type	Waste of interest
MSW	Control
MSW	Control
MSW	E-waste
MSW	E-waste
MSW	Lead based paint
MSW	Wood and tire ash
MSW	Wood and tire ash
C&D	Control
C&D	Lead based paint
Class III	Class III
To be determined	To be determined
To be determined	To be determined

3.0 ASSESSMENT OF BROMINATED FLAME RETARDANTS IN LANDFILL LEACHATES

3.1 Overview

Brominated flame retardants (BFRs) in landfill leachate are of concern because BFRs are organic compounds that are toxic, bioaccumulative, and persistent in the environment. Levels of BFRs in the environment and in humans are increasing in the USA and the levels found in US human breast milk are many times higher than levels found in other parts of the world. Sources of BFRs to the environment include emissions from manufacturing and emissions from products during use, but emissions from landfills are unknown. Since landfills are a depository for many items containing BFRs (E-waste as well as textiles, furniture, and construction products), it is possible that BFRs could accumulate in landfills and landfills could become a long-term source of BFR emissions. BFRs in landfill leachate could be released back to the environment through sewage sludge if the leachate is sent to a wastewater treatment plant. The data presented here is still under analysis; the final report will present a more complete discussion of results.

3.2 Methods and Materials

From May 21, 2003 to July 1, 2003, five sampling trips were conducted for this project collecting samples for BFR and metal analysis and for leaching experiments. In total, 34 landfill leachate samples were collected for BFR analysis, placing into amber glass bottles pre-rinsed with organic solvent. The extraction procedure used was based on continuous liquid – liquid extraction (US EPA SW-846 3520C). One liter of landfill leachate was extracted with 150 – 200 mL methylene chloride. The methylene chloride was then replaced with hexane. The hexane was evaporated to about 0.2 mL using a solvent extraction apparatus (Turbovap II, Zymark Inc.) The concentrated samples were then run on gas chromatography/mass spectrometry (GC/MS) (Finnegan Trace) operated in negative ion chemical ionization mode utilizing gas chromatography with the mass spectrometer operated as a bromine-specific detector. Unlike normal GC/MS, which determines a retention time and a mass spectrum "fingerprint" for each compound, negative ion chemical ionization mode relies on the retention time to identify compounds. The mass spectrometer is limited to detecting bromine atoms. Operating in this mode presents a trade-off; a lower detection limit is possible, but there is less certainty in the identification of compounds. The instrument used achieved a detection limit of 2 ng/L using this method. Without the negative ion chemical ionization mode, the detection limit would have been approximately 1000 times higher. This method has been reported in the literature as successful in determining BFR concentrations in water samples. Other methods for matrices such as breast milk, blood serum and tissue samples involved different extraction and analysis procedures. No method has been reported in the literature for leachate samples or any aqueous sample with the characteristics of landfill leachate.

3.3 Results and Discussion

The results of the analysis were limited by matrix interferences in the landfill leachate and the low detection limits required for the analysis. Unknown organo-bromine compounds were found in many leachate samples that eluted from the GC within the same range as BFRs, but the retention time did not correspond with any compounds in the standard. Since these compounds were extracted using the above method, they would have some characteristics in common with BFRs: they would be lipophillic compounds and could be either polar or non-polar. Since these unknown compounds were detected by the bromine specific detector, bromine was certainly present. The high levels of organic compounds in the leachate also contributed to difficulties in concentration and analysis. The data will be further analyzed to determine what conclusions can be drawn regarding the concentrations of BFRs in landfill leachate.

4.0 ASSESSMENT OF HEAVY METALS IN LANDFILL LEACHATES

4.1 Overview of Experiment

Heavy metals are of interest in landfill leachate due to concerns about potential groundwater contamination and increased leachate treatment costs. Heavy metals may enter landfills through the disposal of metal-contaminated industrial waste byproducts (e.g. ash) and from metal-containing commercial products (e.g. batteries, e-waste). There is currently a debate as to the impact of the disposal of heavy metal containing products on landfill leachate quality (Hooper et al. 1998; Jang and Townsend, 2003). One way to understand this issue is to examine metal concentrations in existing lined landfill leachates, especially landfills that contain known amounts of E-waste, if such facilities can be identified. While regulatory data exists for metal concentrations in landfill leachates, samples were collected specifically for this project, as the point of compliance is often not the sampling point that will give the most useful information about individual landfill cells or give the best idea of the conditions influencing the leaching of compounds inside the landfill. Metal concentrations and conventional water quality parameters were compared to US leachate data, Florida leachate data, and regulatory parameters. The results were also analyzed with respect to operational conditions (active or closed). As this is a preliminary report, the data continues to be analyzed and the results reported here should be viewed as incomplete and preliminary. Further sampling is planned for 2004. The final report for this project will provide a more thorough discussion of the results.

4.2 Methods and Materials

The landfills sampled included landfills receiving only MSW, landfills receiving both MSW and ash, and landfills receiving C&D waste. From the 19 landfill locations visited, 41 discrete landfill leachate samples were collected for metals analysis. Multiple leachate samples were collected at locations where cells with separate leachate collection systems were present. Some samples were collected from leachate sumps or lift stations using a bailer. In other locations, the leachate samples were collected directly from the leachate collection system (LCS) discharge pipe. For one sample, location 24, the leachate sample was collected from within the landfilled waste by lowering a bailer into an unused 2-inch leachate injection well.

The pH and conductivity were measured in the field and the samples were stored in appropriate bottles, depending on the analysis. Samples were stored in coolers until brought to the laboratory, where they were stored in a walk-in cooler. For metals, a portion of each sample was filtered using vacuum filtration with 0.45-μm filters. Both filtered and unfiltered samples from each location were preserved by adding nitric acid to bring the pH below 2. The preserved samples were stored in a refrigerator until digestion. Location 24 was not filtered, as it was too thick to filter through a 0.45-μm filter. Metals samples were acid digested in triplicate following EPA Method 3010A (US EPA, 1996). This method refluxes 100 mL of liquid sample with repeated additions of nitric acid (HNO_3) and finally with hydrochloric acid (HCL). When the digestion was completed, the digestates were filtered through a Whatman 41 filter and the volume was raised to 100 mL by adding de-ionized water. Matrix spike samples were also digested with at least one set of MS/MSD for each 20 samples digested. The digested samples were then analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Jarrell Ash Corporation, Model 95970, US EPA Method 6010B, US EPA, 1996). In addition, the filtered and unfiltered leachate samples were analyzed for mercury following EPA method 7470A (US EPA, 1996). For mercury analysis, a duplicate and a set of matrix spike samples were selected for each set of 20 samples analyzed.

4.3 Results and Discussion

A summary of concentrations for all the metals analyzed is presented in Table 2 and Table 3 for the filtered and unfiltered samples, respectively. For most elements, the concentrations were spread over a large range. To represent the concentration range of each element, the concentrations are presented as 10th percentile, 50th percentile and 90th percentile. Other researchers have used a similar statistical approach to present leachate data (Looser et al., 1999). For calculation purposes, the samples that were below the detection limit were considered as equal to one-half of the detection limit. This method has also been used in literature (Martin et al., 1999).

The metals Ba, Mn, Sr, Zn, Fe, Mg, Ca, K and Na were detected in 100% of tested leachates in both the filtered and unfiltered samples. Ni was detected in 100% of the filtered samples and 95% in unfiltered samples. B, Cr and V also were detected in more than 95% of the samples in both the filtered and unfiltered cases. Co was also detected above 90% in both the cases. As, Cu, Sn, Cd and Pb were detected in 50% or more samples in both filtered and unfiltered conditions.

Some samples were detected differently in filtered and unfiltered samples. Most notably, Al was detected only in 40% of the filtered samples while it was found in 90.2% of the unfiltered samples. Cd was also detected more frequently in the unfiltered samples (78%) than the filtered samples (50%). With respect to the median values, the concentration of metals decreased in the order B, Sr, Na, K, Mn, Ca, Zn, Ba, Ni, Mg, As, Cr, V, Sn, Co, Cu Pb Fe and Cd in filtered samples and B, Sr, Na, Mn, K Al, Ca, Zn, Ba, Ni, Mg, As, Cr, V, Co, Fe, Cu, Pb, and Cd in unfiltered samples. For several metals (Mo, Ni, Sb, Se, Sn, and V), the % detected in the filtered samples was higher than that of unfiltered samples (Table 2 and 3). This may be due to the fact that the samples having low concentrations (close to detection limit) were detected differently in some replicates, making it difficult to account them as detected.

Table 2. Metal Concentrations of Filtered Leachate Samples

Analyte	ICP Detection Limit	# Samples tested	% Detected	10th percentile	50th percentile	90th percentile
Al	50.00	40	40	BDL	BDL	298
As	11.00	40	65	BDL	26.2	96
B	6.00	40	97.5	646	2,358	6,609
Ba	0.60	40	100	16.9	58.5	241
Be	0.20	40	25	BDL	BDL	0.57
Cd	0.30	40	50	BDL	0.14	1.76
Co	0.75	40	92.5	0.92	11.2	39.6
Cr	3.00	40	95	3.31	20.1	74.3
Cu	4.00	40	57.5	BDL	4.96	17.1
Mn	3.00	40	100	35.5	208	1,507
Mo	5.00	40	32.5	BDL	BDL	22.6
Ni	4.00	40	100	8.44	54.0	176
Pb	3.00	40	50	BDL	1.57	20.2
Sb	5.00	40	45	BDL	BDL	26.8
Se	8.00	40	10	BDL	BDL	1.95
Sn	9.00	40	57.5	BDL	11.5	79.9
Sr	17.00	40	100	111	554	2,392
V	0.60	40	97.5	1.48	11.9	55.0
Zn	10.00	40	100	25.8	82.7	157
Hg	0.21	40	22.5	BDL	BDL	0.421
Ca*	0.30	40	100	50.82	122.2	436.4
Fe*	0.11	40	100	0.266	1.334	11.46
K*	0.05	40	100	106.9	434.5	2630
Mg*	0.02	40	100	15.52	36.22	108.7
Na*	1.00	40	100	135.8	494.9	1358

* Units in mg/L, all the other analyte concentrations in ug/L

Table 3. Metal Concentrations of Unfiltered Leachate Samples

Analyte	ICP Detection Limit	# Samples tested	% Detected	10th percentile	50th percentile	90th percentile
Al	50.00	41	90.2	3.29	203	4,652
As	11.00	41	70.7	BDL	33.0	103
B	6.00	41	97.6	676	2,107	6,299
Ba	0.60	41	100.0	31.1	73.4	310
Be	0.20	41	22.0	BDL	BDL	0.58
Cd	0.30	41	78.0	BDL	1.06	3.28
Co	0.75	41	97.6	1.09	10.7	42.9
Cr	3.00	41	95.1	5.45	22.4	89.7
Cu	4.00	41	63.4	BDL	5.16	53.6
Mn	3.00	41	100.0	44.9	237	1,891
Mo	5.00	41	31.7	BDL	BDL	11.3
Ni	4.00	41	95.1	8.72	48.4	186
Pb	3.00	41	53.7	BDL	3.23	28.0
Sb	5.00	41	43.9	BDL	BDL	21.8
Se	8.00	41	0.0	BDL	BDL	BDL
Sn	9.00	41	48.8	BDL	BDL	84.5
Sr	17.00	41	100.0	146	876	6,511
V	0.60	41	95.1	1.43	15.8	64.6
Zn	10.00	41	100.0	30.6	75.3	248
Hg	0.21	41	24.3	BDL	BDL	0.421
Ca*	0.30	41	100.0	55.46	124.3	363.9
Fe*	0.11	41	100.0	0.804	10.42	35.29
K*	0.05	41	100.0	33.69	207.6	1,657
Mg*	0.02	41	100.0	15.68	34.44	100.3
Na*	1.00	41	100.0	107.1	502.9	1,461

* Units in mg/L, all the other analytes concentrations in ug/L

4.3.1 Comparison with Literature

Figures 2, 3 and 4 compare the RCRA metal concentrations from this study to the US and Florida data obtained from the "Leach 2000" database in different percentile values (SAIC, 2000). Only six (As, Ba, Cd, Cr, Hg and Pb) of the eight RCRA metals were plotted. Ag was not plotted due to lack of data and Se was not plotted because all the unfiltered samples were below detection limit for selenium in the current study. The general trend of Cr, Pb, Cd, Hg and Ba concentrations from the 3 sources showed the same pattern. For these five metals, the US values were the highest, followed by the Florida values and finally, the concentrations from this study. This general trend was not observed for As. The upper percentile of As concentration of the current study do not exceed the upper percentile of the US values. Still, the median value of As in this study is above the other two sources. Compared to the regulatory limits, all of the six metals considered show the 95th percentile values far below the TC limit. The current study results do not exceed the drinking water (DW) limit for Ba and Hg. The higher percentile values of the other four metals considered exceeded the drinking water limit. The 75th percentile concentration for As was above DW limit. Arsenic concentrations were further compared with the proposed DW limit (10 ug/L). The 25th percentile of As for US and the FL data exceed the proposed DW limit while the median value exceeded the proposed DW limit for the current study results.

Figure 5 through Figure 10 present the leachate comparison for other metals. Most of them also show the same trend as the RCRA metals (US data are the highest and the current data are the lowest concentrations). Although the median Sr concentration of US data is still higher than the current data, Sr concentrations for the current database, however, occur in a higher range compared to US data. No Florida data for B, Sr, and Mo were available in the “Leach 2000” database for comparison. Some metals were below the drinking water limit while some were well above. Iron concentrations for most of the percentiles were above the drinking water limit for all three databases.

A statistical analysis was conducted to compare the US data and the current study data. Because of the high variability, ANOVA could not be used for the comparison of mean metal concentrations. Therefore, a logarithmic transformation was used by computing the log values (base 10) of concentrations. A hypothesis test was conducted on transformed data using “Z” test. The results indicated at 0.05 of level of significance that the US data was different from the current study for all the metals tested except for As and Sn.

The difference in concentrations in the current study as compared to other two studies may be because of several reasons. The current study samples are more recent. With the regulation changes over the time, the wastes end up in the MSW landfills may also change. There is a possibility that wastes with high concentrations of metals ended up in old landfills and might therefore be included in the previous studies. Jain (2003) found that waste mercury concentrations in a particular landfill were higher in older waste layers compared to newer layers. In addition, Florida landfills may have more diluted leachate because of the climate (heavy rainfall) (Reinhart and Grosh, 1998).

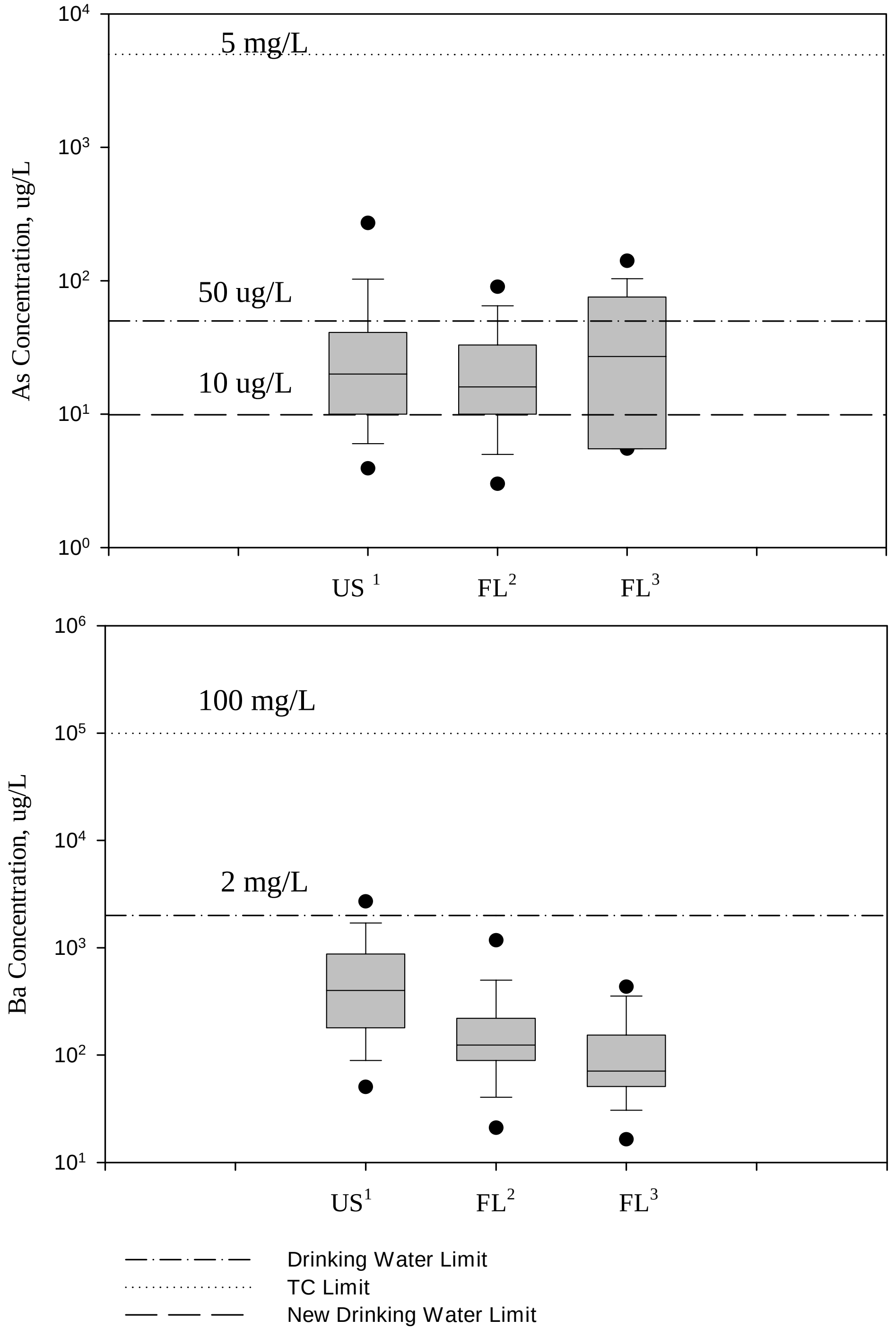

FIGURE 2. Arsenic and barium box and whisker plots for compiled leachate data

[1]US data from Leach 2000 database, [2]Florida data from Leach 2000 database, and [3]Florida data from this study A) Arsenic, B) Barium.

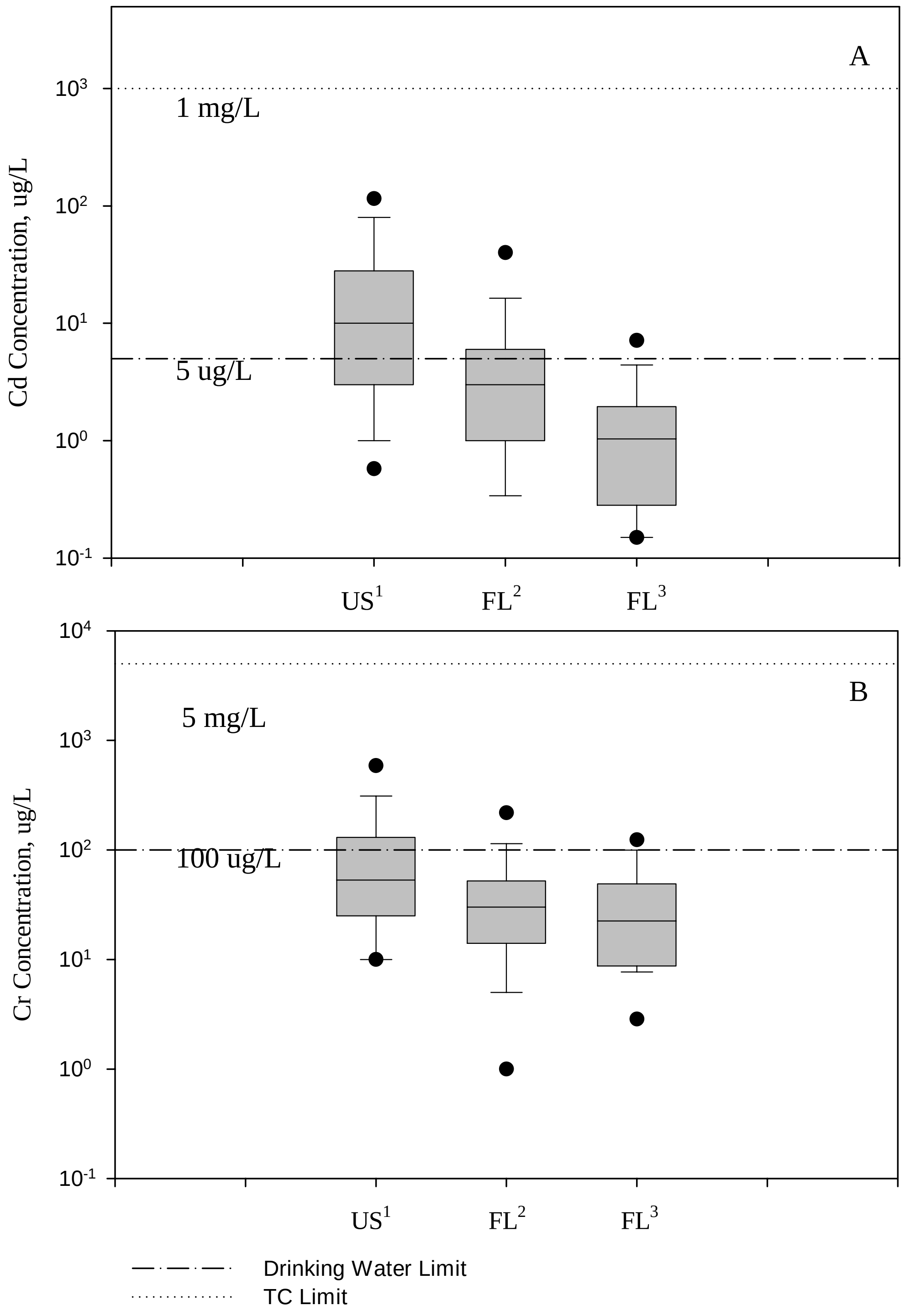

FIGURE 3. Cadmium and chromium box and whisker plots for compiled leachate data

[1]US data from Leach 2000 database, [2]Florida data from Leach 2000 database, and [3]Florida data from this study A) Cadmium, B) Chromium

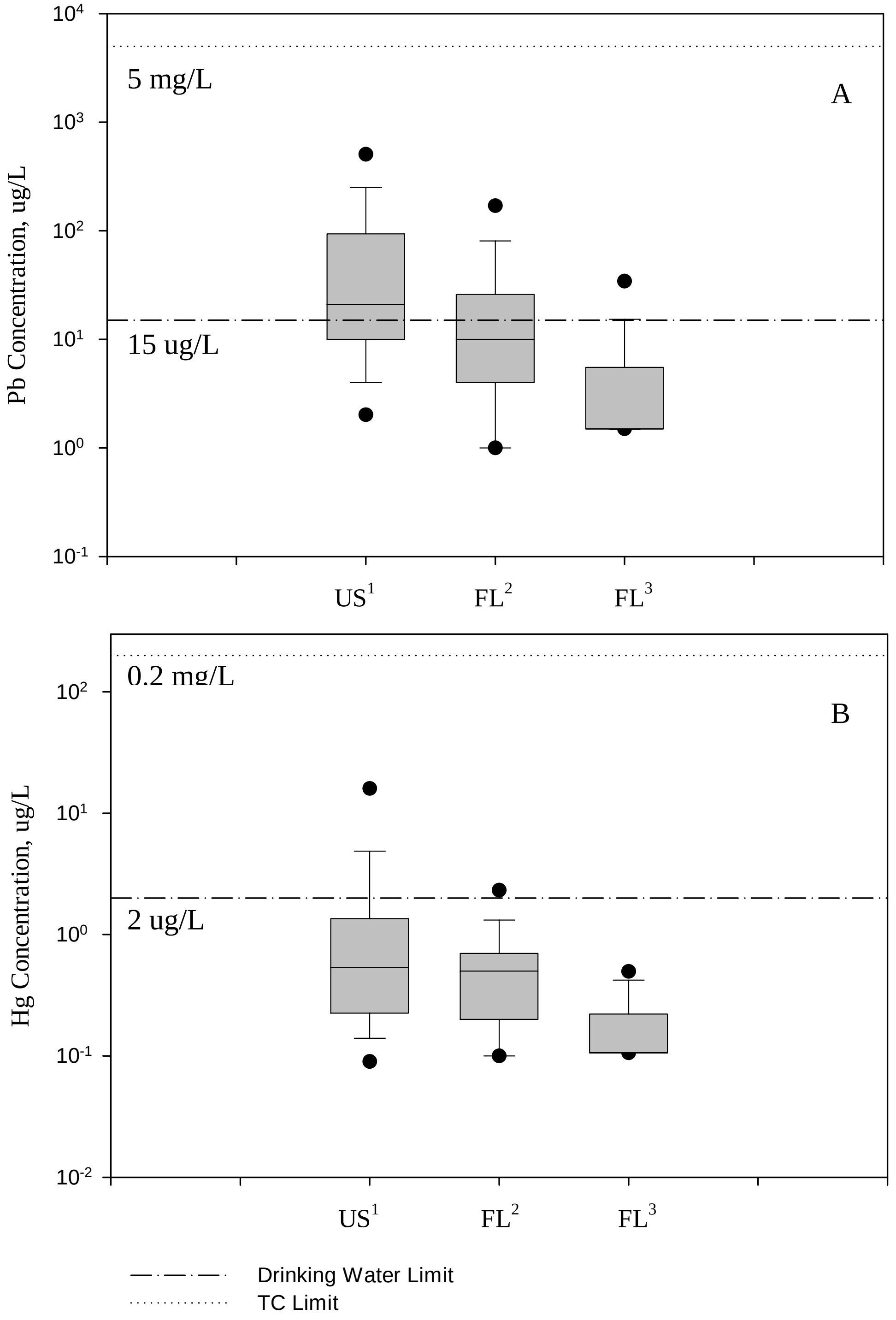

FIGURE 4. Lead and mercury box and whisker plots for compiled leachate data

[1]US data from Leach 2000 database, [2]Florida data from Leach 2000 database, and [3]Florida data from this study A) Lead, B) Mercury

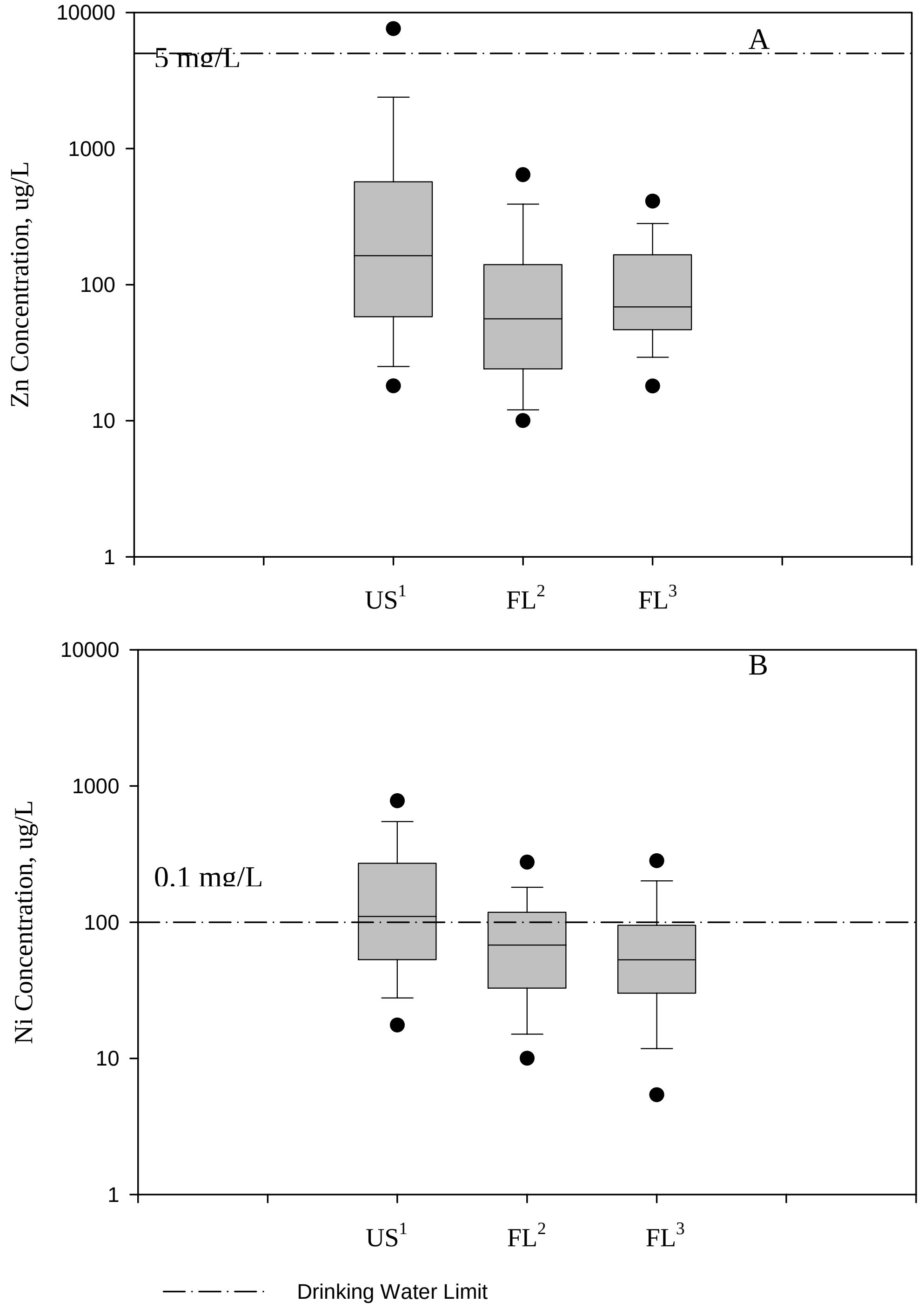

FIGURE 5. Box and Whisker Plots for Compiled leachate for US data from Leach 2000 Database

[1] Florida Data From Leach 2000 Database,[2] and Florida Data from this Study,[3]. A) Zn, B) Nickel

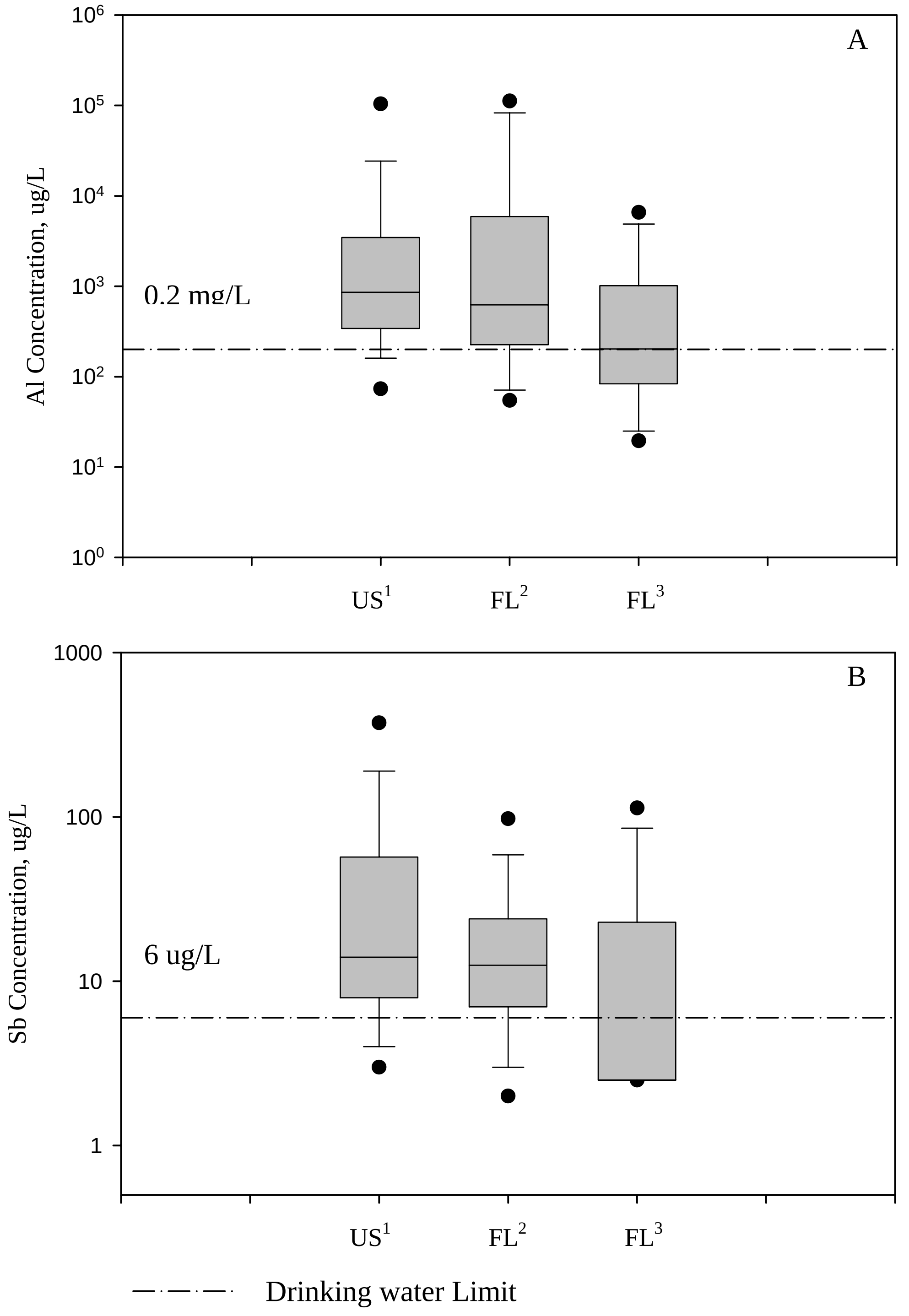

FIGURE 6. Box and Whisker Plots for Compiled leachate for US data from Leach 2000 Database

[1] Florida Data From Leach 2000 Database,[2] and Florida Data from this Study,[3]. A) Aluminum, B) Antimony

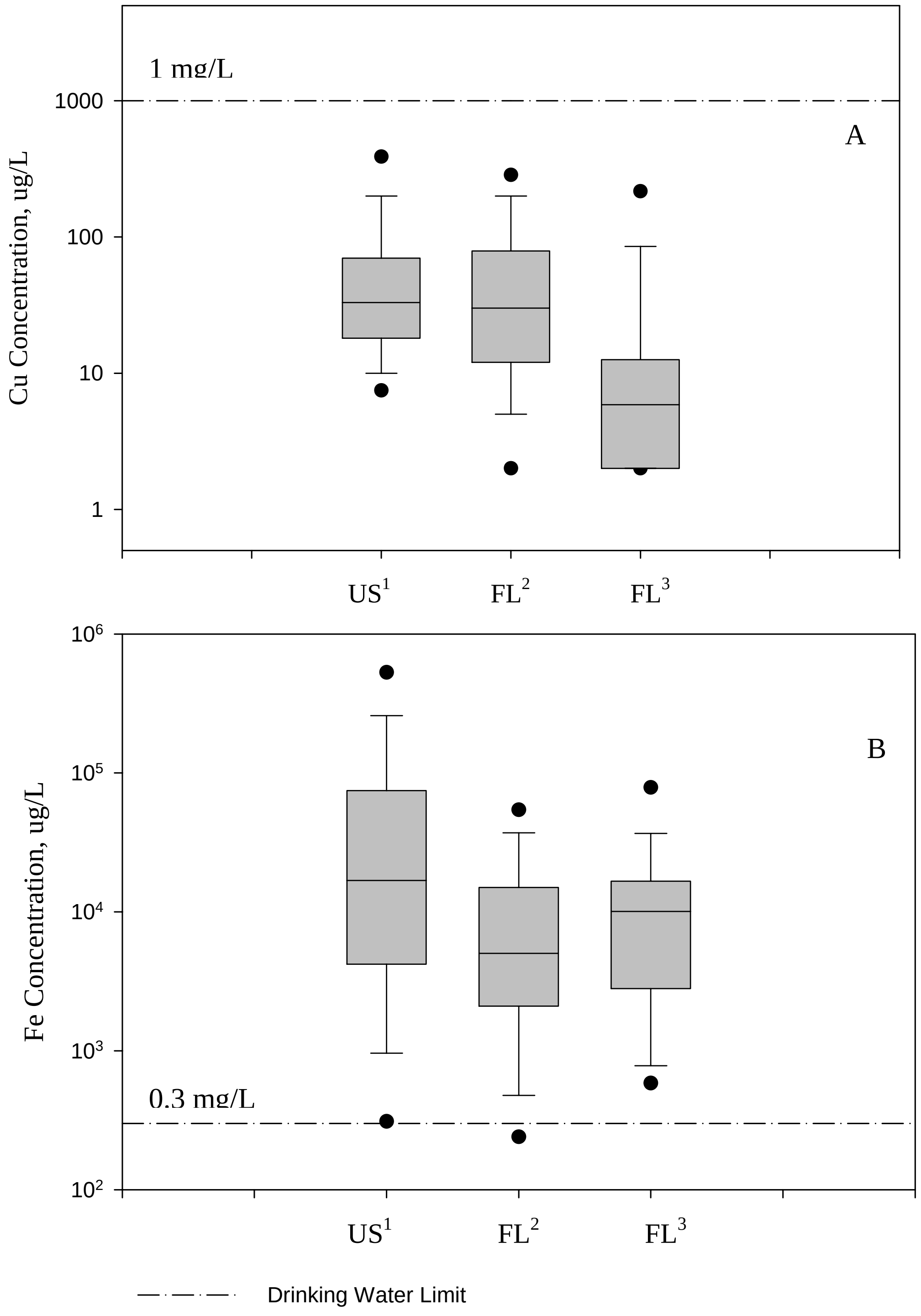

FIGURE 7. Box and Whisker Plots for Compiled leachate for US data from Leach 2000 Database

[1] Florida Data From Leach 2000 Database,[2] and Florida Data from this Study,[3]. A) Copper, B) Iron

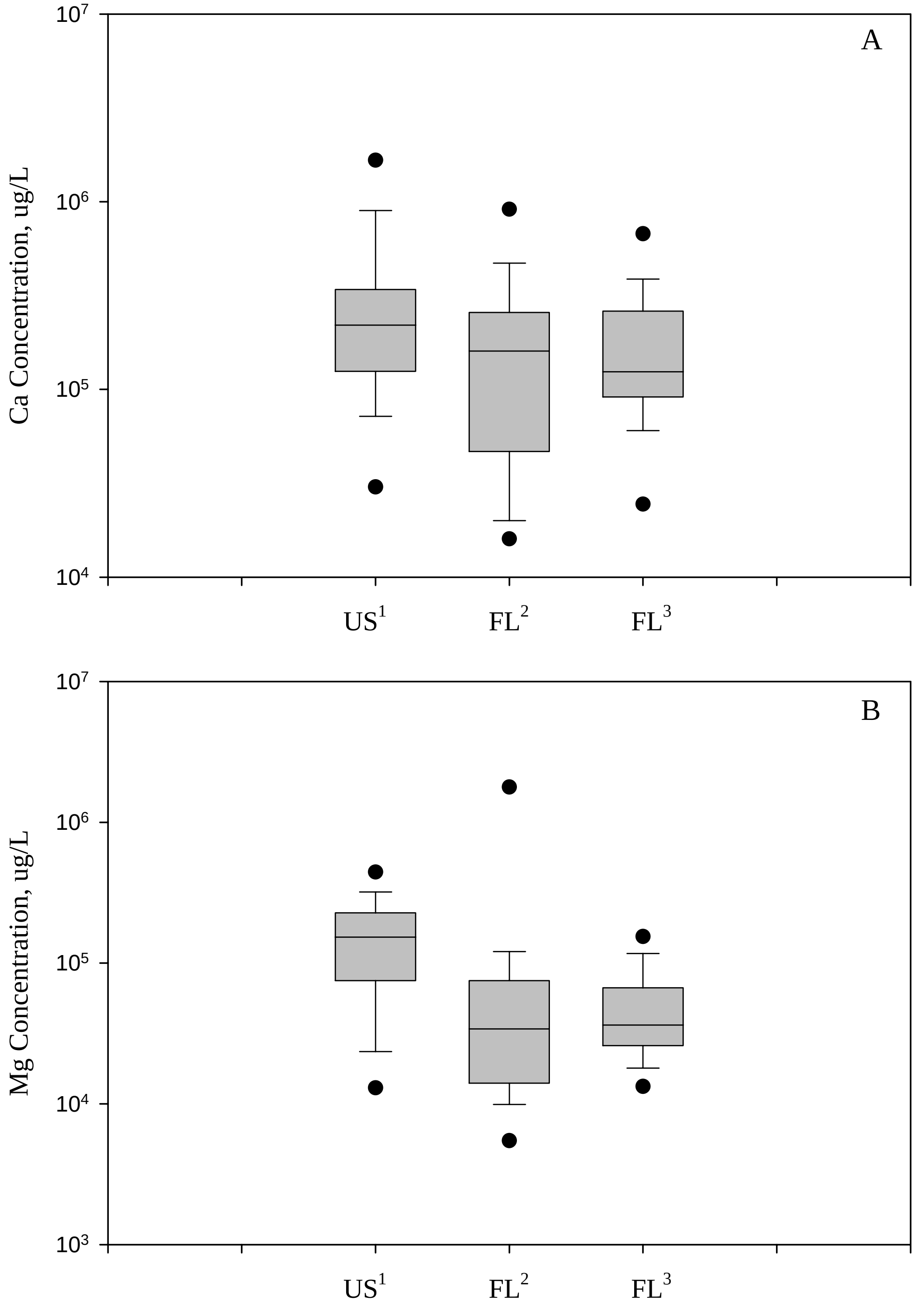

FIGURE 8. Box and Whisker Plots for Compiled leachate for US data from Leach 2000 Database

[1] Florida Data From Leach 2000 Database,[2] and Florida Data from this Study,[3]. A) Calcium, B) Magnesium

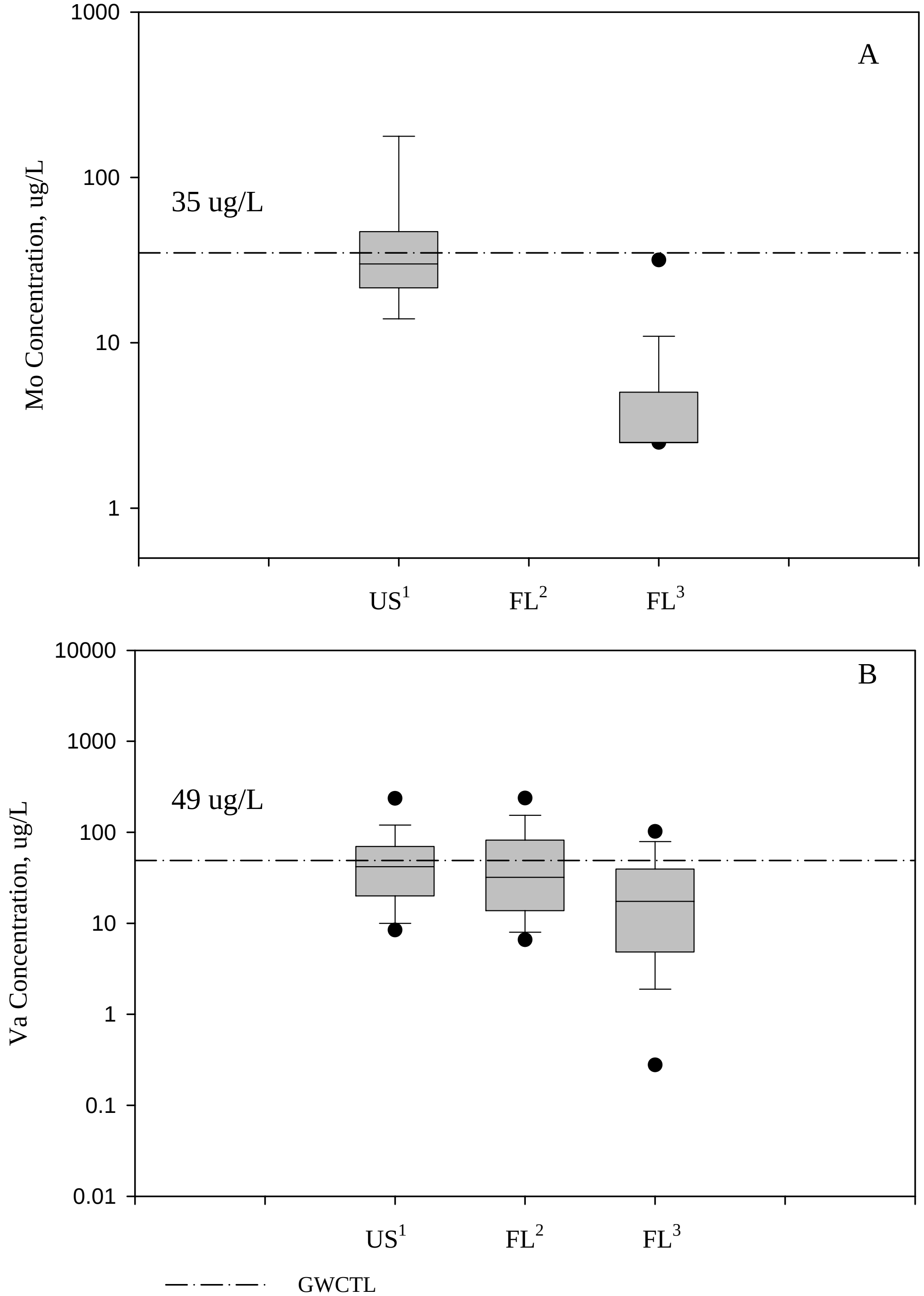

FIGURE 9. Box and Whisker Plots for Compiled leachate for US data from Leach 2000 Database

[1] Florida Data From Leach 2000 Database,[2] and Florida Data from this Study,[3]. A) Molybdenum, B) Vanadium

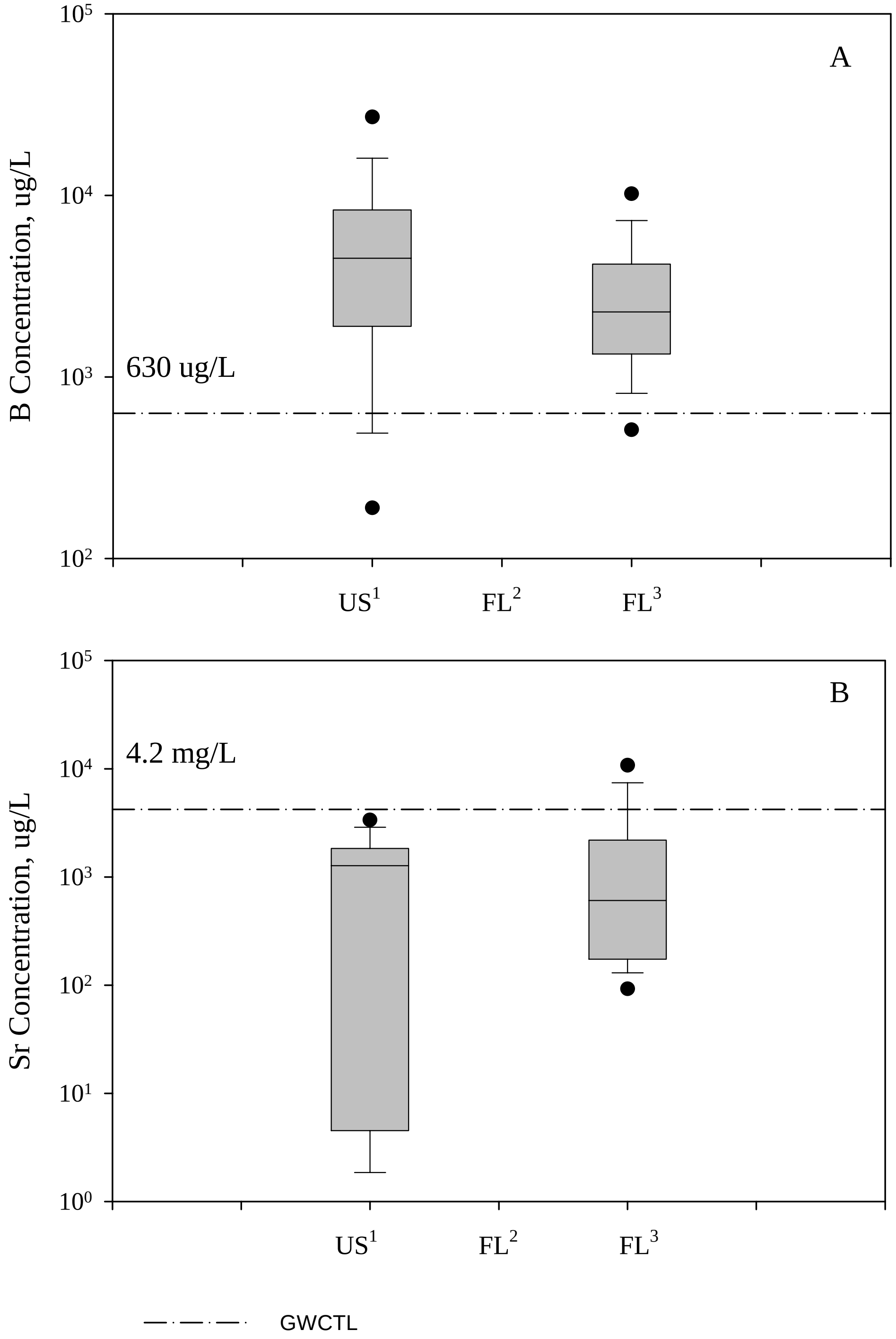

FIGURE 10. Box and Whisker Plots for Compiled leachate for US data from Leach 2000 Database

[1] Florida Data From Leach 2000 Database,[2] and Florida Data from this Study,[3]. A) Boron, B) Strontium

4.3.2 Comparison with Regulatory Levels

The metal concentrations measured in this study were compared to both the RCRA TC limits (where available) and health based water quality standards for human consumption. For all the RCRA metals analyzed in this study, the mean concentrations were far below the TCLP limit (Table 4). The highest ratio of mean measured concentration to TC limit was found for Cr at 1.29%. A similar approach was found in the literature in two other studies (SAIC, 2000; Reinhart and Grosh, 1998). When the median was considered instead of the mean, the ratios became lower. Data in a report prepared for SWANA (2003) also mentioned that five major recent studies concluded that heavy metal concentrations in landfill leachates were very low.

Table 5 presents human consumption based water quality limits for each element, and the number of samples exceeding these limits. Arsenic through Sodium are primary drinking water limits; Al through Zn are secondary drinking water limits. Groundwater cleanup target levels (GWCTL) are a set of water criteria for groundwater in Florida. They include the primary and secondary drinking water limits, as well as limits for other pollutants for which there is no drinking water limit. All the samples exceeded the GWCTL for Fe. B and Mn exceeded the GWCTL in more than 90% of the sample and Na exceeded in 85% of the samples. Arsenic, Sb and Al concentrations in the leachate exceeded the GWCTL in more than 40% of the samples. With the exception of Ba and Se, all other elements exceeded the GWCTL for at least one sample tested.

Table 4. Comparison of RCRA metal concentrations in Leachate with TCLP Limits.

Metal	TCLP Reg. Limit(mg/L)	Mean (mg/L)	Median	% Mean/TCLP	% Median/TCLP
As	5	0.053	0.033	1.06	0.66
Ba	100	0.154	0.073	0.15	0.073
Cd	1	0.003	0.001	0.33	0.106
Cr	5	0.065	0.022	1.29	0.448
Pb	5	0.028	0.003	0.55	0.065
Se	1	BDL	BDL	-	-
Hg	0.2	0.001	BDL	0.27	-

Table 5. Comparison of Metal Concentrations of Landfill leachate with GWCTL

Analyte	GWCTL (mg/L)	# of Samples Exceeding GWCTL	% Exceeding GWCTL
As	0.05	17	41.5
Ba	2	0	0.0
Be	0.004	1	2.4
Cd	0.005	3	7.3
Cr	0.1	4	9.8
Ni	0.1	10	24.4
Pb	0.015	8	19.5
Sb	0.006	17	41.5
Se	0.05	0	0.0
Hg	0.002	1	2.4
Na	160	35	85.4
Al	0.2	22	53.7
Cu	1	1	2.4
Fe	0.3	41	100.0
Mn	0.05	37	90.2
Zn	5	1	2.4
Mo	0.035	3	7.3
B	0.63	38	92.7
Co	0.42	0	0.0
Sn	4.2	0	0.0
Sr	4.2	7	17.1
V	0.049	7	17.1

4.3.3 Comparison of Landfill Types

As stated before, variations exist among MSW landfills. These may be for several reasons. The type of waste at each landfill can affect metal concentrations. In addition, the leachate characteristics can vary with different stages of operation. This study compared metal concentrations of the MSW landfill leachate from active (still receiving waste) landfills with those from closed landfills (defined as not receiving waste). The results are presented using Box and Whisker plots in Figure 11 through Figure 14. The 5th percentile and 95th percentile values for the active landfills are not indicated in the plots because of the limitation of number of samples available for computations. Although the concentrations are in a large range, results indicate that some elements show higher median values in active landfills, some are higher in closed landfills, and others are almost same. B, Ba, Cd, Cr, Hg, Mn, Pb and Ca showed higher median concentrations in active landfills (this include five of the eight RCRA metals). However, Al, As, Co, Fe and K had higher median concentrations for the closed landfills.

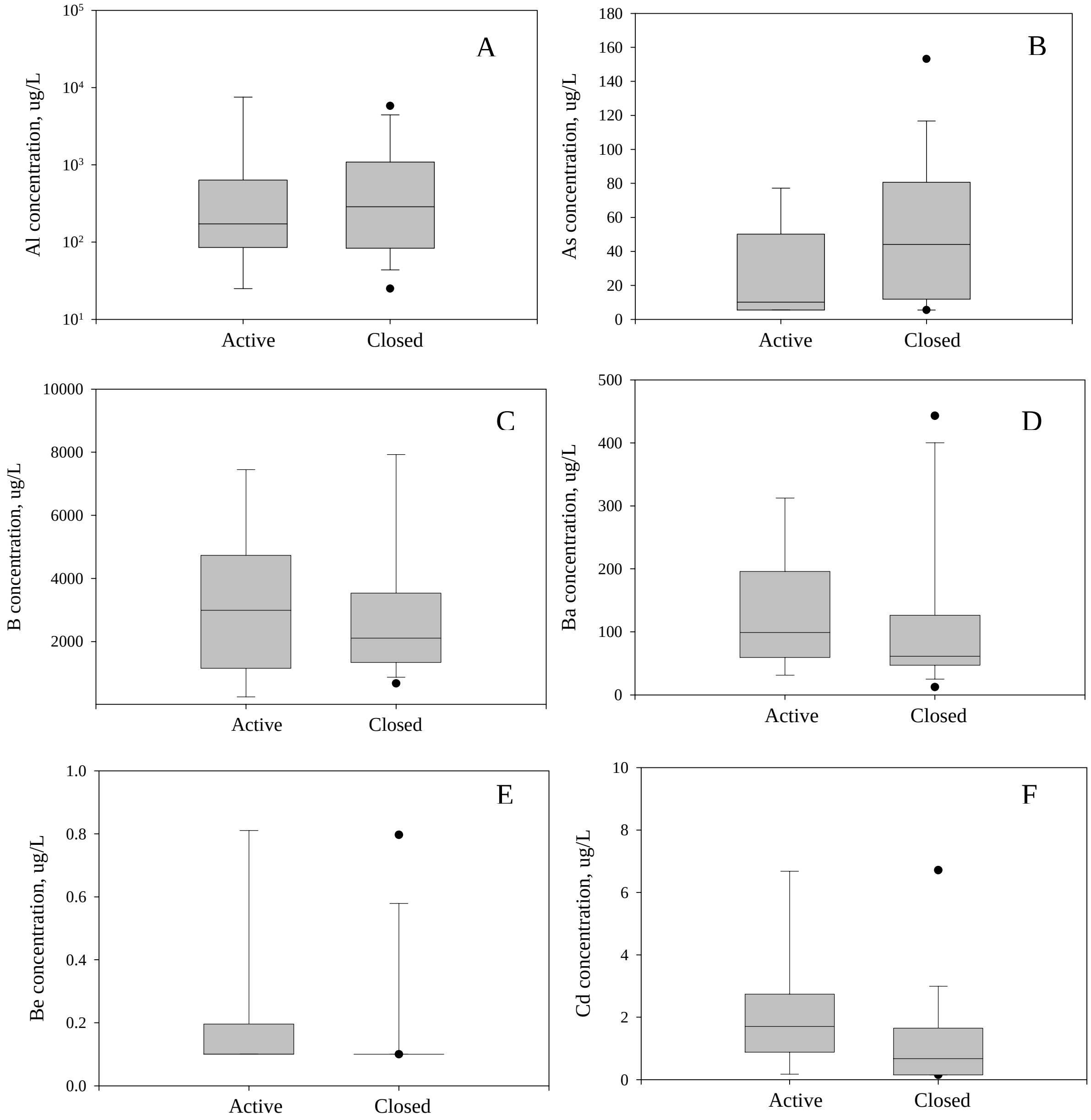

FIGURE 11. Box and Whisker Plots for Comparison of Active and Closed MSW Landfill Leachates for Al, As, B, Ba, Be and Cd.

A) Aluminum B) Arsenic C) Boron D) Barium E) Beryllium F) Cadmium

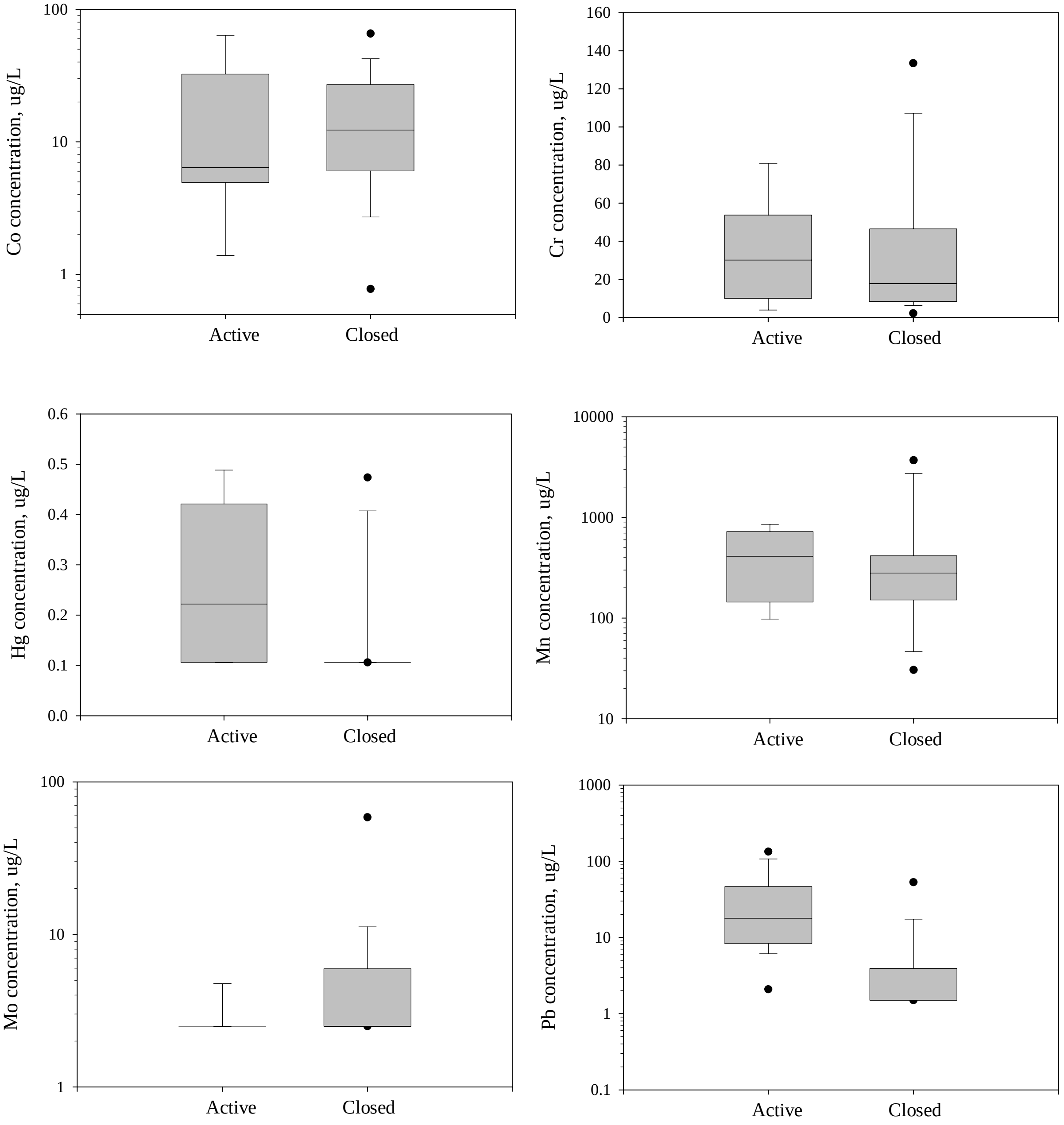

FIGURE 12. Box and Whisker Plots for Comparison of Active and Closed MSW Landfill Leachates for Co, Cr, Hg, Mn, Mo and Pb.

A) Cobalt B) Chromium C) Mercury D) Manganese E) Molybdenum F) Lead

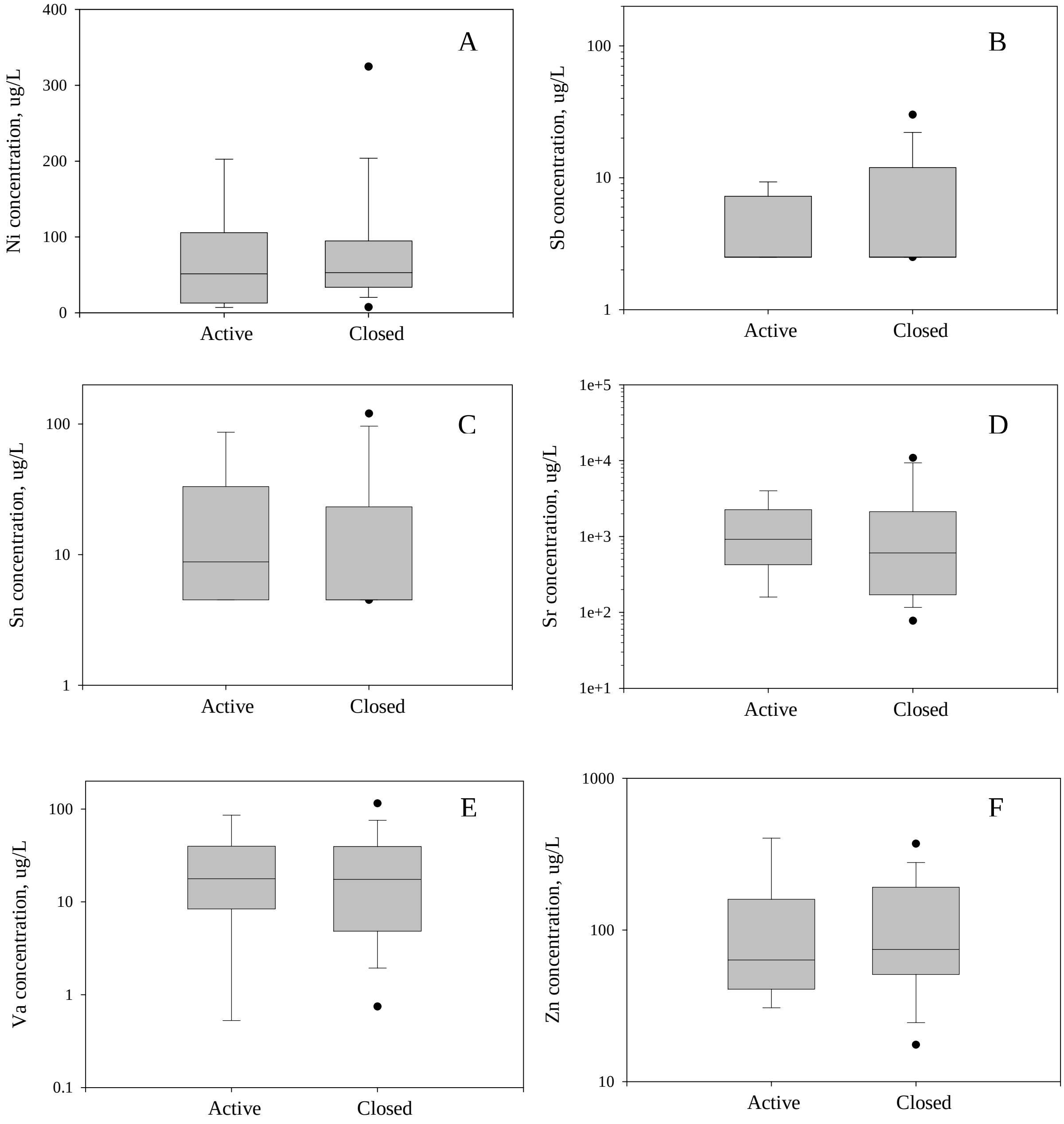

FIGURE 13. Box and Whisker Plots for Comparison of Active and Closed MSW Landfill Leachates for Ni, Sb, Sn, Sr, Va and Zn.

A) Nickel B) Antimony C) Tin D) Strontium E) Vanadium F) Zinc

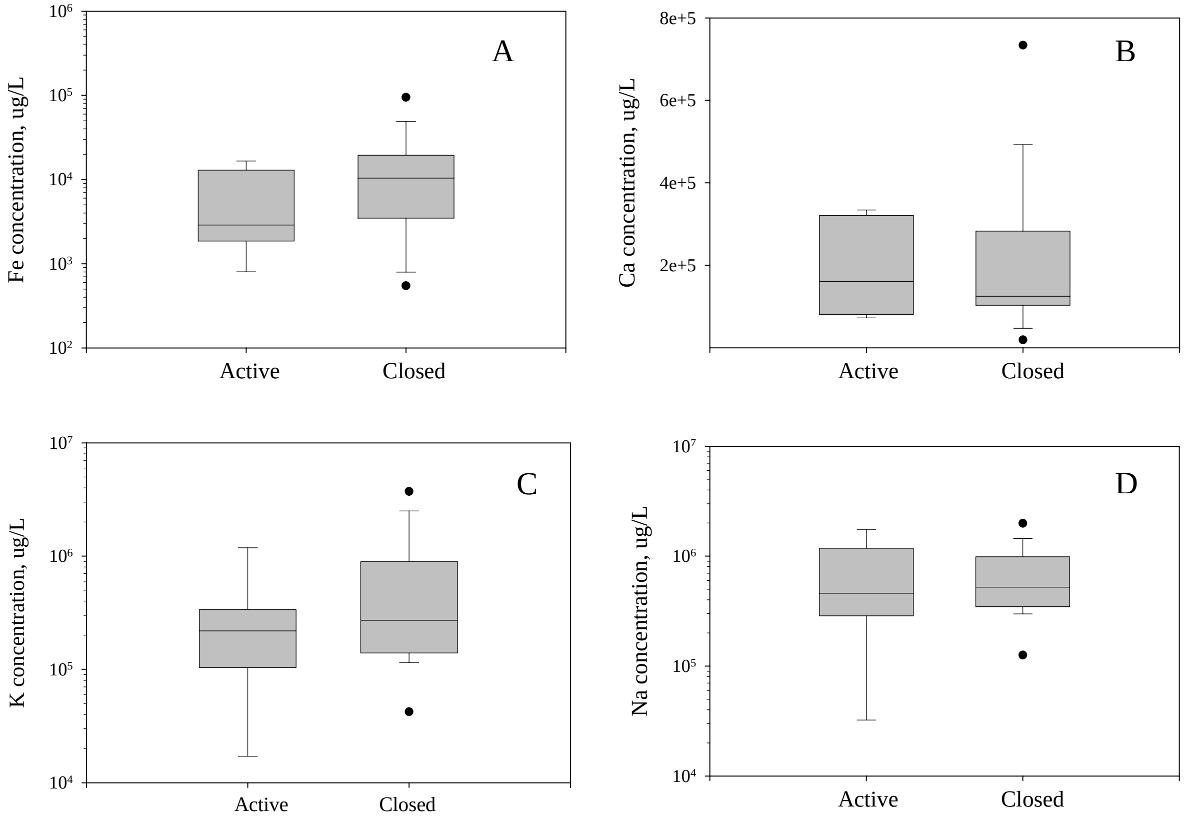

FIGURE 14. Box and Whisker Plots for Comparison of Active and Closed MSW Landfill Leachates for Fe, Ca, K and Na.

A) Iron B) Calcium C) Potassium D) Sodium

Table 6. Comparison of MSW landfills with the Ash receiving landfills (Concentrations in mg/L).

	MSW Landfills			Ash landfills		
Analyte	Minimum	Median	Maximum	Minimum	Median	Maximum
Al	BDL	0.203	574.4	BDL	0.277	9.338
As	BDL	0.029	0.440	BDL	0.060	0.110
B	BDL	2.107	11.36	0.695	1.809	4.851
Ba	0.009	0.071	1.347	0.035	0.190	0.277
Be	BDL	BDL	0.006	BDL	0.00	0.001
Ca	14.44	124.2	777.1	51.88	219.7	1,181
Cd	BDL	0.001	0.076	BDL	0.001	0.002
Co	BDL	0.011	0.113	0.000	0.011	0.027
Cr	BDL	0.022	1.289	0.018	0.027	0.039
Cu	BDL	0.005	1.122	BDL	0.00	0.005
Fe	0.517	10.96	356.6	0.451	4.852	26.83
K	1.140	207.6	4,018	90.4	234.0	3,904
Mg	1.086	34.44	210.5	4.783	28.62	100.5
Mn	0.012	0.280	3.828	0.032	0.086	1.141
Mo	BDL	BDL	0.079	BDL	0.004	0.036
Na	1.639	495.4	2,173	201.2	876	1,529
Ni	BDL	0.048	0.542	0.017	0.048	0.108
Pb	BDL	0.003	0.684	BDL	0.021	0.086
Sb	BDL	BDL	0.055	BDL	0.022	0.024
Se	BDL	BDL	BDL	BDL	BDL	BDL
Sn	BDL	BDL	1.494	BDL	0.034	0.148
Sr	0.066	0.607	10.96	1.798	2.597	33.70
V	BDL	0.016	0.367	0.001	0.016	0.029
Zn	0.017	0.074	24.43	0.073	0.120	0.165

Detection limits are shown in Table 2 and 3.

5.0 COMPARISON OF COMPUTER PWB AND CRT GLASS LEACHING USING TCLP AND MSW LANDFILL LEACHATE

5.1 Overview of Experiment

The objective of this research was to gather information regarding how much lead would leach from PWBs and CRT glass in Florida MSW landfill leachates relative to other leaching tests. The research was not intended to characterize either CRTs or computers for the RCRA toxicity characteristic. Leaching tests were conducted on printed wiring boards (PWBs) and cathode ray tubes (CRTs) using leachates from lined landfills in Florida and three regulatory leaching tests, the TCLP, SPLP, and WET. The TCLP is used by the US EPA to provide a relatively rapid test that could identify solid wastes that warranted special management as a hazardous waste. The US EPA's synthetic precipitation leaching procedure (SPLP) is a synthetic rainwater leaching test (US EPA, 1996) and is sometimes used to assess the leachability of wastes disposed in inert landfills that do not contain large amounts of biodegradable matter. California's Waste Extraction Test (WET) is used to determine hazardous waste status in California (California Code of Regulations, 1985).

5.2 Methods and Materials

Experimental methods included preparation of the PWBs and CRTs, collection and analysis of the MSW leachates, performance of the leaching tests, and analysis of extracted leachates.

5.2.1 Printed Wiring Boards

In 2001 and 2002, 30 personal computers were collected from individual donations, local electronic repair facilities, and a local household hazardous waste collection facility. In 2001, 20 personal computers were disassembled manually and the PWBs were separated from the computers (SET A). Ten computers were collected and disassembled to retrieve PWBs in 2002 (SET B). In both sets, only the large motherboards of the CPUs were collected; future references to PWB analysis refers to the motherboards. No preference was given in the selection of computers or PWBs to any specific type, manufacturer, or age. Manufacturing dates of the computers ranged from 1985 to 1998. The brand, type, and total weight of each computer were recorded. Following disassembly, the total weight of each PWB was recorded. On average, the PWBs (motherboards) made up approximately 6.0% of the total weight of the computers. After weighing, each PWB was size-reduced to approximately 5 cm by 5 cm using hand-held shears. No further size reduction procedure was conducted due to the difficulties in cutting some of the materials affixed to the boards. It is noted that this is larger than the size required by the TCLP (less than 9.5 mm). Again, the purpose of these experiments was to assess leaching of lead-containing components in MSW leachate relative to landfill leachate and other standardized leaching tests, not to characterize for the TC. While the size reduction requirement of the TCLP may result in waste characteristics not representative of actual landfill conditions, it was conservatively designed to minimize the time to reach equilibrium conditions. The pieces of size-reduced PWBs were manually mixed in a 20-liter high-density polyethylene (HDPE) bucket.

5.2.2 Cathode Ray Tubes in Computers and Televisions

A total of 36 CRTs from televisions and computer monitors were collected from individual donations, electronics repair facilities, an electronics manufacturer, and institutional electronics disposal. A CRT consists of three major glass fractions: the neck, the funnel, and the faceplate. The CRT display unit was dismantled, and the different sections of the CRT were separated. Each section was placed in a stainless steel bowl and manually crushed with a hammer. The 36 CRTs tested were the same ones used in the previous study performed to determine if CRTs were TC hazardous wastes (Musson et al., 2000; Townsend et al, 1999). Thirty of the CRTs were color and 6 were monochrome. In the previous study, each fraction of each CRT was leached using the TCLP. In this study, all of the crushed glass from the funnel sections of the 30 color CRTs was combined and mixed in a stainless steel bowl. The mixed glass was then separated by size using stainless steel sieves. Figure 15 presents the particle size distribution of the glass. The glass pieces ranging from 4.75 mm to 6.3 mm were used for the leaching experiments in this study. This size range does meet the requirements of the TCLP. Again, it is noted that the purpose was not to perform a TC characterization; the glass tested was not representative of an entire CRT.

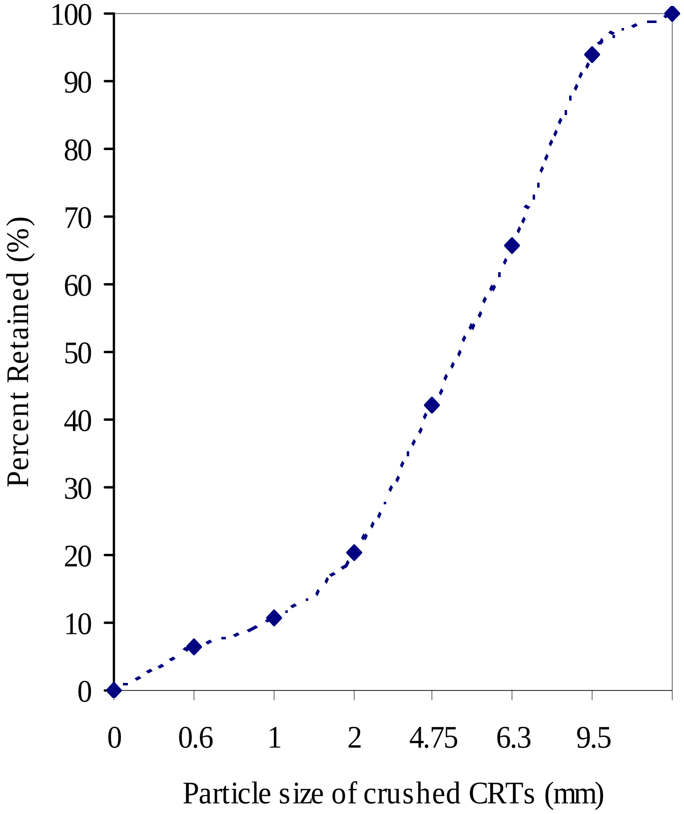

FIGURE 15. Particle size distribution of cathode ray tubes.

5.2.3 MSW Leachate Sampling and Characteristics

In 2001, leachates from five lined solid waste landfills in Florida (designated as Sites A through E) were collected from leachate collection sumps using Teflon bailers. The sites selected consisted of four MSW landfills and one class III landfill (Site D). In Florida, class III landfills receive yard trash, construction and demolition debris, carpet, cardboard, furniture, and other materials not expected to produce leachate that poses a threat to public health or the environment. In 2002, six different leachates were collected from six active MSW landfills (designated as Sites F through I, and 2002 sites A and B). Two landfills (Sites A and B) were sampled in both 2001 and 2002.

After collection of the leachate samples, parameters immediately measured in the field included pH and oxidation reduction potential (Accumet portable AP10), dissolved oxygen (DO) (YSI Inc. Model 55/12 FT), and specific conductance (HANNA Instruments, Model H19033). Three samples from each site were collected in one-liter glass bottles to accommodate different chemical analyses. One sample was preserved with sulfuric acid (pH <2) for organic content analysis (e.g., COD and TOC). Another sample was acidified with nitric acid (pH <2) for metals analysis. A third sample used for conventional water quality parameter analysis was not preserved. All samples were stored on ice and transported to a refrigerated room until a chemical analysis was performed. In addition, approximately 20 liters of leachate were collected in a HDPE container. The amount of headspace was minimized by filling the containers as much as possible. The leaching tests with landfill leachates were conducted within 24 hours of collection to minimize possible changes in leachate characteristics.

The leachate samples collected were analyzed for various leachate parameters, including metals, anions, sulfides, alkalinity, total dissolved solids, and organic acids. US EPA methods (US EPA, 1996) and other standard methods (APHA et al., 1995) were employed. After sample filtration (0.45-μm membrane filter), an ion chromatograph (Dionex DX-500) was used for ion analysis. Heavy metals in the leachate were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Jarrell Ash Corporation, Model 95970, US EPA Method 6010B) after metals digestion for liquid samples (US EPA Method 3020A). Volatile fatty acids (VFAs) were measured by gas chromatography (year 2002 leachate samples only) using a Shimadzu gas chromatograph (Shimadzu GC 9-AM) with a flame ionization detector (FID). Samples for VFAs were centrifuged at 10,000 rpm for 10 min and the resultant supernatant was acidified with 1:9 v/v parts sample to 20% H_3PO_4 containing 1000 mg/L of isobutryate. Two micro-liters of sample were injected onto a 2-m long, 3.2-mm wide internal diameter glass column packed with 10% SP1000 and 1% H_3PO_4 in Chromosorb WAW 100/120. Table 7 presents the parameters analyzed and the chemical characteristics of the leachates.

Table 7. Characteristics of Landfill Leachates

Parameters		2001 Site A	2001 Site B	Site C	Site D	Site E	Site F	Site G	Site H	Site I	2002 Site A	2002 Site B
pH		7.74	7.74	6.80	7.30	7.48	6.53	8.10	8.22	7.92	7.97	7.89
TDS (mg/L)		6320	4610	16830	2450	3780	2620	9610	1960	5540	7960	5880
Alkalinity (mg/L as CaCO$_3$)		5210	3120	7400	1800	3450	1250	6850	1550	5300	8050	4350
	COD (mg/L)	2770	1320	2650	2230	1020	792	9570	1260	2150	3080	2530
Anions and cations (mg/L)	Sulfide	0.20	0.09	0.07	0.03	0.04	< 0.008	31.65	0.072	0.132	0.225	7.75
	Chloride	1610	748	9160	406	1070	296	2150	1500	402	1950	1270
	Sulfate	< 1.0	< 1.0	< 1.0	< 1.0	< 1.0	7.91	33.0	11.0	2.42	17.6	141
	Ammonia	814	441	437	97.3	614	20.6	1490	125	833	2630	1160
	Calcium	59.5	89.9	1190	278	110	275	177	174	67	44.1	128
	Sodium	1100	1190	3410	274	1010	532	1920	367	1390	1990	1550
Organic Acid (mg/L)	Acetate	--[a]	--	--	--	--	35.0	582	273	13.5	40	366
	Propionate	--	--	--	--	--	22.6	176	32	11.3	19	13
	Isobutyrate	--	--	--	--	--	74.0	172	129	101	100	126
	Butyrate	--	--	--	--	--	< 1.0	82	29	1.8	23	7.5
	Isovalerate	--	--	--	--	--	< 1.0	159	56	0.4	13.3	59
	Valerate	--	--	--	--	--	< 1.0	52	36	0.26	3.0	<1.0
Metal (mg/L)	Iron	30.7	4.2	26.4	7.4	3.6	13.1	5.8	16.2	13.1	5.1	5.0
	Lead	<0.04	<0.04	<0.04	0.07	<0.04	<0.04	<0.04	<0.04	<0.04	0.06	<0.04
	Zinc	0.11	<0.1	<0.1	<0.1	<0.1	0.24	<0.1	0.23	0.24	0.12	<0.1

[a] Indicates that the parameter was not measured.

5.2.4 Leaching Test Protocols

The leaching tests performed in this study included the TCLP, SPLP, and WET. Table 8 summarizes the three standardized batch test protocols used as well as the extraction test protocol that utilized landfill leachates. TCLP, SPLP, and WET were performed on every sample. The same source of CRT glass was leached using the MSW landfill leachates collected in 2001 and 2002. The set A PWBs were leached using the 2001 landfill leachate samples and the set B PWBs were leached using the 2002 landfill leachate samples. The extraction process included placing 100 g of sample (PWBs or CRTs) into a 2.2-liter extraction vessel, adding 2 liters (or 1 liter for WET) of leaching solution to the vessel, tumbling for 18 ± 2 hrs (or 48 hours for WET), and filtering the extract using a pressurized filtration apparatus with a 0.7-µm borosilicate glass fiber filter (Environmental Express TCLP filters). After filtration, the extract was digested (US EPA Method 3020A) and analyzed for lead by ICP-AES. All samples were leached in triplicate. Laboratory blanks, sample spikes, duplicates, and calibration check samples were performed as appropriate.

Table 8. Summary of Leaching Test Procedures for CRT and PWB Leaching

	Standardized Leaching Test			MSW leachate
	TCLP	WET	SPLP	
pH of leaching solution	4.93 ± 0.05 (acetic acid and sodium hydroxide)	5.00 ± 0.05 (citric acid and sodium hydroxide)	4.20 ± 0.05 (sulfuric and nitric acids)	7.60[a]
No. of CRTs and PWBs used	30/10[b]	30/10[b]	30/10[b]	30/ (20 or 10)[c]
Solid to liquid ratio (gram of waste to liter of solution)	100 g / 2 L	100 g / 1 L	100 g / 2 L	100 g / 2 L
Extraction period	18 ± 2 hrs	48 hrs	18 ± 2 hrs	18 ± 2 hrs

[a] On average of 11 landfill leachates. [b] SET A-10 PWBs [c] SET A – 10 PWBs in 2001 and SET B-20 PWBs in 2002.

5.3 Results and Discussion

5.3.1 Leaching Results Using MSW Landfill Leachates

The results of the batch leaching tests for the PWB pieces and the CRT glass using MSW landfill leachates are presented in Figure 16. In the PWB leaching experiments, lead concentrations ranged from 0.53 to 5.0 mg/L, with an average of 2.2 mg/L. For the CRT samples, lead concentrations ranged from 1.7 to 6.0 mg/L, with an average of 4.1 mg/L. Background levels of lead in the landfill leachates ranged from less than detection limit (0.04

mg/L) to 0.07 mg/L, as shown in Table 7. Lead concentrations in the extracts for Site D and 2002 Site A were corrected for the background lead concentrations.

The MSW leachates varied to some extent in their ability to extract lead from the PWB and the CRT samples, as presented in Figure 16.

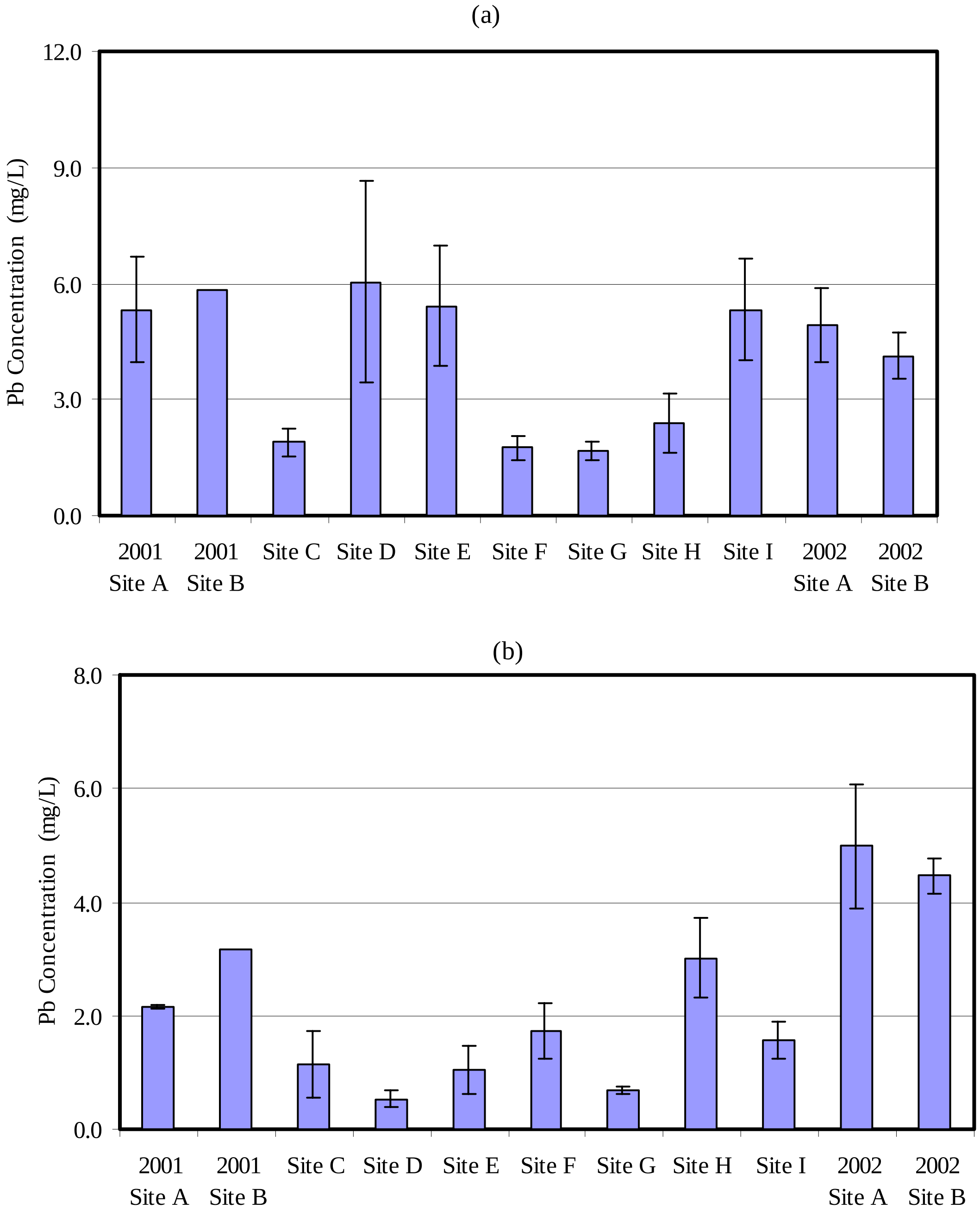

FIGURE 16. Lead leaching from (a) CRTs and (b) PWBs using MSW landfill leachates

(Error bars represent standard deviation of triplicate leaching tests; the 2001 Site B leachate was tested in duplicate only).

An analysis of variance (ANOVA) was conducted to determine whether there was any significant difference in lead concentration among the MSW leachate extracts. The critical value of the F-distribution (α= 0.05, df1 = 10, df2 = 22) was 2.30.

The computed values of F for the PWB and CRT samples were 5.0 and 2.7, respectively. This suggests that at least one of the mean lead concentrations in the MSW leachate extracts differed from the others. Fisher's least significant difference (LSD) test was then performed to determine differences among possible pair wise combinations. In the case of the PWB data analysis, 2002 Site A and 2002 Site B were significantly greater than all other sites. For the CRT data analysis, Sites D, E, I, A (2001 and 2002), and B (2001 and 2002) were significantly greater than those obtained by Sites H, C, F, and G. For the same sites with different years (Sites A and B), lead concentrations were different for the PWB extracts, but not significantly different for the CRT samples. While the Class III landfill leachate (Site D) extracted lead from the PWB samples at the lowest level, the average lead concentration of the CRT samples using the Class III landfill leachate was among the highest.

Several factors can influence how a given leachate will extract lead. There were not enough leachate samples to perform a detailed analysis of all the factors affecting lead leaching. Some factors, however, will be discussed further. Previous leaching studies have shown that lead exhibits a marked increase in leachability at both low and high pH values. Minimum leachability is observed at neutral pH values and an increase in leachability is observed at pH values less than 6 and greater than 10 (van der Sloot et al., 1991; Groot and van der Sloot, 1992; Eighmy et al., 1995; van der Sloot et al., 1997). In this study, the leachate pH values of all the leachates fell within the range 6 to 8; the change in pH during the leaching test was minor, with only slight increases noted from the original leachates. When lead concentrations were compared to final leachate pH values to evaluate a possible relationship, no significant correlation was found. This is largely a result of the very narrow pH range encountered among the leachate samples. The presence of organic acids (e.g., volatile fatty acids) in landfill leachate may also enhance metal mobility due to complexation (Clevenger and Rao, 1996; Gould et al., 1998). Volatile fatty acids were measured only for Sites F through I, and 2002 Site A and 2002 Site B. No clear evidence of a correlation between organic acid concentrations and the amounts of lead extracted was found. Other factors that could impact metal leaching include dissolved organic matter, hardness, oxidation-reduction potential, ionic strength, and species that might result in precipitation (sulfides, hydroxides). Additional experimentation using more leachate samples with a more complete analysis is needed to explore the possible relationships further.

5.3.2 Comparison of MSW Leachate Results to Standardized Tests Results

Figure 17 presents a comparison of the average lead concentrations measured using MSW landfill leachate with the concentrations measured using the standardized leaching tests. The MSW landfill leachate results represent an average of all 11 samples tested. In all cases the TCLP extracted more lead from the size-reduced PWBs and the CRT glass than did the MSW leachate. The greater lead concentrations measured using the TCLP can be attributed to two primary factors. The higher affinity of acetate ions in TCLP for lead complexation resulted in higher levels of lead in the extracts. Acetate, a component of the TCLP leaching solution, is a monodentate ligand with an affinity for transition metal ions such as lead. Acetate, which chelates strongly with lead, enhances dissolution and complexation of metals (Majone et al., 1996; Lagier et al., 1999; Flyhammar and Hakansson, 1999). The concentration of acetate in the

TCLP fluid is 5,990 mg/L. This compares to the measured acetate concentrations in the range of 13 to 580 mg/L in the 2002 Florida MSW landfill leachate samples.

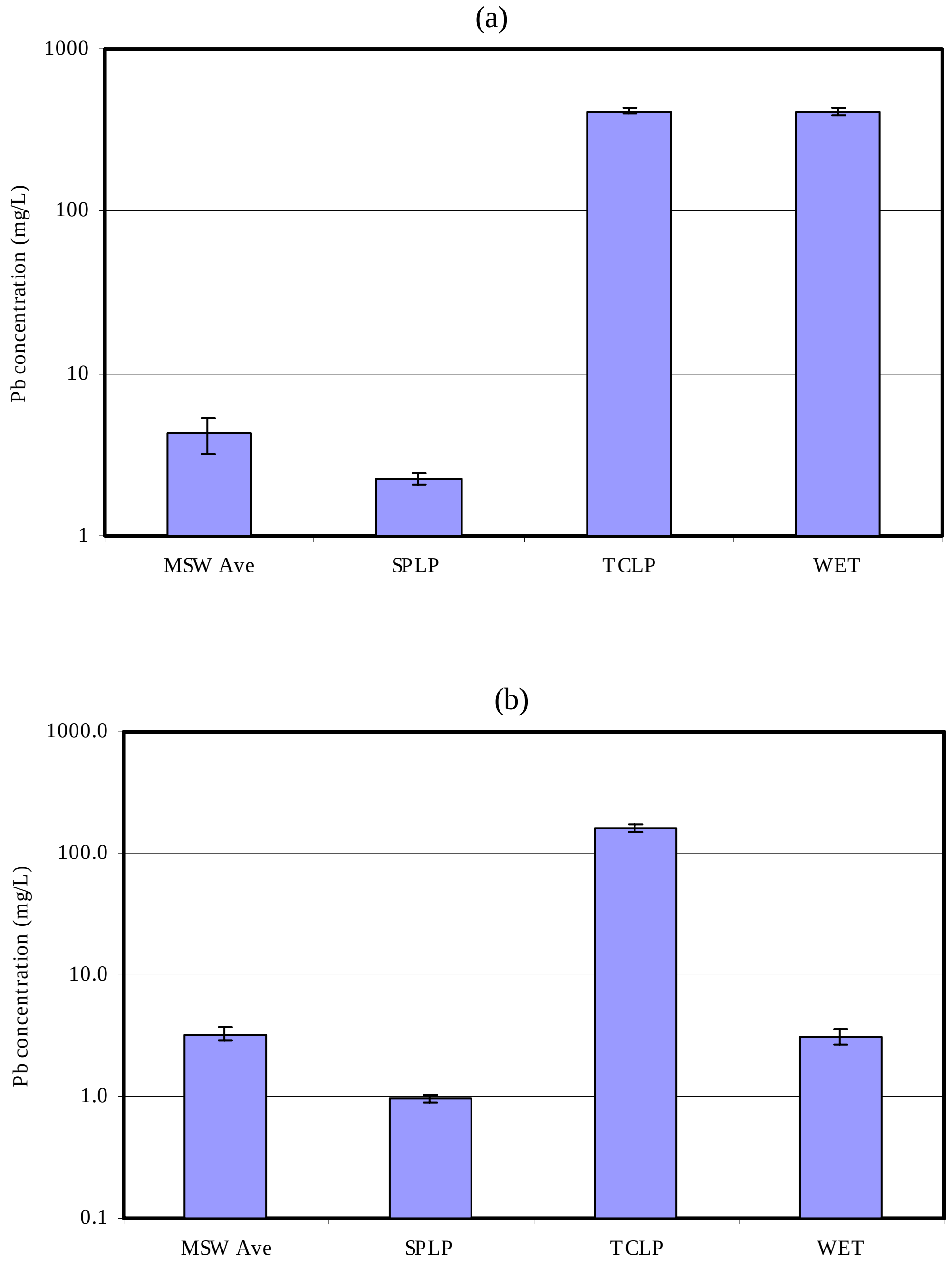

FIGURE 17. Comparisons of Pb leaching from CRTs (a) and PWBs (b) using MSW leachates with SPLP, TCLP, and WET results.

As discussed previously, pH plays an important role in the leachability of lead. The initial and final pH values for the MSW landfill leachates were higher than those in the TCLP and WET. The initial pH of all MSW leachates was neutral, ranging from 6.5 to 8.2 (Table 7). This is typical for MSW landfill leachate pH (Farquhar, 1989; Tchobanoglous et al., 1993). Leaching tests with MSW leachate yielded slightly higher pH values than the initial pH values. As stated previously, the TCLP leaching solution was buffered with sodium hydroxide at a pH of 4.93. The TCLP final pH values were close to the initial pH values: 4.97 for printed wire boards and 5.08 for CRTs (Table 9). This indicated that the alkalinity released by the PWB pieces and CRT glass was not large enough to change the pH greatly during the 18-hour TCLP extraction. The MSW leachate leaching tests were conducted at a pH that was higher than the pH value for the TCLP, resulting in less lead leaching (Table 9). In the California study that compared the leaching of multiple metals from a number of solid wastes using the TCLP and MSW leachates, the pH values of the MSW leachate extraction solution were also generally higher than the TCLP (Hopper et al., 1998), but the pH effect on lead leaching was not as clearly observed.

Table 9. Summary of Leaching Test Results

		MSW leachate	**Standardized Leaching Test**		
			TCLP	**WET**	**SPLP**
Initial pH		7.60 [a]	4.93	5.00	4.20
CRT	Ave. Pb Conc. (mg/L)	4.06	413	350	2.27
	Ave. Final pH	7.67	5.08	5.07	9.73
PWB	Ave. Pb Conc. (mg/L)	2.23 [a]	162	3.15	0.95
	Ave. Final pH	7.69	4.97	5.14	7.70

[a] Average of 11 landfill leachates

When the average concentration of lead in MSW leachate extracts was compared to that of the WET (Figure 17), the results for CRT glass were similar to those obtained with the TCLP. Citrate, a component of the WET leaching solution, is a tridentate ligand which chelates with metal ions such as lead (Kjeldsen et al., 2002). The final pH value of the WET for CRTs was close to the initial pH of 5.0 (Table 9). As was the case with the acetic acid-based TCLP, the use of citric acid in the WET coupled with lower pH values resulted in higher concentrations of lead from the CRT glass when compared to MSW leachate extracts. In the case of computer PWBs, the leaching results from the WET differed; the average lead concentration was close to that of the MSW leachate extracts. It is uncertain whether the mechanism for relatively low leachability of lead was precipitation or interference with other chemicals in the circuit boards. Further study is needed to determine the cause of the lower concentrations of lead in the WET extract. Hooper et al. (Hopper et al., 1998) found lead to leach from several waste streams at significantly greater concentrations using the WET relative those extracted by California MSW leachates.

The lead concentrations measured in the SPLP leachates were lower than the TCLP, WET, and the MSW landfill leachates. When comparing the SPLP results with those from the TCLP and WET, a similar rationale as previously mentioned can be used to explain the lower concentrations of lead in the SPLP. The synthetic acid rain used in the SPLP was not buffered; this resulted in an increase in pH during the leaching test. The pH increased from an initial value of 4.2 to final values of 7.7 for PWBs and 9.7 for CRTs (Table 9). The E-waste components, especially the CRT glass, neutralized the acid found in the SPLP leaching solution. The lower lead concentrations in the SPLP extract resulted from the higher pH values, along with the absence of chelating or complexing agents (as found in the TCLP and WET). The MSW landfill leachates extracted somewhat more lead than SPLP, especially in the CRT glass. The final pH of the MSW leachates was similar to that in the SPLP for the leaching of the PWBs. The increased lead concentration in the MSW leachate at the same pH as the SPLP indicates that some additional factors in the landfill leachates contributed to extracting the lead beyond pH. The difference was less pronounced with the CRT glass because of the increased pH of the SPLP leachates. Both lead concentrations extracted from the PWBs and CRTs by the SPLP were statistically lower than the average concentrations of lead extracted by the MSW leachates ($\alpha = 0.05$).

6.0 LEACHING OF METALS FROM CELLULAR PHONES, MERCURY LAMPS AND NICKEL CADMIUM BATTERIES USING TCLP, SPLP AND MSW LANDFILL LEACHATES

6.1 Overview of Experiment

The objective of this research was to gather information regarding how heavy metals leach from cellular phones, mercury lamps and nickel cadmium batteries under typical Florida MSW landfill leachate conditions relative to other leaching tests. This chapter deals with the same issues as the previous chapter, but the leachate samples collected in 2003 were used for the leaching tests. Twenty-seven cell phones, eighteen nickel-cadmium batteries and eighteen mercury lamp samples were leached in MSW landfill leachate. The TCLP and SPLP were also performed on the samples. The objective of this research is not to characterize the wastes for the RCRA Toxicity Characteristic, rather to estimate the concentrations of lead, cadmium, and mercury that may potentially leach from these devices when disposed of in a typical Florida MSW landfill.

6.2 Methods and Materials

Experimental methods included preparation of the samples, collection and analysis of the MSW leachates and analysis of extracted leachates. Since each group of E-waste was processed differently, the following sections discuss each in detail.

6.2.1 Cellular Phones

During the summer of 2003, seventy-eight cell phones were collected from a recycling facility located in Tampa, Florida. All cell phones used for this study were Motorola model i600. The cellular phones were disassembled into five component categories and weighed. The five categories used for sample categorization were; plastic, printed wire board, ferrous metal, non-ferrous metal and liquid crystal display (LCD). The samples were reduced to a final weight of 100 g by proportionally reducing each category by its appropriate percentage composition. Size reduction was conducted manually with hand shears for all samples.

6.2.2 Nickel-Cadmium Batteries

The nickel-cadmium batteries used for this study were collected from the Alachua County Transfer Station, Household Hazardous Waste facility. The nickel-cadmium batteries used for this study were manufactured by Alexander Battery Company, model S522. Each cell weighed approximately 70 g. To prepare the samples, each battery was cut in half to expose the contents of the battery. Next, the cell was placed in a 2 liter TCLP vessel with enough leaching solution to yield a 20:1 liquid-to-solid ratio. It is important to note that the sample preparation deviated from the TCLP method in that the samples were not size reduced to below 0.95 cm so this is considered a modified TCLP. The modified TCLP method is described further in Section 6.2.5 of this report. The architecture of the battery cells prevented a uniform size reduction and it is thought that the method used is more appropriate for this study. A total of twenty-two samples were used for this study. The samples were leached in nine different MSW landfill leachates, TCLP solution, and SPLP solution.

6.2.3 Mercury Florescent Lamps

Discarded household mercury florescent lamps were collected for this study. They were obtained at the Alachua County Transfer Station, Household Hazardous Waste facility. The lamps were size reduced using a fluorescent bulb crusher. The bulbs were size reduced to below 0.95 cm. The samples were weighed out to 100 g, and placed in 2 L of leaching solution. Currently, only leaching tests in MSW leachates have been performed on the mercury florescent lamp samples. TCLP and SPLP leaching tests will be carried out in the future as part of this study.

6.2.4 MSW Landfill Leachate Collection

During the summer of 2003, 41 MSW landfill leachate samples were collected. Nine of the leachates were used as leaching fluid for cell phones, nickel-cadmium batteries, and mercury florescent lamps. The leachates used were from locations 24, 26, 27, 32, 33, 34, 36, 37, and 40. Upon collection, the leachate samples were taken to the laboratory and tested for a variety of parameters.

6.2.5 Leaching Test Protocols

The leaching tests used for this study included the TCLP, SPLP, a modified TCLP and a modified SPLP method. Table 10 summarizes the different methods employed for testing each waste and the number of samples tested. All samples were rotated at 28 rpm in 2 L HDPE vessels for 18 ± 2 hrs. A 20:1 liquid-to-solid ratio was used for all leaching tests. After rotation, samples were pressure filtered using 0.7 μm borosilicate glass fiber filters (Environmental Express TCLP filters). After filtration, the filtrate was digested (US EPA Method 3015-H, Microwave Assisted Reaction System, CEM Mars 5, Model ESP 1500) and analyzed using inductively coupled plasma-atomic emission spectroscopy (ICP-AES, Thermo Jarrell Ash Corporation, Model 95970). Laboratory blanks, sample spikes, duplicates and calibration check samples were performed as appropriate.

Standard TCLP leaching followed the methods outlined in EPA method 1311. The standard TCLP method was used for five cell phone samples. To meet the size reduction and weight requirements, all samples are disassembled and separated into five categories; plastic, printed wire board, ferrous metal, non-ferrous metal, and liquid-crystal display. Next, the mass of each sample was reduced to 100 g by removing a proportional mass of each categories. Each sample was then size-reduced to below 0.95 cm by means of cutting with hand shears.

A modified TCLP was used for testing five cellular phones and two nickel-cadmium batteries. This method follows all of the requirements of EPA method 1311, except that the devices were not size-reduced to below 0.95 cm.

Standard SPLP leaching tests followed the prescribed methods outlined in EPA method 1312. The standard SPLP method was used for five cell phones and two nickel-cadmium batteries. The method is similar to the TCLP described above, but varies in the extraction fluid used. SPLP leaching solution is comprised of nitric and sulfuric acid. A modified SPLP was used for testing two nickel-cadmium batteries. This method follows all of the requirements of EPA method 1312, except that the devices were not size-reduced

MSW Leaching. The leaching test using landfill leachate stayed as close as possible to the TCLP, with the substitution of MSW landfill leachate for the leaching solution. The pH of the leachates ranged from 6.190 to 8.096. The size reduction differed by device.

Table 10. Summary of Sample Numbers and Size-reduction

Cell Phones

Leaching Test	TCLP	Modified TCLP	SPLP	Modified SPLP	MSW Leaching
Number of Samples Leached	5	5	5	0	27
Size-reduced	Yes	No	Yes	-	No

Ni-Cadmium Batteries

Leaching Test	TCLP	Modified TCLP	SPLP	Modified SPLP	MSW Leaching
Number of Samples Leached	0	2	2	2	18
Size-reduced	-	No	No	No	No

Mercury Florescent Lamps

Leaching Test	TCLP	Modified TCLP	SPLP	Modified SPLP	MSW Leaching
Number of Samples Leached	0	0	0	0	18
Size-reduced	-	-	-	-	Yes

6.3 Results and Discussion

The results of the leaching tests for the cellular phones, nickel-cadmium batteries, and mercury florescent lamps are shown in Figure 18 through 20. Lead, cadmium and mercury concentrations presented were corrected for background concentrations in the landfill leachates.

The lead leaching results for cell phones are presented in Figure 18. Among the cell phones tested, lead leached from 0.01-1.65 mg/L in MSW leachate. The mean value for the TCLP was 52.86 mg/L and the mean value for the SPLP was 3.22 mg/L. Background levels of lead in landfill leachates ranged from below detection limit (0.04 mg/L) to 0.105 mg/L.

The cadmium leaching results for nickel-cadmium batteries are summarized in Figure 19. Among the nickel-cadmium batteries tested, lead leached from 0.11-11.54 mg/L in MSW leachate. The mean value for TCLP was 15.01 mg/L and the mean value for SPLP was 0.02 mg/L. Background levels for cadmium in the landfill leachates ranged from 0.03 mg/L to 0.29 mg/L.

The mercury leaching results for florescent lamps are summarized in Figure 20. Among the florescent lamps tested, mercury leached from a range of below detection limit (<0.002 mg/L) to 0.06 mg/L. Background levels for mercury in the landfill leachates ranged from below detection limit to 0.005 mg/L. TCLP and SPLP tests have not yet been conducted.

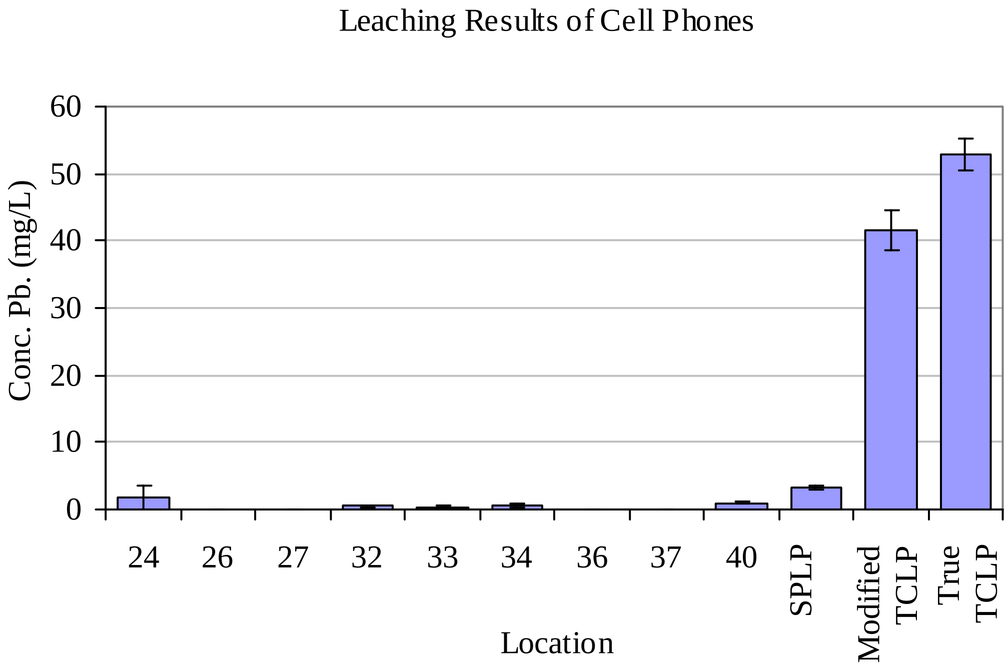

FIGURE 18. Lead leaching results from cellular phones.

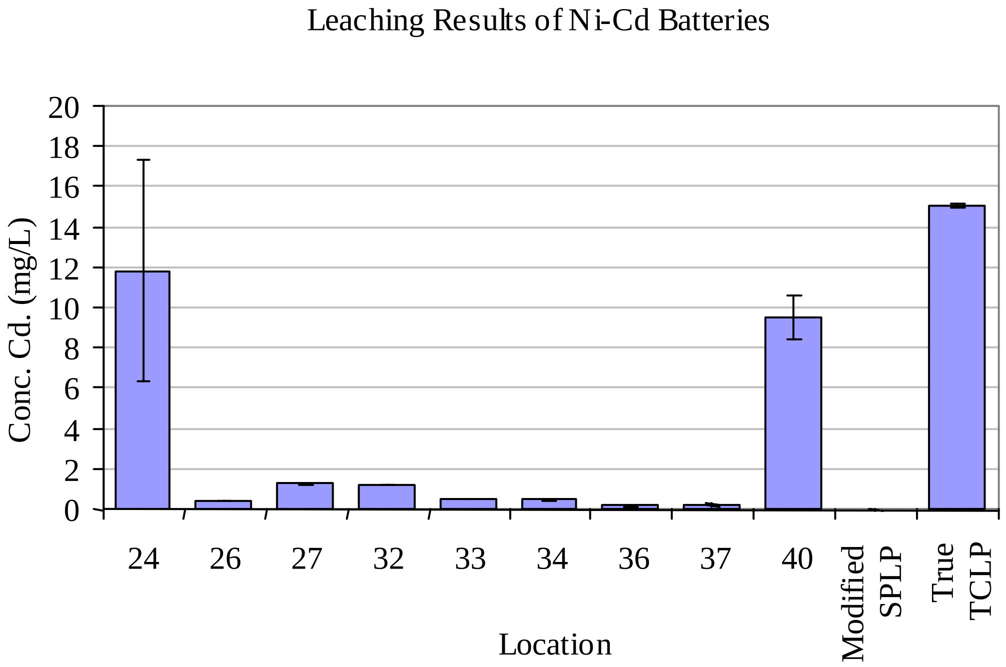

FIGURE 19. Cadmium leaching results from nickel-cadmium batteries.

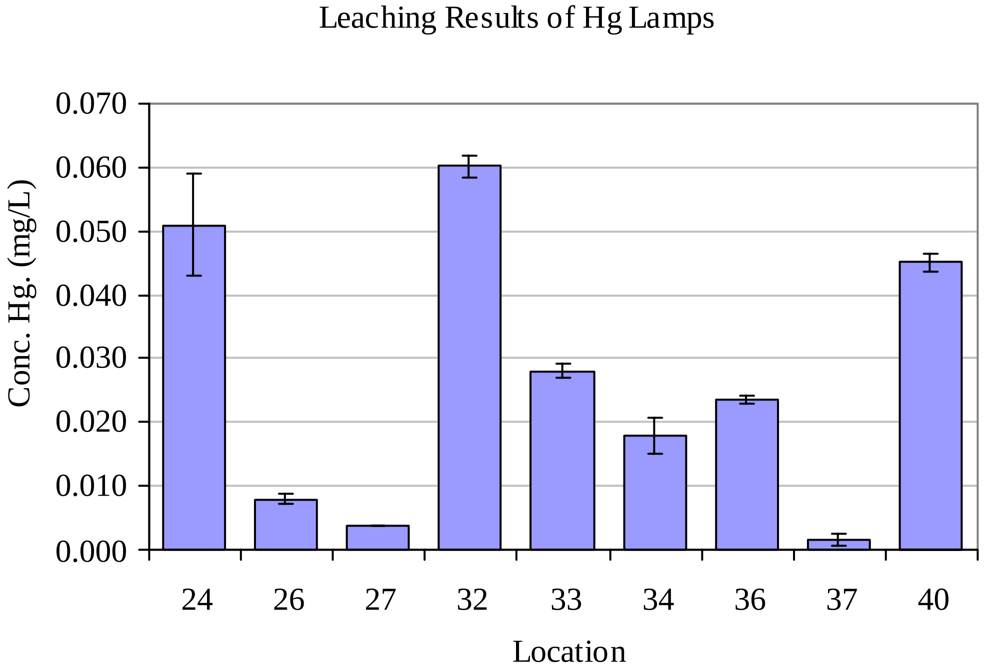

FIGURE 20. Mercury leaching results from mercury florescent lamps.

7.0 ASSESSMENT OF POTENTIAL IMPACT OF E-WASTE ON WASTE-TO-ENERGY ASH

An analysis of the potential impact of E-waste on Waste-to-Energy ash will be conducted using data compiled from FDEP, literature values for metals content of E-waste, and information from WTE facilities. The final report will contain the completed analysis.

8.0 PRELIMINARY OBSERVATIONS AND PLANS FOR YEAR 2

This research aims to produce a deeper understanding of the impact of E-waste on disposal using leaching tests, simulated landfills, landfill leachate data, and MSW incinerator ash data. In year 2, simulated landfills or “lysimeters” will be filled with a known amount of E-waste to observe the leaching behavior of E-wastes in a simulated MSW mixture. Also, in year 2, regulatory Waste-to-Energy ash data will be analyzed to assess the potential impact of E-waste on metals concentrations. The lysimeters for this project are under construction and will be installed in February 2004. The Waste-to-Energy analysis is in the data gathering stage and analysis will begin in Spring 2004. What follows is a discussion of the results from year 1 and some preliminary observations drawn from the current data.

In total, 34 Florida landfill leachate samples were analyzed for brominated flame retardants. At this point, the data is still being analyzed, but some preliminary conclusions can be drawn. First, there are unexpected levels of unknown organo-bromine compounds in landfill leachate. These compounds may be BFRs, BFR breakdown products, other organo-bromine compounds or their breakdown products. One concern with BFRs is the breakdown of high molecular weight BFRs, which are less bioaccumulative, into lower molecular weight BFRs, which are more bioaccumulative. Recent research has indicated the debromination (loss of bromine atoms) of Deca-BDE, the second most widely used BFR and the highest molecular weight and most widely used polybrominated diphenyl ether (PBDE), in carp (Stapleton et al., 2003). Considering the chemically active nature of landfills, the conversion of BFRs to other chemicals could be a possibility. Second, it appears that BFRs may be able to migrate out of landfills through the leachate collection system, but to quantify the amount of BFRs in landfill leachate, High Resolution GC/MS, coupled with further cleanup procedures may be required. At this point, there are no plans to pursue this option, as no instrument is available at UF capable of this analysis.

In total, 41 landfill leachate samples were analyzed for the occurrence and concentration of heavy metals. Metal concentrations obtained from samples filtered using a 0.45-micron filter were compared to concentrations from unfiltered samples. Some elements (e.g. aluminum, iron) were statistically greater in many of the unfiltered samples, indicating that sediments and other particulate matter were contributing to the metals occurring in the leachate sample. Other elements (e.g. beryllium, antimony, tin, zinc, molybdenum, lead and cobalt) were found to occur relatively consistently among the filtered and unfiltered samples. The results indicate that sampling point selection and sample handling can influence the concentrations of metals. Landfill operators, therefore, may want to select sampling points according to the purpose of the sampling i.e. groundwater monitoring versus leachate bound for offsite treatment.

In general, the heavy metal concentrations found in current study were lower than reported in the literature, especially when compared to a US database that includes more than 200 MSW landfills (including 65 Florida MSW landfills). Different percentile values (e.g. 90th percentile) were calculated from the range of concentrations for each element. Several of the RCRA heavy metals occurred at concentrations predominantly below human consumption limits (e.g. drinking water standards), while the other elements exceeded these limits for some samples. None of these however exceeded their TC limit. Thus, concentrations of heavy metals in landfill leachates were relatively low. This corroborates results from previous studies. Concentrations of elements such as arsenic, however, are sufficiently high that landfills might have difficulty meeting leachate pretreatment requirements if the limits based on drinking water standards. Planned work for year 2 in this area includes collecting further samples and comparing factors such as landfill age, cover soil type, leachate generation rates, management techniques, and disposal bans.

In total, # leaching tests were conducted to assess the leaching behavior of different E-wastes. The dramatic difference between the lead concentrations measured using the TCLP and those measured using Florida landfill leachates merits further discussion. The TCLP was designed to simulate worse-case leaching conditions in a municipal waste landfill. The amount of acetic acid used in the TCLP solution corresponds to the maximum amount expected to be produced under a given co-disposal scenario. Acetic and other fatty acids are produced during anaerobic waste decomposition in landfills, as a result, landfills with leachates containing large amounts of fatty acids and lower pH values are often classified as being in the acid phase. Landfills where methane production has begun are classified as being in the methanogenic phase with lower amounts of fatty acids and a pH that tends to be neutral (Kjeldsen et al., 2002). This classification system can be misleading as the sequential layering of waste in landfills means that fresher waste overlays older and one landfill can be simultaneously in multiple stages. Once the lower layers of a landfill enter the methanogenic phase, acids formed in upper layers that travel downward could be utilized by microorganisms to produce CH_4, CO_2, and a more neutral pH. For reasons discussed earlier, lead would tend to leach less in leachates with lower levels of organic acids and a neutral pH. When compared to leachate concentrations summarized in the literature (Kjeldsen et al., 2002), most Florida landfills were similar to landfills characterized as being in the methanogenic phase.

From a regulatory perspective, the TCLP was designed to be a conservative test, and thus one would expect such a test to result in greater leaching levels. The very large difference in lead leaching suggests that the test might be over-conservative (especially in light of other conservative features built into the test such as size reduction). On the other hand, in Hooper et al.'s work (1998), many elements leached more when using landfill leachate relative to the TCLP. The TCLP may thus be more conservative for some elements (and some wastes) and less conservative for others. The US EPA has been examining the applicability and shortcomings of TCLP for a number of years, and this research adds to this complicated issue. For those state and local governmental agencies wrestling with whether to ban discarded electronics from landfills, the results of this work suggest that lead leaching from PWBs and CRTs will be less than might be estimated using TCLP results. It is also important to note that other factors affect the migration of leached lead from a disposed device to the leachate collection system of a landfill (e.g. sorption, reduction, precipitation).

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