
Arsenic and Chromium Speciation of Leachates from CCA-Treated Wood

(FINAL)

Submitted September 27, 2004

Helena Solo-Gabriele, Ph.D., P.E.
Bernine Khan, Ph.D.
University of Miami, Coral Gables, FL

Timothy Townsend, Ph.D., P.E.
Jin-Kun Song, M.S.
Jenna Jambeck, Ph.D.
Brajesh Dubey, M.S.
Yong-Chul Jang, Ph.D.
University of Florida, Gainesville, FL

Yong Cai, Ph.D.
Florida International University
Miami, FL

State University System of Florida
FLORIDA CENTER
FOR SOLID AND HAZARDOUS WASTE MANAGEMENT
2207 NW 13 Street, Suite D
Gainesville, FL 32609

Report #03-07

This page left intentionally blank.

This document is formatted for 2-sided copies.

TABLE OF CONTENTS

TABLE OF CONTENTS	iii
LIST OF FIGURES	v
LIST OF TABLES	viii
LIST OF ABBREVIATIONS AND ACRONYMS	xi
UNITS OF MEASURE	xiii
ABSTRACT	xiv
CHAPTER I, BACKGROUND, MOTIVATION, AND OBJECTIVES	
I.1 Motivation	3
I.2 Background	3
I.3 Objectives	10
CHAPTER II, LABORATORY ANALYTICAL METHODS	
II.1 Arsenic Analysis of Liquid Leachates	13
II.2 Chromium Analysis of Liquid Leachates	17
II.3 Metal Analysis in Solid Samples	18
CHAPTER III, RESULTS FROM “pH STAT” EXPERIMENTS	
III.1 Sample Preparation	25
III.2 Results	26
CHAPTER IV, RESULTS FROM TCLP AND SPLP FOR UNBURNED WOOD AND CCA-TREATED WOOD ASH	
IV.1 Sample Descriptions and Pre-processing	37
IV.2 Sample Processing for SPLP and TCLP Analysis	42
IV.3 Results from Unburned CCA-Treated Wood	44
IV.4 Results from CCA-Treated Wood Ash	49
IV.5 Comparison Between SPLP and TCLP Tests and Between Unburned CCA- Treated Wood and CCA-Treated Wood Ash	56

TABLE OF CONTENTS (Con'd)

CHAPTER V, LYSIMETER STUDY

V.1 Lysimeter Construction	63
V.2 Operation and Monitoring of Lysimeters	68
V.3 Results	69

CHAPTER VI, ANALYSIS OF GROUNDWATER NEAR C&D DEBRIS DISPOSAL FACILITIES

VI.1 Preliminary Efforts	81
VI.2 New Strategy	82
VI.3 Results	83

CHAPTER VII, SUMMARY, CONCLUSIONS, RECOMMENDATIONS, & ACKNOWLEDGMENTS

VII.1 Summary and Conclusions	91
VII.2 Recommendations	94
VII.3 Acknowledgments	95

REFERENCES

APPENDIX A: Separation of Arsenic Species by Ion-Exchange Cartridges	101
APPENDIX B: Data Log Sheet for Groundwater Sampling Study	109
APPENDIX C: Supplemental Data from Lysimeter Study	113
APPENDIX D: Supplemental QA/QC Information	121

LIST OF FIGURES

- Figure I.1 Eh-pH Diagram for Arsenic (Schnoor 1996)
- Figure I.2 Eh-pH Diagram for Chromium (Adapted from Ball and Nordstrom 1998)
- Figure II.1 Summary of Laboratory Methods Used for Arsenic Analysis for Liquid Leachates
- Figure II.2 HPLC-HG-AFS Setup
- Figure II.3 Chromatogram of the Four Major Arsenic Species using HPLC-HG-AFS
- Figure II.4 Summary of Laboratory Methods Used for Chromium Analysis of Liquid Leachates
- Figure II.5 Summary of Laboratory Methods Used for the Analysis of Solid Samples
- Figure III.1 Leaching of Arsenic from New Wood at Varying pH Values, Total Arsenic as Measured by AFS is in the Form of As(V)
- Figure III.2 Leaching of Chromium from New Wood at Varying pH Values
- Figure III.3 Leaching of Arsenic from Weathered Wood at Different pH Values
- Figure III.4 Leaching of Chromium from Weathered Wood at Different pH Values
- Figure III.5 Total Arsenic Concentrations for New and Weathered CCA-treated Wood Across the pH Range (HPLC-HG-AFS Analysis Method)
- Figure III.6 Distribution of Arsenic Among As(V) and As(III) Across the pH Range for Weathered Wood
- Figure III.7 Total Chromium Concentrations for New and Weathered CCA-treated Wood Across the pH Range
- Figure III.8 Distribution of Chromium Among Cr(III) and Cr(VI) Across the pH Range for Weathered Wood
- Figure IV.1 Layout of the TCLP and SPLP Experiments
- Figure IV.2 Processing Steps for the TCLP/SPLP Experiments

LIST OF FIGURES (con'd)

- Figure IV.3 Arsenic Species Observed In SPLP Leachates From Unburned Wood Samples
- Figure IV.4 Chromium Species Observed In SPLP Leachates From Unburned Wood Samples
- Figure IV.5 Arsenic Species Observed In TCLP Leachates From Unburned Wood Samples
- Figure IV.6 Arsenic Species Observed In SPLP Leachates From CCA-Treated Wood Ash
- Figure IV.7 Chromium Species Observed In SPLP Leachates From CCA-Treated Wood Ash
- Figure IV.8 Chromium Concentration Versus Final pH of Leaching Solution for SPLP Leachates From CCA-Treated Wood Ash
- Figure IV.9 Arsenic Species Observed In TCLP Leachates From CCA-Treated Wood Ash
- Figure IV.10 Chromium Species Observed In TCLP Leachates From CCA-Treated Wood Ash
- Figure IV.11 Comparison of Arsenic Species in Unburned Wood Between between the TCLP and SPLP Tests
- Figure IV.12 Comparison of Arsenic Species in CCA-Treated Wood Ash Between between the TCLP and SPLP Tests
- Figure IV.13 Chromium Concentrations in Unburned Wood As Observed During the SPLP Test
- Figure IV.14 Comparison of Cr(VI) Concentrations in CCA-Treated Wood Ash Between between the TCLP and SPLP Tests
- Figure V.1 Schematic of Lysimeter
- Figure V.2 Comparison to Cumulative Total Arsenic Between Each Set of Lysimeters Using Data from HPLC-ICP-MS Analysis
- Figure V.3 Cumulative Quantities of Various Arsenic Species from Lysimeter 1
- Figure V.4 Cumulative Quantities of Various Arsenic Species from Lysimeter 2
- Figure V.5 Cumulative Quantities of Various Arsenic Species from Lysimeter 3
- Figure V.6 Cumulative Quantities of Various Arsenic Species from Lysimeter 4

LIST OF FIGURES (con'd)

- Figure V.7 Cumulative Quantities of Various Arsenic Species from Lysimeter 5
- Figure V.8 Cumulative Quantities of Various Arsenic Species from Lysimeter 6
- Figure VI.1 Total Arsenic for Background Wells as Measured by HPLC-ICP-MS and Independent Commercial Laboratories
- Figure VI.2 Total Arsenic for Compliance/Detection Wells as Measured by HPLC-ICP-MS and Independent Commercial Laboratories
- Figure VI.3 Arsenic Species of Compliance/Detection Wells that Tested Above Detection Limits
- Figure A.1 Ion-exchange Cartridge in Series
- Figure A.2 Fractional Concentrations of Arsenic Species Plotted as a Function of pH (Korte and Fernando, 1991)
- Figure A.3 Outline of the Cation-Exchange Cartridge Experiment
- Figure A.4 Outline of the Anion-Exchange Cartridge Experiment

LIST OF TABLES

Table I.1	Formulas of the Principal Arsenic Compounds (Benramdane et al. 1999)
Table I.2	Formulas of Typical Chromium Compounds
Table II.1	Experimental Conditions for Arsenic Speciation by HPLC-HG-AFS System
Table II.2	Experimental Conditions for Cr(VI) Analysis Using Ion Chromatography
Table III.1	Results from the Analysis of the Solid Sawdust Samples Used in pH Stat Tests
Table III.2	Leaching of Arsenic and Chromium from New Wood at Varying pH Values
Table III.3	Leaching of Arsenic and Chromium from Weathered Wood at Varying pH Values
Table IV.1	Samples Utilized for TCLP and SPLP Analysis
Table IV.2	Measured Retention Level of the Outer 6/10” of the Unburned Wood Samples Used in TCLP and SPLP Experiments
Table IV.3	Metals Concentrations of Unburned Wood Samples Used in TCLP and SPLP Experiments
Table IV.4	Metals Concentrations of Solid Ash Samples Used in TCLP and SPLP Experiments
Table IV.5	SPLP Results for Unburned Wood
Table IV.6	TCLP Results for Unburned Wood
Table IV.7	SPLP Results for CCA-Treated Wood Ash
Table IV.8	TCLP Results for CCA-Treated Wood Ash
Table V.1	Summary of Wood Types Contained Within Each Lysimeter
Table V.2	Layers of Each Lysimeter
Table V.3	Composition of Wood Monofill Lysimeters
Table V.4	Composition of C&D Lysimeters

LIST OF TABLES (Con'd)

Table IV.5	SPLP Results for Unburned Wood
Table IV.6	TCLP Results for Unburned Wood
Table IV.7	SPLP Results for CCA-Treated Wood Ash
Table IV.8	TCLP Results for CCA-Treated Wood Ash
Table V.1	Summary of Wood Types Contained Within Each Lysimeter
Table V.2	Layers of Each Lysimeter
Table V.3	Composition of Wood Monofill Lysimeters
Table V.4	Composition of C&D Lysimeters
Table V.5	Composition of MSW Lysimeters
Table V.6	Average Total Arsenic Concentrations From Each Lysimeter
Table V.7	Arsenic Results for Lysimeters 1 & 2 (Monofills)
Table V.8	Arsenic Results for Lysimeters 3 & 4 (Simulated C&D)
Table V.9	Arsenic Results for Lysimeters 5 & 6 (MSW)
Table VI.1	Groundwater Data for Background Wells at C&D Debris Disposal Facilities
Table VI.1	Groundwater Data for Detection/Compliance Wells at C&D Debris Disposal Facilities
Table A.1	Percent Recovery of Arsenic Species from Experiments with Ion-Exchange Cartridges
Table C.1	Results for Lysimeter 1 (Monofill no CCA)
Table C.2	Results for Lysimeter 2 (Monofill with CCA)
Table C.3	Results for Lysimeter 3 (C&D Untreated Wood Only)
Table C.4	Results for Lysimeter 4 (C&D With CCA-Treated Wood)
Table C.5	Results for Lysimeter 5 (MSW Untreated Wood Added)
Table C.6	Results for Lysimeter 6 (C&D With CCA-Treated Wood Added)

LIST OF TABLES (Con'd)

Table D.1	Methods Employed for Analyses that have been Standardized by Regulatory/Standardization Agencies
Table D.2	Methods Employed for Analysis which are Utilized by the Research Community
Table D.3	Reproducibility of Lysimeter Leachate Results Based Upon Duplicate Acid Digestion and Analysis
Table D.4	Results from Spike Analysis on Samples from the pH stat Experiments
Table D.5	Results from Spike Analysis for Total Chromium in CCA-treated Wood and CCA-treated Wood Ash
Table D.6	Matrix Spike Recoveries for the Lysimeter Samples
Table D.7	Results for CrVI Spike Analysis on CCA-treated Wood & Ash

LIST OF ABBREVIATIONS AND ACRONYMS

AES	Atomic Emission Spectrometry
AFS	Atomic Fluorescence Spectroscopy
As	Arsenic
As(III)	Trivalent Arsenic, Arsenite
As(V)	Pentavalent Arsenic, Arsenate
AsB	Arsenobetaine
AsC	Arsenocholine
Ave.	Average
AWPA	American Wood Preservers Association
AWPI	American Wood Preservers' Institute
BDL	Below Detection Limit
CCA	Chromated Copper Arsenate
C&D	Construction and Demolition
Cr	Chromium
Cr(III)	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
Cu	Copper
DMAA	Dimethylarsinic Acid
DO	Dissolved Oxygen
Eh	Measure of the Oxidation and Reduction Potential of A Solution
FDEP	Florida Department of Environmental Protection
FIU	Florida International University
FPL	Florida Power and Light
GW	Groundwater
HG	Hydride Generation
HPLC	High Performance Liquid Chromatography
HPLC-HG-AFS	High Performance Liquid Chromatography coupled with Hydride Generation and Atomic Fluorescence Spectrometry
HPLC-ICP-MS	High Performance Liquid Chromatography coupled with Inductively Coupled Plasma – Mass Spectrometry

LIST OF ABBREVIATIONS AND ACRONYMS (Con'd)

IC	Ion Chromatography
ICP	Inductively Coupled Plasma
ICP-AES	Inductively Coupled Plasma-Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
MDL	Minimum Detection Limit
LMAC	Minnesota's Listed Metals Advisory Council
MMAA	Monomethylarsonic Acid
MPCA	Minnesota Pollution Control Agency
MS	Mass Spectrometry
MSW	Municipal Solid Waste
NA	Not Analyzed
NS	Not Sampled
ORP	Oxidation Reduction Potential
pcf	Pounds per Cubic Foot
pH	Measure of the hydrogen ion activity in water. Measure of the acidity of water.
RCRA	Resource Conservation and Recovery Act
RDF	Refuse Derived Fuel
SPLP	Synthetic Precipitation Leaching Procedure
Std. Dev.	Standard Deviation
SWA	Solid Waste Authority
SYP	Southern Yellow Pine
TAG	Technical Awareness Group
TCLP	Toxicity Characteristic Leaching Procedure
TMAO	Trimethylarsine Oxide
UF	University of Florida
UM	University of Miami
USEPA	U.S. Environmental Protection Agency
XRF	X-ray fluorescence spectroscopy

UNITS OF MEASURE

“	Inches
%	Parts Per Hundred, Percent
ug	Micrograms
ug/L	Micrograms Per Liter
um	Micron (1 millionth of a meter)
°C	Degrees Celcius
cm	Centimeters
°F	Degrees Farenheit
ft ³	Cubic Feet
g	Grams
L	Liter
lb/ft ³	Pounds Per Cubic Foot
LD ₅₀	A measure of toxicity. Lethal dose at which 50% of the test population dies. The lower the LD ₅₀ the more toxic the chemical.
kg	Kilograms
mg	Milligrams
mg/kg	Milligrams of Chemical Per Kilogram of Wood or Woil
mg/L	Milligrams Per Liter
mV	MilliVolts
nm	Nanometer
M	Molar Concentration Units
N	Normality (equivalents per liter)
pcf	Pounds of Chemical Per Cubic Foot of Wood
pH	Measure of the hydrogen ion activity. Measure of the acidity of water.

ABSTRACT

Different species of arsenic and chromium are characterized by different toxicities and different mobilities. The environmental impacts of CCA-treated wood would therefore be a function of the chemical forms of the metal releases. As a consequence a series of tasks were undertaken to evaluate arsenic and chromium species from CCA-treated wood. The intent of these tasks was to quantify the total quantity metals released under different environmental conditions and to obtain some insight concerning the speciation of these releases. Samples evaluated in this study were speciated for arsenic as As(V), As(III), DMAA, and MMAA. Chromium speciation focused on evaluating the relative distribution of total chromium between Cr(III) and Cr(VI). Analyses were conducted on solid wood samples and on leachates from these wood samples using a series of different analytical techniques including HPLC-HG-AFS, HPLC-ICP-MS, ICP-AES, and ion chromatography. Tasks described in this study include: a) a “pH stat” experiment, b) SPLP and TCLP experiments, c) a set of lysimeter experiments, and d) analysis of groundwater in the vicinity of C&D debris disposal facilities.

The “pH stat” experiment focused on evaluating the distribution of different arsenic and chromium species with changes in pH. Two types of CCA-treated wood were evaluated, new CCA-treated wood and weathered CCA-treated wood. Results indicate that leaching of arsenic and chromium is enhanced at the pH extremes. The weathered wood sample leached greater quantities of arsenic and chromium within the near neutral pH range with total arsenic concentrations between 4 and 5 mg/L and total chromium concentrations between 1 and 2 mg/L range. The enhanced leaching of weathered wood may be due to the higher retention level and/or due to the age of the wood. Of interest is the finding that As(III) was observed to leach only from the weathered wood sample between a pH of 1 to 7. Cr(VI) was observed in both new and weathered wood at pH values greater than 9.

The SPLP and TCLP experiments simulate leaching due to rainfall and landfill conditions. Samples evaluated in this portion of the study included unburned wood and wood ash. Results for unburned wood indicated that the weathered pole sample consistently leached a significant fraction of arsenic as As(III) in both the TCLP and SPLP tests, whereas the unweathered samples leached much smaller quantities of As(III). Upon sample ashing, As(III) was observed in significant quantities within the leachates from the 2.5 pcf-ash sample. Chromium was leached from unburned wood as Cr(III) and from the ash as Cr(VI). Chromium leaching from the ash was found to be strongly dependent upon pH. The pH effect for chromium is likely influenced by the acidity of the CCA chemical added to the wood.

Six lysimeters (two that simulate wood monofills, two that simulate C&D debris landfills, and two that simulate MSW landfills) were operated for a period of 18 months. Each set of two lysimeters were identical except that the wood component in one was untreated and the other was CCA-treated. Results showed that the quantities of arsenic leached from the CCA set of lysimeters was significantly higher than the quantities leached from the lysimeters containing solely untreated wood. The organic arsenic species, DMAA, predominated the speciation of arsenic from the untreated control lysimeters. Either As(V) or As(III) predominated the speciation of the lysimeters containing CCA-treated wood.

Groundwater samples were collected in the vicinity of 21 unlined C&D debris disposal facilities in an effort to determine whether or not arsenic is elevated in the groundwater at these facilities beyond background concentrations. The presumption was that CCA-treated wood had been disposed at these facilities and that the arsenic from the CCA-treated wood may be starting to impact groundwater at the monitoring wells located at the sites. Of the 48 samples collected from compliance/detection wells, 21 were found to contain total arsenic concentrations greater than the 5 ug/L detection limit. Of these samples, 6 were characterized by concentrations greater than 20 ug/L. These 6 samples came from 3 separate facilities. Of interest is that the organic arsenic species (DMAA and MMAA) were the predominant arsenic species from the one landfill with elevated background concentrations. The predominant arsenic species in groundwater from the other two landfills were As(III) and As(V). This difference in speciation was interesting and suggests perhaps a difference in source.

Overall results of this study suggest that arsenic which leaches from CCA-treated wood leaches primarily as either As(V) or As(III). Chromium predominantly leaches as Cr(III). If the wood is burned, arsenic speciation of the leachates remains consistent with that of the unburned wood with As(V) and As(III) predominating, but chromium speciation of the leachates converts almost exclusively to Cr(VI). The degree of Cr(VI) leaching from ash is highly dependent upon the pH of the ash leachate, with higher leachate concentrations for samples with lower retention levels. Results of this study also showed that more As(III) leaches from weathered wood than from unweathered wood. The conversion of arsenic in the leachate towards As(III) may enhance the leaching of arsenic as wood structures increase in age. Furthermore, results also suggest that arsenic that leaches from untreated wood is primarily in the less toxic organic form (DMAA), whereas arsenic that leaches from CCA-treated wood is in the more toxic As(V) and As(III) forms. This difference in speciation is important when evaluating the relative impacts of arsenic.

This page left intentionally blank.

CHAPTER I
MOTIVATION, BACKGROUND, OBJECTIVES

This page left intentionally blank.

CHAPTER I, MOTIVATION, BACKGROUND, OBJECTIVES

I.1 MOTIVATION

During August 18 and 19, 1999, four individuals involved in Florida's CCA-treated wood research (William Hinkley, John Schert, Helena Solo-Gabriele, and Timothy Townsend) were invited by the Minnesota Pollution Control Agency (MPCA) located in St. Paul, Minnesota, to participate in the deliberations of Minnesota's Listed Metals Advisory Council (LMAC). The research team was invited for the purpose of sharing their research on the disposal aspects of CCA-treated wood. Minnesota's LMAC has the authority to make recommendations to MPCA's Commissioner concerning the following four listed metals: cadmium, lead, mercury, and hexavalent chromium. It was the presence of hexavalent chromium within the CCA chemical that initiated the CCA discussion in Minnesota. Given the focus on hexavalent chromium many discussions ensued during the deliberations concerning speciation of chromium, where speciation refers to the chemical form of the chromium. Furthermore, many questions were also raised about arsenic and its speciation in the environment. Although Minnesota's Listed Advisory Council did not vote for a ban on the CCA chemical, the research team from Florida recognized the need for studies focusing on arsenic and chromium speciation from CCA-treated wood leachates, especially given the different toxicities and mobilities of different species in the environment. As a consequence, the research team requested and received supplemental funds in September 1999 which among other work was to include a literature review aimed at identifying speciation methods. The results of that literature review were documented in Townsend et al. 2001. The work presented herein is a result of subsequent funding received from the Florida Center for Solid and Hazardous Waste Management (FCSHWM) from 2000 through 2003 that focused on speciation analyses of leachates from CCA-treated wood. The FCSHWM provided funds specifically for arsenic speciation analysis. Some funds were also provided towards the arsenic speciation work from the National Institutes of Environmental Health Sciences. A separate concurrent source of funding with a different research focus was used to finance the chromium speciation research and so where the research focuses from the arsenic and chromium speciation studies overlapped samples were split and used in both studies. The predominant focus of the report presented herein is therefore the arsenic speciation work. Chromium speciation data are provided and discussed for samples that were split among the studies.

I.2 BACKGROUND

Chromated copper arsenate (CCA) is a chemical wood preservative used to prolong the service life of the wood thereby extending its service life 20 to 40 years beyond that without the preservative. The CCA chemical contains copper which serves as a fungicide, arsenic which serves as an insecticide, and chromium which is used to "fix" the copper and arsenic into the wood. There are three types of CCA-treated wood: Type A, Type B, and Type C. The most common type is CCA-Type C, which is composed of 34.0% As_2O_5 , 47.5% CrO_3 , and 18.5% CuO , by weight. The amount of CCA utilized to treat the wood or "retention level" depends upon the particular application for the wood product. Typical retention levels utilized by the industry are 0.25 pcf, 0.40 pcf, 0.60 pcf, 0.8 pcf, and 2.50 pcf. (Note: pcf = pounds of chemical per cubic foot of wood). Low retention values (0.25 pcf) are permissible for plywood, lumber,

and timbers if the wood is used for above ground applications. Higher retention values are required for load bearing wood components such as pilings, structural poles, and columns. The highest retention levels (0.8 and 2.5 pcf) are required for wood components that are used for foundations or saltwater applications (AWPA 1999).

CCA-treated wood has been the most widely used type of treated wood (AWPI 1999) representing about 80% of the U.S. wood preservation market through about 2002. A phase-out of this product has been implemented nation-wide for CCA-treated wood which will prohibit the CCA treatment of wood that is intended for residential uses after December 2003. Products not included within the phase-out include wood used for marine and some farm applications, poles, piles, round posts, and plywood. Even with these exceptions, the amount of CCA-treated wood produced in the U.S. is expected to decrease significantly and major changes will likely occur within the wood treatment industry. It is important to emphasize that even with the phase-out, CCA-treated structures manufactured prior to the phase-out will remain in the environment for many years into the future given the long service life of the wood. Furthermore, products exempted from the phase out will continue to be produced and discarded CCA-treated wood will continue to impact the environment during its disposal, if it is not managed properly. Thus quantifying the leachates from this product will continue to be relevant in order to assess its environmental impacts.

CCA-treated wood is composed of three metals: arsenic, chromium, and copper. Two of these metals, arsenic and chromium, are capable of transformations under ambient conditions. These transformation impact the toxicity of the metal to humans. These transformations include a change in valence (which in simple terms is a measure of the metal's "willingness" to exchange electrons) or its association with organic compounds (compounds containing a reduced form of carbon or carbon that is "willing" to release electrons). Arsenic is capable of changing valence in the natural environment between a +3 valence and between a +5 valence. Arsenic in the +3 valence is also referred herein as As(III) and arsenic in the +5 valence is referred to as As(V). In a simplified chemical sense, As(III) prefers to be associated with other atoms such that it is able to share 3 electrons. As(V) prefers to be associated with other atoms such that it is able to share 5 electrons. As(III) is generally more toxic to humans than As(V). Arsenic also forms complexes with organic compounds which generally make the arsenic less reactive and thus less toxic to humans. Chromium in the natural ambient environment is capable of changing valence states between +3 and +6. Similar to arsenic, chromium in the +3 valence is referred to as Cr(III) and in the +6 valence is referred to Cr(VI). In general, Cr(VI) tends to be more toxic than Cr(III). It is important to note that metals cannot be destroyed in the environment. They can simply alter their valence state or the way in which they are bound to other elements to form molecules. Thus the transformation of these metals is of importance in evaluating the potential impacts of CCA releases to the environment, given that the metals can not be destroyed.

The information provided above concerning arsenic and chromium speciation is oversimplified. The remaining portion of this background section provides more details concerning arsenic and chromium speciation for the readers interested in getting a more in-depth understanding concerning speciation, including some of the nuances associated with the ability of the species to convert from one form to another and the toxicity of the different species.

I.2.a Basic Arsenic Chemistry

Arsenic in the natural environment exists in many different chemical forms or species. The four major arsenic species of importance are the inorganic species, arsenite (As(III)) and arsenate (As(V)), and the organic species, monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA); with each specie varying in toxicity with the inorganic species being generally the more toxic. In general, As(III) is more mobile than As(V). Other organic forms of arsenic include, arsenobetaine (AsB) and its reduced form, arsenocholine (AsC) (both found in marine invertebrates, shellfish, and fish) and trimethylarsine oxide (TMAO) also found in marine samples (Francesconi and Edmonds, 1994). A very toxic and gaseous form of arsenic, arsine gas (AsH_3) can be formed under extreme reducing conditions. The formulas for the different arsenic species are provided in Table I.1. The most toxic forms of arsenic are at the top of the table and toxicity decreases as one proceeds down the table in the following order $\text{AsH}_3 > \text{As(III)} > \text{As(V)} > \text{MMAA} > \text{DMAA} > \text{AsB, AsC, TMAO}$. Arsenic, as As(III), is considered to be very toxic. AsB and AsC, the forms typically found in shellfish, are considered to be virtually non-toxic in humans. In order to provide a sense for the relative toxicity between the different arsenic species, data from scientific studies are quoted in terms of LD_{50} where LD_{50} represents the lethal dose at which 50% of the test population dies. The lower the LD_{50} the more toxic the compound. LD_{50} values quoted by Seiler et al. (1994) for humans are 1.43, 50 and 500 mg/kg for As(III), MMAA, and DMAA, respectively. Naqvi et al. (1994) report an LD_{50} of up to 10,000 mg/kg in mice for AsB. Although, As(III) has been found to be considerably much more toxic than As(V) in most animal studies (Yamauchi and Fowler, 1994), other studies indicate that this may not hold true for humans in all cases (Squibb and Fowler, 1983) and both inorganic species (As(III) and As(V)) should be regarded as being very toxic. Furthermore, the general supposition that the inorganic species are more toxic should be considered in light of the fact that the organic species can be degraded to the more toxic inorganic forms, depending upon the environmental conditions. Also, recent findings show that the organic species can be extremely toxic to humans, in particular organic complexes of arsenic with arsenic in the +3 valence (Del Razo et al., 2001). The organic complexes with arsenic in the +3 valence are not listed in Table I.1.

Arsenic in CCA and in the treated wood product is predominantly in the +5 valence. Chemical and biological conditions in the environment affect the transformation between these different forms including the possible conversion to As(III) and MMAA and DMAA. Chemical conditions of importance include pH and redox potential. Figure I.1 shows the arsenic species of significance under varying pH and redox conditions. These species include the inorganic arsenious acids or arsenites (H_3AsO_3 , H_2AsO_3^- , HAsO_3^{2-}) collectively referred to as As(III) where the arsenic atom possesses a valence of +3, inorganic arsenic acids or arsenates (H_3AsO_4 , H_2AsO_4^- , HAsO_4^{2-}) collectively referred to as As(V) where the arsenic atom possesses a valence of +5. In aerobic waters (high Eh values), inorganic arsenic acid or arsenate, H_3AsO_4 predominates at extremely low pH (<2); within a pH range of 2 to 11, it is replaced by H_2AsO_4^- , and HAsO_4^{2-} . Inorganic arsenious acid or arsenite, H_3AsO_3 , exists at low pH and under mildly reduced conditions, but as the pH increases it is replaced by H_2AsO_3^- . Only after the pH exceeds 12, HAsO_3^{2-} can be seen. In the presence of sulfide and at low pH, HAsS_2 can form and under extreme reducing conditions; and arsine, arsine derivatives, and arsenic metal can occur under extreme reducing conditions (Figure I.1).

Compound	Formula
Arsine, AsH ₃ Gaseous Form with As in the -3 Valence	$\begin{array}{c} \text{H} \\ \\ \text{H} - \text{As} - \text{H} \end{array}$
Arsenious acid As(III), Form in Water with As in the +3 Valence	$\begin{array}{c} \text{OH} - \text{As} - \text{OH} \\ \\ \text{OH} \end{array}$
Arsenic acid As(V), Form in Water with As in the +5 Valence	$\begin{array}{c} \text{OH} \\ \\ \text{OH} - \text{As} = \text{O} \\ \\ \text{OH} \end{array}$
Monomethylarsonic acid MMAA, Form in Water with As in the +5 Valence	$\begin{array}{c} \text{OH} \\ \\ \text{CH}_3 - \text{As} = \text{O} \\ \\ \text{OH} \end{array}$
Dimethylarsonic acid DMAA, Form in Water with As in the +5 Valence	$\begin{array}{c} \text{CH}_3 \\ \\ \text{O} = \text{As} - \text{OH} \\ \\ \text{CH}_3 \end{array}$
Arsenobetaine AsB	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{As}^+ - \text{CH}_2 - \text{C} = \text{O} \\ \qquad \qquad \\ \text{CH}_3 \qquad \qquad \text{OH} \end{array}$
Arsenocholine AsC	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{As}^+ - \text{CH}_2 - \text{CH}_2 - \text{OH} \\ \\ \text{CH}_3 \end{array}$
Trimethylarsine oxide TMAO	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 - \text{As} = \text{O} \\ \\ \text{CH}_3 \end{array}$

Table I.1: Formulas of the Principal Arsenic Compounds (Benramdane et al. 1999)

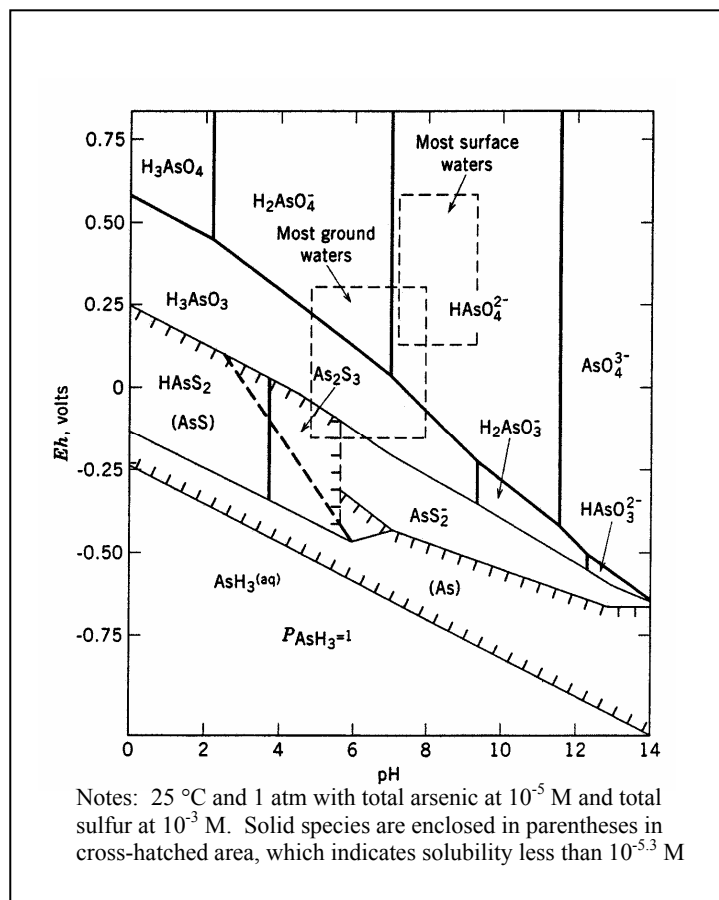


Figure I.1: Eh-pH Diagram for Arsenic (Schnoor 1996)

I.2.b Basic Chromium Chemistry

Chromium is a unique metal in that the two primary species encountered in the environment have drastically different properties. Hexavalent chromium, Cr(VI), is much more toxic than trivalent chromium, Cr(III), and also tends to be more mobile in the environment than Cr(III) due to its higher solubility in water. Chromium can exist in other valence states in the environment including 0, +2, and +4. From the point of view of CCA, however, the +3 and +6 states are the most relevant. The composition of typical molecules and ions that contain Cr(III) and Cr(VI) are provided in Table I.2.

Chromium in the CCA solution is present primarily as Cr(VI). Once the CCA chemical is impregnated into the wood it reacts with the wood fibers and transforms over time to Cr(III). It is important to note that under strong oxidizing conditions, Cr(III) can be converted to Cr(VI). The difference in toxicity between the two forms of chromium is significant. Katz and Salem, 1993, reported that hexavalent chromium compounds appear to be 10 to 100 times more toxic than trivalent chromium compounds when ingested orally.

Valence	Name	Chemical Formula
0	Chromium	Cr
+3 or Cr(III)	Hydroxyl species	CrOH^{+2} , Cr(OH)_2^{+1} , Cr(OH)_3 , Cr(OH)_4^{-1}
	Chromic chloride	CrCl_3
	Chromic oxide	Cr_2O_3
	Chromic nitrate	$\text{Cr(NO}_3)_3$
+6 or Cr(VI)	Hydroxyl species	HCrO_4^{-1} , CrO_4^{-2}
	Chromic acid	H_2CrO_4
	Ammonium chromate	$(\text{NH}_4)_2\text{CrO}_4$
	Chromium trioxide	CrO_3
	Chromyl chloride	CrO_2Cl_2
	Sodium chromate	NaCrO_4
	Sodium dichromate	$\text{Na}_2\text{Cr}_2\text{O}_7$

Table I.2: Formulas of Typical Chromium Compounds

There are three main points to consider in chromium chemistry. First, the dominant naturally occurring form of chromium is the trivalent oxide (Barnhart, 1997; Barceloux, 1999) and this form is not very biologically reactive thus resulting in low toxicities. The second is that other valence forms of chromium will tend to be converted to the trivalent oxide when in contact with the natural environment. Hexavalent chromium tends to be reduced to trivalent chromium by organic matter, divalent iron, and sulfides. This becomes a major consideration when sampling and testing environmental samples for hexavalent chromium. Trivalent chromium will not be generally oxidized to Cr(VI) with one exception, manganese oxides in soil can oxidize Cr(III) to Cr(VI) (Kim et al., 2002, James, 1996, Rai et al, 1989, Eary and Rai, 1987). In the case of CCA-treated wood, it has been found that oxidants used to clean treated wood decks will also convert the chromium in CCA to Cr(VI) (Reference Paper by Paul Cooper). Lastly,

trivalent chromium is very slow to react. Hexavalent chromium can also persist in the environment for long periods of time if it does not reduce to Cr(III).

Chromium reduction-oxidation potential Eh-pH diagrams graphically describe equilibrium data and oxidation states that exist within certain Eh and pH ranges in aqueous solutions. Although Figure I.2 describes chromium compounds in aqueous conditions, concentration, pressure, temperature, and the presence of other ions can affect the presence of various hydroxyl chromium species. Cr(III) exists in wide Eh and pH ranges, with the specific species varying with pH, as seen in Figure I.2. Cr^{+3} exists when pH is less than 3, and trivalent chromium hydroxyl species [$\text{Cr}(\text{OH})^{+2}$, $\text{Cr}(\text{OH})_2^{+1}$, $\text{Cr}(\text{OH})_3$, and $\text{Cr}(\text{OH})_4^{-1}$] exist at pH greater than 3.5. Of special interest is the predominance of Cr(VI) species as CrO_4^{-2} at alkaline pH levels which emphasizes the possibility for converting Cr(III) to Cr(VI) under basic conditions.

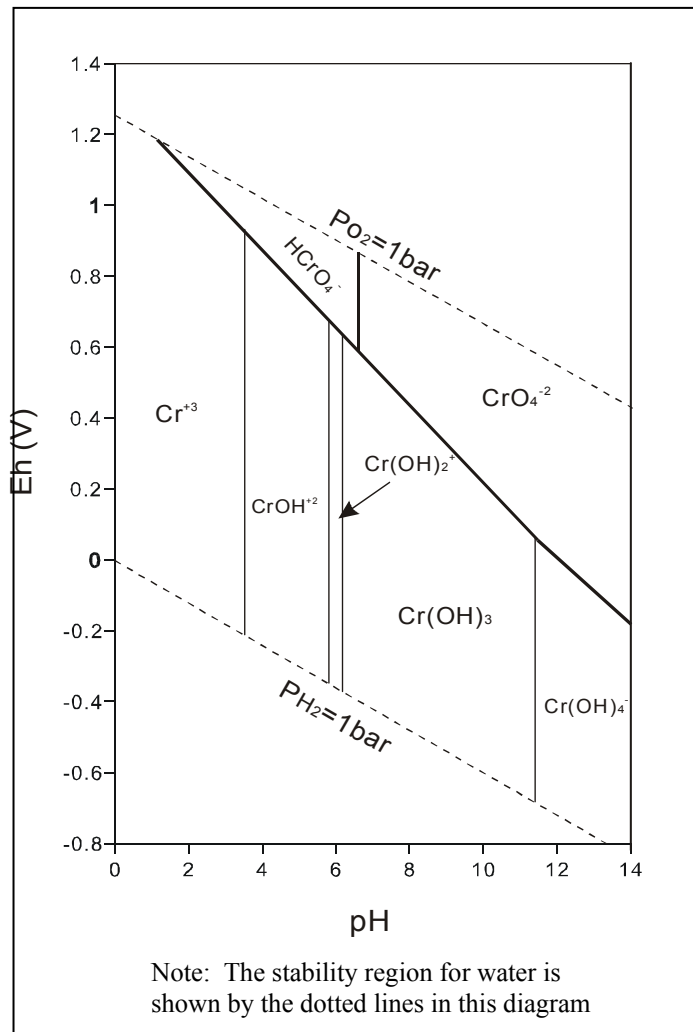


Figure I.2: Eh-pH Diagram for Chromium (Adapted from Ball and Nordstrom 1998)

I.3 OBJECTIVES

The primary objective of this study was to evaluate the arsenic species of leachates from CCA-treated wood. Where possible, common results from a separate chromium speciation study funded through the Florida Department of Environmental Protection, are presented herein. Specifically the study includes the following tasks.

- Evaluate the effects of pH on arsenic and chromium species from CCA-treated wood leachates. (Chapter III)
- Evaluate SPLP and TCLP leachates from unburned wood and wood ash for arsenic and chromium species. (Chapter IV)
- Evaluate arsenic species of leachates from a set of 6 lysimeters designed to simulate wood monofills, C&D landfills, and MSW landfills. (Chapter V)
- Evaluate arsenic species of groundwater in the vicinity of C&D debris disposal facilities. (Chapter VI)

The tasks outlined above progress from controlled laboratory scale experiments (pH study), towards laboratory scale experiments designed to simulate specific environments such as areas impacted by rainfall (SPLP tests) or within landfill conditions (TCLP tests). The lysimeter work represents a large field-scale controlled experiment designed to evaluate various landfill scenarios and the sampling program for groundwater at C&D debris disposal facilities represents an actual field scenario which may include indirect impacts from CCA-treated wood. So the tasks described in this report represent a large range in scale and experimental control, from the small-scale laboratory experiments which are highly controlled to field-scale sampling with minimal control over the possible source of contamination. The ultimate intent of this work is to quantify the amounts of arsenic and chromium leached from CCA-treated wood and to assess the suitability of various disposal scenarios for the treated wood product.

This report is organized in terms of the tasks outlined above (Chapters III through VI). Since many of the laboratory methods are common across different tasks a separate chapter (Chapter II) was dedicated to describing the laboratory methods. A summary, conclusion, and a set of recommendations are provided at the end of the report (Chapter VII).

In addition to the tasks described within this report, several other studies were conducted by the research team that focused on arsenic and chromium speciation. These studies include work evaluating the arsenic species leached from CCA-treated wood that is currently in service, arsenic species in soil column tests, arsenic speciation methods for soils, chromium speciation of soils, and chromium speciation of leachates under alkaline conditions simulating the potential effects of concurrent concrete disposal on leachate quality. Contacts for these other studies include Helena Solo-Gabriele of the University of Miami for arsenic speciation of in-service wood and from soil column tests, Yong Cai of Florida International University for work focusing on arsenic speciation methods for soil, and Timothy Townsend of the University of Florida for all of the chromium speciation work. The reader is encouraged to contact these individuals if they are interested in getting more information on these other related studies.

**CHAPTER II,
ANALYTICAL LABORATORY METHODS**

This page left intentionally blank.

CHAPTER II, ANALYTICAL LABORATORY METHODS

A significant effort in this study involved the development of laboratory methods for quantifying and speciating arsenic and chromium within both liquid extracts and solid wood or solid ash samples. Depending upon the sample matrix and experiments conducted, different analytical methods were used. These methods are described in detail below for arsenic analysis in liquid leachates (Section II.1), chromium analysis in liquid leachates (Section II.2), and chromium, arsenic, and copper analysis in solid wood sawdust or solid ash samples (Section II.3).

II.1 ARSENIC ANALYSIS OF LIQUID LEACHATES

Total arsenic analysis in liquid leachates included an acid digestion step prior to analysis to degrade bonds within the sample matrix. Once the samples were digested they were analyzed using an arsenic-specific detection instrument, an inductively coupled plasma-atomic emission spectrometer (ICP-AES). It should be noted that once a sample has undergone digestion it cannot undergo speciation analysis and can only be analyzed for total arsenic concentrations.

Although the determination of total metal concentrations in environmental samples is challenging, speciation is much more difficult since species are to be separated without changing their chemical forms. The most common approach for arsenic speciation involves the coupling of separation techniques with detection instrumentations. High performance liquid chromatography (HPLC) was used in this study for species separation. Once the species were separated, they were quantified using an arsenic-specific detection system including inductively coupled plasma – mass spectrometry (ICP-MS) or atomic fluorescence spectroscopy (AFS). Use of AFS requires that the sample be introduced in a gaseous form so AFS is typically preceded by hydride generation (HG) to convert the arsenic into a gaseous hydride form. HPLC-HG-AFS was used for the analysis of relatively simple matrices. HPLC-ICP-MS was used for the analysis of samples in more complex matrices. The distinction between simple matrices and complex matrices is important since some of the less common forms of arsenic, which can be found in complex matrices, may not convert to hydrides.

Figure II.1 outlines the analytical techniques used in this study to determine total arsenic and arsenic species concentrations. Speciation analysis by HPLC-HG-AFS and HPLC-ICP-MS were conducted at Florida International University, Miami, Florida. Total arsenic analysis, including a digestion step and analysis by ICP-AES, was completed at the University of Florida, Gainesville, FL. A basic overview of these analytical techniques used is provided below.

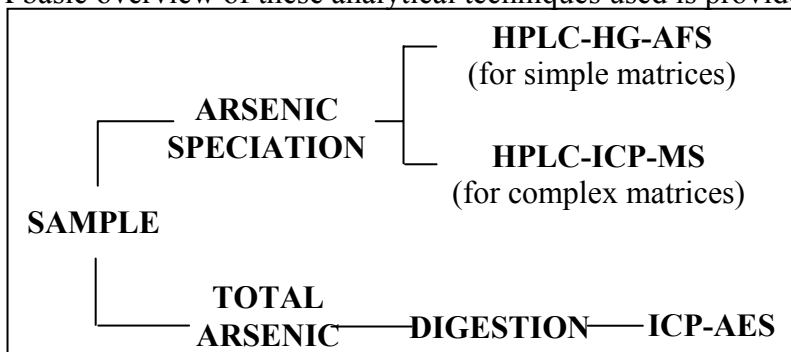


Figure II.1: Summary of Laboratory Methods Used for Arsenic Analysis for Liquid Leachates

II.1.a HPLC-HG-AFS (Arsenic Speciation)

High performance liquid chromatography coupled with hydride generation and atomic fluorescence spectrometry (HPLC-HG-AFS) (Figure II.2) was the technique used for arsenic speciation analysis in the “pH Stat” experiment (Chapter III) and in the TCLP and SPLP tests (Chapter IV). As previously mentioned, HPLC-HG-AFS is best utilized for samples containing a simple matrix, such as laboratory-based solvent-extracted leachate, but falls short in its ability to speciate samples of more complex matrices.

HPLC is a separation technique that partitions species within a sample. When used with a suitable element-specific detector, in this case AFS, the very low concentrations found in environmental samples can be detected. Samples must be introduced to the AFS in a gaseous form and as a result the AFS is preceded by hydride generation (HG). Hydride generation utilizes a reducing agent, sodium borohydride, NaBH_4 , to convert the separated arsenic species to their respective gaseous hydrides that can then be detected by AFS. HG is the preferred method of sample introduction to the AFS; however, it possesses the disadvantage in that it converts only those arsenic species which are capable of forming gaseous arsines or hydrides. The most common arsenic species, As(III), As(V), DMAA, and MMAA, are converted to their corresponding gaseous form using HG (arsine for both As(III) and As(V)). However, in very complex matrices there can be forms of arsenic that do not form gaseous hydrides. These forms of arsenic are termed “hidden” arsenic in the scientific literature.

It is important to emphasize that AFS is a very sensitive and selective method. Its advantage over other detection instruments, such as, atomic absorption spectrometry, in terms of sensitivity, linear range and spectral interferences, is well documented. AFS uses a miniature argon-hydrogen diffusion flame for atomization while the analyte element is introduced from the hydride generator as a gaseous hydride. AFS can only analyze for gases and hence the analyte must first be converted to a gaseous state (hydride) before detection. The hydrogen necessary to keep the flame lit is a by-product of the NaBH_4 reduction reaction and a boosted-hollow cathode lamp is used to attain excitation. The detection limit via this method for arsenic is approximately $2 \mu\text{g/L}$ based on a 3σ . The detection limit is defined as the largest value among “2.5 times the blank value” or “3 times the standard deviation of the blank value”.

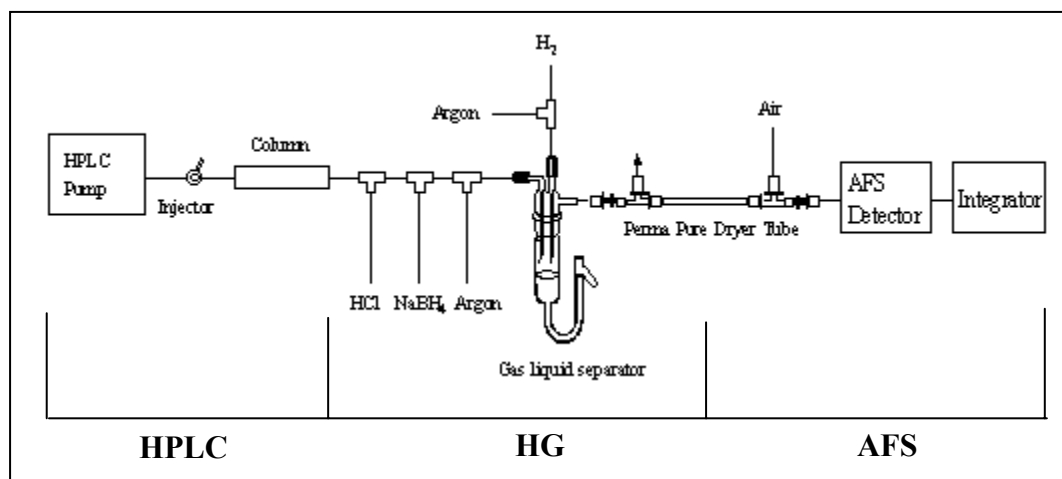


Figure II.2: HPLC-HG-AFS Setup

The final result of an analysis by HPLC-HG-AFS is graphically displayed using the computer integrator software AvalonTM. Figure II.3 shows a typical output file of the four major arsenic species of interest, As(III), As(V), MMAA, and DMAA, at a concentration of 20 µg/L each. The separated arsenic species can be identified based on their retention time (the time at which their peak shows up on the chromatogram). Retention times are usually expressed in units of seconds. The species are eluted in the following order: As(III), DMAA, MMAA and As(V). The area under each peak corresponds to the concentration of that particular specie. The 20 µg/L standard solution was analyzed several times to test the stability of the HPLC-HG-AFS technique. The peak area fluctuated no more than 8 to 10% between any two runs. Table II.1 outlines the experimental parameters for arsenic speciation used for the HPLC-HG-AFS system.

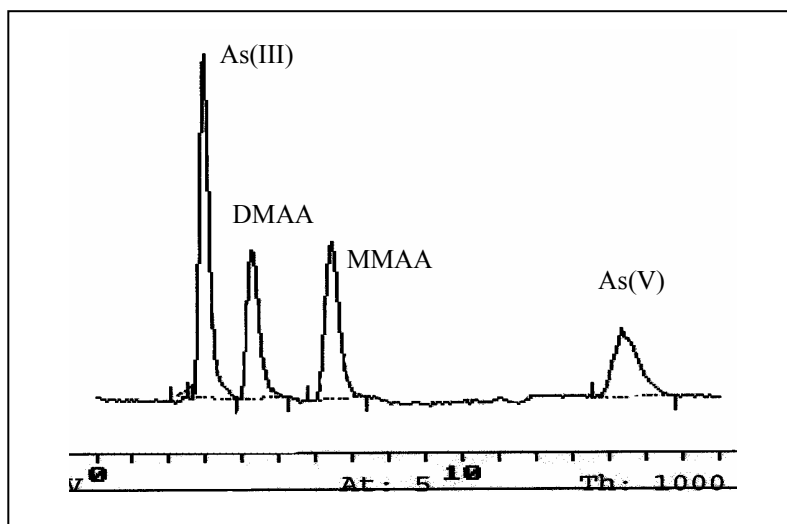


Figure II.3: Chromatogram of the Four Major Arsenic Species using HPLC-HG-AFS

HPLC - SpectraSYSTEM P4000 with a SpectraSYSTEM AS 3000 Autosampler	
Anion exchange:	
Column	Hamilton PRP-X100, 250 mm x 4.6 mm i.d., 10µm particle size
Mobile Phase	15 mM KH ₂ PO ₄ / 15 mM K ₂ HPO ₄ solution, pH 5.8
Injected Volume	100 µL
Flow Rate	1.0 mL min ⁻¹
HG-AFS - Millenium Excalibur (PS Analytical, Kent, UK)	
HCl (Pump 1)	12.5% (v/v), half (2 mL min ⁻¹)
NaBH ₄ (Pump 1)	1.4% (m/v) in 0.1 M (m/v) NaOH, half (2 mL min ⁻¹)
Carrier Gas	Argon, 235 mL min ⁻¹
Dryer Gas	Nitrogen, 3000 mL min ⁻¹
Pump 2	Off
Lamp	Arsenic, 197.3 nm, 193.7 nm, 189.0 nm
Primary Current	27.5 mA
Boost Current	35 mA
Range	100
Filter	12
Auto Zero	On
Recorder Output	0-1 V

Table II.1: Experimental Conditions for Arsenic Speciation by HPLC-HG-AFS System

II.1.b HPLC-ICP-MS (Arsenic Speciation)

HPLC can be coupled with ICP-MS for arsenic speciation analysis. This technique was used for arsenic speciation of the lysimeter leachate (Chapter V) and for the speciation of groundwater in the vicinity of C&D debris disposal facilities (Chapter VI). The ICP-MS used in this study was a Hewlett Packard HP4500 Plus equipped with HP ChemStation Software WinNT for ICP-MS. Since the HPLC is described in the previous section (HPLC-HG-AFS) and its function does not change with the detector to which it is coupled, this section will be dedicated to describing the ICP-MS instrumentation.

ICP-MS is a highly sensitive multi-element technique and today's method of choice for multi-element trace analysis. Samples introduced from the HPLC to the ICP-MS are first dispersed into a stream of argon gas and carried to an ICP where they are ionized. ICP-MS uses a high temperature plasma source, commonly argon, to atomize the sample into its constituent atoms or ions. For liquids, this is achieved by aspirating the sample into the flow of argon gas using a nebulizer. ICP-MS detects the ions themselves. The ions are passed into a vacuum via a sample and skimmer cone interface, where a lens stack focuses the ion beam into a quadrupole mass spectrometer that separates the ions based on their atomic mass-to-charge ratio and detects them using a scanning electron multiplier.

The chromatogram output file of the HPLC-ICP-MS is similar to that of the HPLC-HG-AFS, with the same retention times and order of species elution.

II.1.c ICP-AES (Total Arsenic)

Samples were split to conduct separate analysis for both total arsenic and arsenic species concentrations. The splits intended for total arsenic analysis were preprocessed prior to analysis using an acid digestion method with analyses carried out with an ICP-AES.

Digestion

Samples analyzed for total arsenic analysis by ICP-AES (at the University of Florida) were digested using EPA's method SW 846-3010A entitled "*Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy*" (U.S. EPA 1996). The procedure involves refluxing a mixture of 100-mL aliquot of the sample and 3 mL of concentrated nitric acid in a watch glass covered Griffin beaker on a hot plate. The sample was evaporated to a low volume (5 mL), cooled and another 3 mL concentrated nitric acid added. Again the sample was returned to the hot plate and refluxed until the digestate became light in color or until its color stabilized. After the digestate was brought to a low volume, it was refluxed with hydrochloric acid (HCl) (10 mL/100 mL of the final solution) for about 15 minutes to dissolve any precipitate or residue resulting from evaporation. The final sample was filtered and adjusted to 100 mL with reagent water (an HCl acid concentration of 10%). The sample was then analyzed by ICP-AES.

ICP-AES

ICP-AES analysis was conducted at the University of Florida laboratory in accordance with U.S. EPA SW-846 Method 6010B (U.S. EPA 1996). The instrument utilized was manufactured by Thermal Jarrel Ash (Model: Enviro 36). The results obtained from the ICP-AES were used to confirm the sum of the arsenic species measured during the "pH Stat"

experiments (Chapter III), the TCLP/SPLP experiments (Chapter IV) and from the lysimeter samples (Chapter V).

Inductively Coupled Plasma - Atomic Emission Spectroscopy (ICP-AES) is a multi-element analytical technique that dissociates a sample into its constituent atoms and ions and causes them to emit light at a characteristic wavelength by exciting them to a higher energy level. This excitation is accomplished by the use of an ICP source, usually an argon plasma. A monochromator separates specific wavelengths of interest, and a detector measures the intensity of the emitted light. This information is used to calculate the concentration of that particular element in the sample. The ICP-AES instrument consists of a sample delivery system that includes a peristaltic pump and a capillary tube to deliver a constant flow of analyte liquid into the nebulizer; an ICP to generate the signal; an optical spectrometer to measure the signal; and a computer for controlling the analysis. The advantages of this technique are its sensitivity, minimum interference and multi-element detection capability on a single sample.

II.2 CHROMIUM ANALYSIS OF LIQUID LEACHATES

Chromium analysis of liquid leachates involved two steps: total analysis using ICP-AES following an acid digestion step and analysis of Cr(VI) by ion chromatography. Cr(III) was determined as the difference between total chromium and Cr(VI). A schematic of the chromium analytical procedure is provided in Figure II.4. The same procedures for chromium analysis were employed for all the liquid leachate samples described in this report. These include the pH Stat leachates (Chapter III) and the SPLP and TCLP leachates from CCA-treated wood and CCA-treated wood ash (Chapter IV).

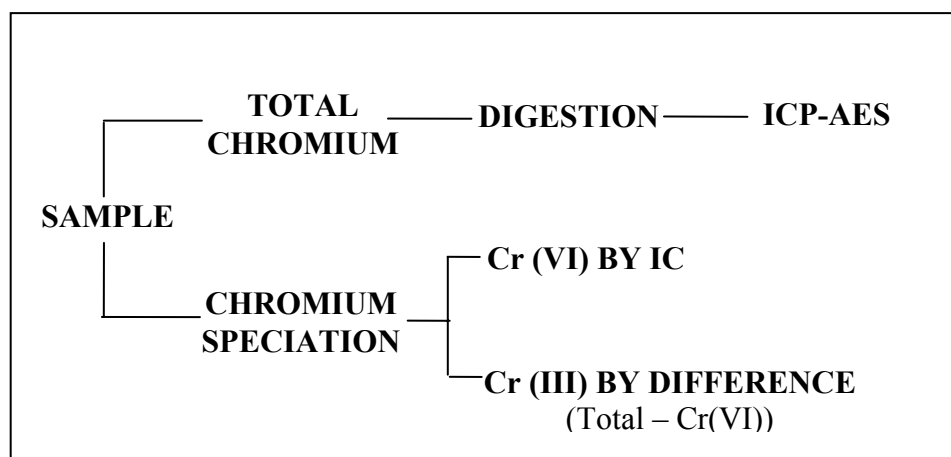


Figure II.4: Summary of Laboratory Methods Used for Chromium Analysis of Liquid Leachates

II.2.a Ion Chromatography (Cr(VI) Analysis)

Hexavalent chromium was measured by ion chromatograph (IC) following the USEPA SW-846 Method 7199 (U.S. EPA 1996). Table II.2 presents the experimental conditions for chromium speciation by IC system. A Perkin Elmer Series 40 liquid chromatograph pump was

employed to carry the eluent and the sample at a flow rate of 1.3 mL/min. A Gilson model 1302 pump was used to carry the post-column reagent at a flow rate of 0.6 mL/min. Dionex IonPac NG1 and IonPac AS7 columns were utilized to block organics and separate hexavalent chromium, respectively. A Hitachi UV detector L-7400 was used to detect the presence of Cr(VI). A Hewlett Packard HP3396A integrator was connected with the detector. The detection limit for this equipment was 0.04 mg/l of hexavalent chromium. Approximately 250 ml of filtered aqueous sample were injected at an injection port with a syringe. The injected sample was carried by the eluent, which contained 33 g of ammonium sulfate and 6.5 ml of ammonium hydroxide in one liter of deionized water at a flow rate of 1.5 ml/min. Organics in the injected sample, if present, were removed with a guard column. Hexavalent chromium was separated on an analytical column. The separated hexavalent chromium reacted with diphenylcarbazide, and was then detected at a wavelength of 520 nm.

Ion Chromatography Component	Experimental Conditions
Eluent Pump	Perkin Elmer Series 40 liquid chromatograph pump
Postcolumn Reagent Pump	Gilson model 1302 pump
Integrator	Hewlett Packard HP 3396A integrator
Detector	Hitachi UV detector L-7400
Guard Column	IonPac NG1
Analytical Column	IonPac AS7
Eluent	250 mM Ammonium sulfate / 100 mM Ammonium hydroxide, Eluent Flow Rate-1.5 ml/min
Eluent Flow Rate	1.3 ml/min
Postcolumn Reagent	2mM diphenylcarbazide, 10 % Methanol, 1 N Sulfuric acid
Postcolumn Reagent Flow Rate	0.6 ml/min
Detection Wavelength	520 nm
Sample Volume	250 μ L

Table II.2: Experimental Conditions for Cr(VI) Analysis Using Ion Chromatography

II.2.b ICP-AES (Total Chromium)

The analysis of total chromium in liquid leachates by ICP-AES required an acid digestion step followed by analysis using an ICP-AES. This procedure is the same as that described in section II.1.c except that chromium was analyzed instead of arsenic. In most instances, the analysis of total chromium and arsenic was conducted on the same sample.

II.3 METAL ANALYSIS IN SOLID SAMPLES

Solid samples evaluated in this study included sawdust samples and ash samples. Sawdust samples were analyzed for total metals (arsenic, chromium, and copper) and for hexavalent chromium. Analysis for total metals was conducted using two different methods: X-ray fluorescence spectroscopy (XRF) and ICP-AES. The XRF analysis was conducted on sawdust obtained from the entire cross section of the wood or from sawdust generated from the outer 6/10". The 6/10" sample corresponds to the "rated" retention level of the wood sample in accordance with American Wood Preservers' Association (AWPA) standard procedures. The rated retention level is the retention level quoted during commercial sale of the wood. The ICP-AES method, which was conducted after sample digestion, was performed exclusively on sawdust obtained from the entire cross section of the wood. Analysis of sawdust collected from

the entire cross-section is a more direct measure of the metals concentrations throughout the wood sample and is a more useful value when performing mass balance computations to evaluate metals releases from the wood samples. Given that the concentration of wood preservatives is generally greater near the outer portion of the wood cross-section, it is anticipated that retention levels obtained from analyzing the outer 6/10" would be greater than the retention levels obtained from analyzing the entire cross-section of the wood samples.

The analysis of hexavalent chromium on sawdust required the extraction of chromium using a special alkaline digestion method which preserves and solubilizes the chromium species of the original wood samples. The digestates were then analyzed for hexavalent chromium using an ion chromatography (IC) method. Trivalent chromium is determined by difference between total chromium and hexavalent chromium. A schematic diagram of the procedures used to evaluate solid sawdust samples is provided in Figure II.5.

Ash samples were analyzed through a prior study (Solo-Gabriele et al. 1999 and 2002) using neutron activation analysis. Neutron activation is a non-destructive analytical method which is capable of analyzing total metals in solid samples. Furthermore, as part of the current study, these same samples were evaluated for total metals using ICP-AES following an acid digestion step (Figure II.5)

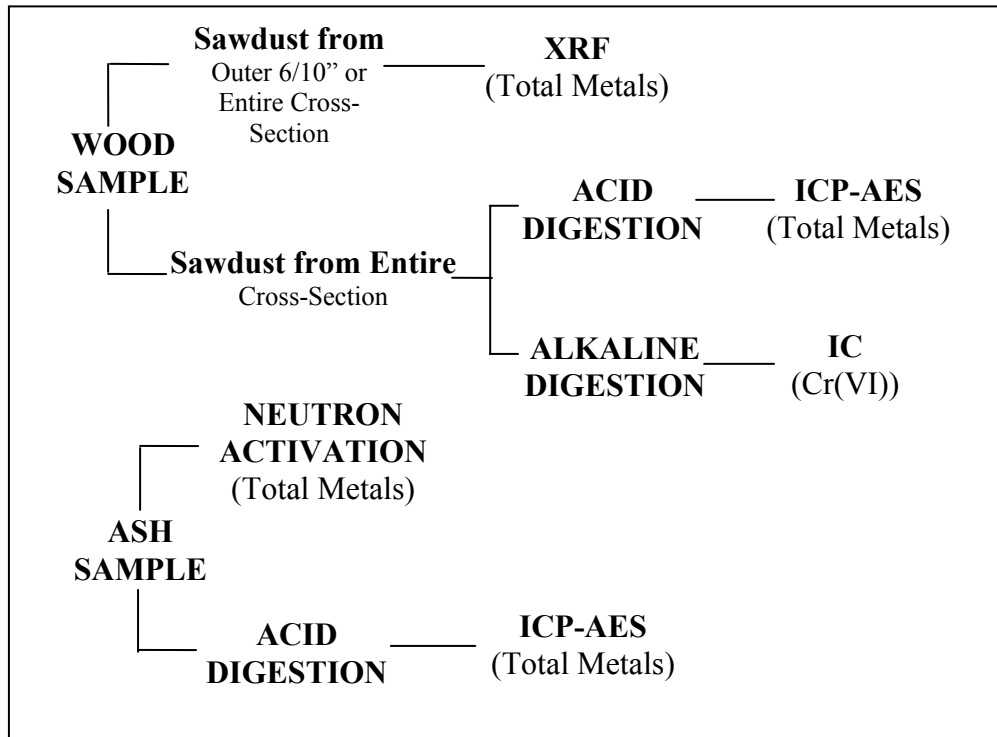


Figure II.5: Summary of Laboratory Methods Used for the Analysis of Solid Samples

II.3.a Ion Chromatography (Cr(VI) Analysis, sawdust)

The analytical procedure used for hexavalent chromium analysis of sawdust samples requires the extraction of hexavalent chromium using an alkaline digestion procedure which preserves the chromium species and thus transfers the chromium from the solid sawdust to a liquid digestate solution. This solution is then analyzed using ion chromatography (IC) to quantify Cr(VI). The ion chromatography procedure utilized for the analysis of these digestates is the same as that used for liquid leachate samples (See sub-section II.2.a). The alkaline digestion procedure is described below.

Alkaline Digestion

The alkaline digestion procedure used for the digestion of samples for hexavalent chromium analysis was SW-846 Method 3060A (U.S. EPA 1996). This procedure begins with the addition of two grams of soil into a 250 ml Erlenmeyer flask containing 50 ml of digestion solution and 0.5 ml of 1-M phosphate buffer solution. The digestion solution was prepared with 20 g of sodium hydroxide and 30 g of sodium bicarbonate in one liter of deionized water. The pH of the digestion solution was greater than 11.5. The 1-M phosphate buffer solution was made with 87.09 g of dibasic potassium phosphate and 68.04 g of monobasic potassium phosphate in one liter of deionized water. The flask was covered by a watch glass, heated at 90-95°C, and stirred with a magnetic stirrer bar on a hot plate for more than one hour without boiling. After cooling, the digestate was transferred into the filtration apparatus and filtered using a 0.45 um membrane filter. The pH of the filtered digestate was adjusted to pH 9.0 ± 0.5 using 5-M nitric acid. The digestate was transferred into a 100 ml volumetric flask and diluted to 100 ml with deionized water. The hexavalent chromium was measured by ion chromatograph as described in sub-section II.2.a.

II.3.b XRF (Total Metals, sawdust)

X-ray fluorescence (XRF) is a technique utilized by many wood treating plants to determine the “rated” retention value of treated wood. The analytical method for determining the rated retention value requires the analysis of the outer 6/10” of the wood (AWPA 1999); however, the same technique can be used to analyze sawdust collected from the entire cross-section of the wood.

XRF operates by emitting X-rays which then releases electrons from atoms within the wood creating a vacancy in the electron shell in these atoms. Next an electron from a higher energy falls to the created vacancy, and in the process excess X-ray energy is emitted that is equal to the difference of energy between those shells. An XRF analyzer registers the emitted energy and compares it to the known energies of a given element. Different elements are distinguished by the wavelength of the energy that is emitted. The intensity of that energy, measured in units of “counts”, is a measure of the amount of that element within the sample.

XRF was used to analyze the wood samples used in the pH Stat experiment (Chapter III) and for the wood samples used in the TCLP and SPLP experiments (Chapter IV). The sawdust utilized for this analysis came from the entire cross-section of the wood samples. The wood samples used for the pH Stat experiments came from the same batch as those used for the lysimeter study (Chapter V). The samples used in the pH Stat experiment/lysimeter study (Chapters III and V), were analyzed using an XRF instrument (Asoma, model 100) owned by Koppers Inc. located in Gainesville, Florida. The samples used in the TCLP and SPLP experiments (Chapter IV) were evaluated by XRF through an earlier study (Solo-Gabriele et al. 1999), with the exception of samples C&D 1 and C&D 3. The sawdust utilized for this analysis came from the outer 6/10" of the wood samples. The analyses for this set of samples were first conducted at Langsdale Forest Products, Valdosta, Georgia, by utilizing a ASOMA X-ray Spectrometer Model 111. Then the same samples were sent to Hickson Corporation, Smyrna, Georgia, for confirmatory analysis. Hickson Corporation (now known as Arch Wood Protection Inc.) analyzed the samples four times; two sets using an ASOMA X-ray Spectrometer Model 200 and two sets using an ASOMA X-ray Spectrometer Model 200T.

II.3.c ICP-AES (Total Metals, sawdust and ash)

The ICP-AES analysis for total metals in sawdust and ash samples is the same as that used for liquid leachate samples (as described in sub-section II.1.c) except for the digestion method used corresponds to SW-846 Method 3050B which is a digestion procedure for solid samples instead of Method 3010A which is a digestion procedure for liquid samples (U.S. EPA 1996). The two digestion procedures are very similar. The method used for the solid samples differs from the methods used for the liquid leachates in that 1 to 2 grams of sawdust or ash were analyzed instead of 100 ml of liquid leachate. Furthermore, the solid digestion requires repetitive acid additions plus the addition of hydrogen peroxide, which is not required by the liquid digestion method.

II.3.d Neutron Activation (Total Metals, ash)

Neutron activation analysis is based upon the bombardment of a sample with accelerated neutrons. After bombardment a sample will then emit a characteristic form of radiation that is dependent upon the amount and types of elements within a particular sample. Results from such analyses are considered to provide the absolute total metal concentration within a sample.

Ash samples used in the TCLP and SPLP tests (Chapter IV) were analyzed using neutron activation analysis through a prior study (Solo-Gabriele et al. 2002). Two sets of 1 gram ash samples were prepared. One set was provided on March 16, 1999 to Dr. William Vernetson, Director of the University of Florida's Nuclear Reactor Facility located at the University of Florida campus in Gainesville, Florida. The second set was provided on September 1, 1999 to Dr. Michael Ames, Director of the Massachusetts Institute of Technology's Nuclear Reactor Facility located at the Massachusetts Institute of Technology campus in Cambridge, Massachusetts. Both sets were irradiated and counted during the month of October 1999.

This page left intentionally blank.

**CHAPTER III,
RESULTS FROM pH STAT EXPERIMENT**

This page left intentionally blank.

CHAPTER III, RESULTS FROM pH STAT EXPERIMENT

For the “pH Stat” experiment, measurements of As and Cr species were made on new and weathered CCA-treated wood at pH values ranging from 1 to 13. These experiments require that samples be pre-processed and extracted into a deionized water solution of a given pH (section III.1). Once extracted samples were analyzed for arsenic species using HPLC-HG-AFS and for hexavalent chromium using an IC as described in Chapter II. Total arsenic and chromium were analyzed using ICP-AES. Results for arsenic and chromium (section III.2) were then plotted for analysis.

III.1 SAMPLE PREPARATION

Samples used in the pH stat experiment included new and weathered CCA-treated wood at a rated retention of 0.4 pcf as indicated during the purchase of the wood. The new CCA-treated wood was obtained from a home improvement store. The “rated” retention level of the new wood was 0.4 pcf as indicated during the purchase of the wood. The weathered CCA-treated wood was taken from a playground demolition in Gainesville, Florida. The playground was built from Nov. 18th to 22nd 1987, making the wood approximately 14 years of age at the time this experiment was conducted during 2001. The demolition took place in 1998, from which time the used wood had been lying in dumpsters under cover.

Before analysis, the solid sawdust samples were evaluated for Cr(VI) and for total Cr, Cu, and As to obtain the true retention values (See Section II.3 for a description). Two sets of sawdust samples were collected: one set corresponding to the entire cross-section of the wood and another corresponding to the outer 0.6 inches of the wood. The outer 0.6 inches corresponds to the depth utilized by the industry to established the “rated” value (AWPA 1999). Cr(VI) concentrations were evaluated in triplicate using the IC method described in sub-section II.3.a. The retention value measurements for Cr(VI) were based upon sawdust collected from the entire cross-section of the wood. XRF and ICP-AES were used to analyze this sawdust (see sub-sections II.3.b and II.3.c) corresponding to the entire cross-section of the wood. Single analyses were conducted using XRF and analyses were conducted in quintuplicate (5 different digestates) using ICP-AES. Samples collected from the outer 0.6 inch of the wood were analyzed by atomic absorption in duplicate. Results from these analyses are summarized in Table III.1 below. As observed from this table, the rated retention level indicated during the purchase of the treated wood (0.4 pcf) was significantly different than the retention level for new wood as measured for sawdust collected from the outer 0.6 inches (0.32 pcf) and sawdust collected from the entire cross-section (XRF: 0.214 pcf, ICP-AES: 0.19 pcf). Furthermore, Cr(VI) was found to represent less than 2% of the total chromium within the new and weathered solid sawdust samples.

As part of the sample pre-processing, the wood samples were reduced to a particle size smaller than 9.75 mm which is consistent with EPA’s TCLP and SPLP methods. The leaching solution consisted of deionized water to which an acid or a base was added to obtain the desired pH. The acid used was 1N nitric acid and the base used was 1 N sodium hydroxide. This acid was selected after careful evaluation of similar leaching tests conducted by other researchers (Warner and Solomon, 1990; Cooper, 1991). Unlike acetic, citric and hydrochloric acids, nitric

acid is less likely to cause complexation with heavy metals that can lead to an increase in metal leaching.

The leaching procedure utilized is consistent with the U.S. EPA’s TCLP and SPLP test methods with the exception of the solvent utilized. The pH stat extraction begins by adding one hundred grams of each sample to about 1 liter of leaching solution. Nitric acid (1N) was used to lower the extraction fluid pH to simulate acidic conditions and sodium hydroxide (1 N) was used to increase the pH. The solution was rotated to mix thoroughly and the pH of that solution was adjusted, if needed, in 15 minute intervals for an hour. After an hour of mixing, the solution was brought up to a final of 2 liters and the pH was re-checked and re-adjusted, if necessary. The final 2 L volume (20:1 liquid to solid ratio) was rotated for approximately 18 hours with periodic pH correction, after which time the solution was filtered through a 0.7 um filter. The University of Florida team conducted the experiment in their laboratory and ran duplicates of all the samples. The final filtrate was split between the University of Miami and the University of Florida teams. The University of Miami team conducted arsenic speciation analysis by HPLC-HG-AFS on the filtrate and summed the concentrations of the individual species to obtain the total arsenic concentration. The University of Florida team analyzed the filtrate for total arsenic by ICP-AES. Chromium speciation analysis was also conducted by the University of Florida team using their sample split. Total chromium analysis was conducted using ICP-AES. Cr(VI) was analyzed using ion chromatography. See Chapter II for more specifics for the methods utilized for arsenic and chromium speciation analysis.

Sample ID	IC (full-cross section)	ICP-AES (full-cross section)					XRF (full-cross section)	AA (outer 0.6")
	pcf as Cr ^{VI} O ₃	pcf ¹ as CuO	pcf as CrO ₃	pcf as As ₂ O ₅	pcf CCA	Average pcf CCA	pcf CCA	pcf CCA
New	0.00090	0.032	0.087	0.065	0.184	0.190	0.214	0.32
	0.00180	0.033	0.088	0.066	0.187			
	0.00271	0.034	0.094	0.070	0.198			
		0.032	0.089	0.066	0.188			
		0.033	0.086	0.073	0.192			
Weathered	0.00151	0.053	0.155	0.096	0.304	0.307	0.386	0.41
	0.00084	0.053	0.155	0.094	0.301			
	0.00075	0.053	0.154	0.095	0.302			
		0.055	0.158	0.098	0.312			
		0.055	0.162	0.099	0.316			

¹ Conversion of units from mg/kg is based upon an assumed density of SYP of 32 lb/ft³

Table III.1: Results from the Analysis of the Solid Sawdust Samples Used in pH Stat Tests

III.2 RESULTS

Results of the pH stat experiment are presented for both new wood (sub-section III.2.a) and weathered wood (sub-section III.2.b). A comparison of the results for new and weathered wood is provided in sub-section II.2.c.

III.2.a Results for New CCA-Treated Wood

Table III.2 provides the results obtained from the pH stat experiment conducted on the new CCA-treated wood. The only arsenic species detected was inorganic arsenate, As(V). As(III) and the organic arsenic species (MMAA and DMAA) were not detected. The highest arsenic concentrations were observed at the lowest and highest pH values, with about 40 mg/L at pH 1 and an average of 12 mg/L at pH 13. In the pH region, 6 to 10, at which environmental samples are generally found, arsenic concentrations were relatively constant with an average of 4.4 mg/L. Figure III.1 shows the graphical relationship between both analytical instruments, HPLC-HG-AFS and ICP-AES for comparative purposes. Since As(V) was the only species observed leaching from the new wood, the total concentration of As(V) for each pH value was compared to the total arsenic concentration analyzed by ICP-AES. Both sets of results match fairly well with a standard deviation no greater than 3.7 mg/L. The slight difference in concentration between both curves may be attributed to the difference in analytical techniques.

Chromium, as for arsenic, leached the most at the pH extremes (Figure III.2). The highest concentrations were observed in the highly acidic region (pH = 1) with 27 mg/L chromium. Concentrations were not as high at the alkaline extreme (3.4 mg/L total chromium). Within the mid-range near neutral pH region, total chromium concentrations were in the 1 to 2 mg/L range. All of the chromium in the acidic and neutral regions was present as Cr(III). Only under alkaline conditions, at pH > 9, was Cr(VI) observed.

III.2.b Results for Weathered CCA-Treated Wood

Table III.3 shows the results obtained from the pH Stat test conducted on weathered CCA-treated wood. Unlike new wood, both As(III) and As(V) species were observed. MMAA and DMAA in these samples were not detected. Figure III.3 shows a graphical relationship between As(III) and As(V) for each pH value and a comparison of the overall total arsenic concentration between the analytical techniques, HPLC-HG-AFS and ICP-AES. To obtain the total arsenic concentration for HPLC-HG-AFS, the individual arsenic species were summed together. When the results of both techniques were compared, a slight difference in concentration was noticed. This difference is not severe and may be attributed to the difference in analytical techniques. As(III) leached from the used wood up to a pH of about 9, after which no As(III) was observed. As(V), however, was detected across the entire pH range. The highest concentrations of arsenic were observed at the lowest and highest pH values, with an average of 27.8 mg/L at pH 1 and 26.5 mg/L at pH 13. Similar results about arsenic behavior have also been observed when Pansar-Kallio and Manninen (1997) extracted arsenic from soil across the pH range. They noted the highest concentrations of arsenic being released at the extreme pH values of 1 and 13 and detected both As(III) and As(V) from soils collected from wood preservative plants that were contaminated with As(V) in the form of As₂O₅. Results similar to that of new wood were observed at the pH region of 6 to 10. As(III) and As(V) concentrations were relatively constant with an average of 1.2 and 6.5 mg/L, respectively, with As(V) as the predominate species.

Chromium results for weathered wood were similar to that of new wood with the highest leachate concentrations observed at the extreme pH values (Figure III.4). At a pH of 1,

chromium which was present as Cr(III), was observed at a value of 32 mg/L. At the other pH extreme (pH = 12.8) total chromium was observed at 20 mg/L. Within the near neutral pH range, total chromium concentrations were relatively constant between values of 5 and 6 mg/L. Only Cr(III) was observed in the acidic and neutral ranges. Cr(VI) was observed at pH values greater than 9. Although the amount of Cr(VI) at the alkaline pH extreme was significant, the majority of the chromium leached was in the form of Cr(III).

III.2.c Comparison Between New and Weathered CCA-Treated Wood

Results indicate that the overall arsenic concentration leached from new wood was greater at a pH from 1 to 3 (Figure III.5), which is contrary to what would be expected given that the retention value was lower than that of weathered wood. At a pH of about 4, there is a shift with weathered wood leaching greater concentrations of arsenic than new wood. This shift increases with increasing pH values. This increase in leaching may be attributed to 1) the higher measured retention in the weathered wood and/or 2) the age of the wood. In addition, the presence of As(III) may also play a role in the greater leaching of arsenic from the weathered wood (Figure III.6), as As(III) is a more soluble specie and may not bind as strongly to the wood as As(V). It appears from this limited data set that a portion of the As is converted to As(III) as the wood ages. Further work is needed with additional wood samples to reconfirm this observation.

Greater quantities of total chromium were leached from weathered wood consistently throughout the entire pH range (Figure III.7). As for arsenic, this increase in leaching is likely due to the higher measured retention in the weathered wood and also possibly due to the effects of wood aging. Leaching at the alkaline pH range is enhanced by the conversion of Cr(III) to Cr(VI) (Figure III.8).

pH	Arsenic				Chromium				
	HPLC-HG-AFS ^c			ICP-AES	ICP-AES			IC	By Difference
	As(V) Runs 1 & 2 (mg/L)	As(V) Average (mg/L)	Std. Dev. (mg/L)	Total As (mg/L)	Total Cr Runs 1 & 2 (mg/L)	Total Cr Average (mg/L)	Std. Dev. (mg/L)	Cr(VI) Average (mg/L)	Cr(III) Average (mg/L)
1	37.21 42.44	39.82	3.7	34.94	27.8 25.8	26.8	1.4	BDL	26.8
2	15.1 18.31	16.71	2.27	16.2	7.8 8.1	7.9	0.2	BDL	7.9
3	9.02 8.64	8.83	0.26	12.38	3.5 3.7	3.6	0.1	BDL	3.6
4	6.84 7.95	7.4	0.79	9.12	2.0 2.0	2.0	0.0	BDL	2.0
5	4.8 5.01	4.91	0.15	5.4	1.2 1.5	1.4	0.2	BDL	1.4
6	3.84 3.14	3.49	0.49	4.52	1.4 1.4	1.4	0.0	BDL	1.4
6.3	2.67 3.66	3.17	0.7	4.71	1.1 1.3	1.2	0.1	BDL	1.2
6.9	2.56 2.91	2.73	0.25	4.2	1.1 1.2	1.1	0.1	BDL	1.1
7.5	2.51 3.14	2.82	0.44	3.58	0.7 1.3	1.0	0.4	BDL	1.0
8.0	2.54 2.81	2.67	0.19	4.54	1.0 1.3	1.2	0.2	BDL	1.2
9.1	2.88 3.67	3.28	0.56	4.61	1.5 1.5	1.5	0.0	0.3	1.2
10.9	4.93 5.46	5.19	0.38	7.22	4.0 2.3	3.1	1.2	1.9	1.2
12.6	10.48 NA	10.48	--	13.68	4.6 4.6	4.6	0.0	1.2	3.4

^aBelow Detection Limit

^bNot Analyzed

^c As(III), MMAA, and DMAA were not detected

Table III.2: Leaching of Arsenic and Chromium from New Wood at Varying pH Values

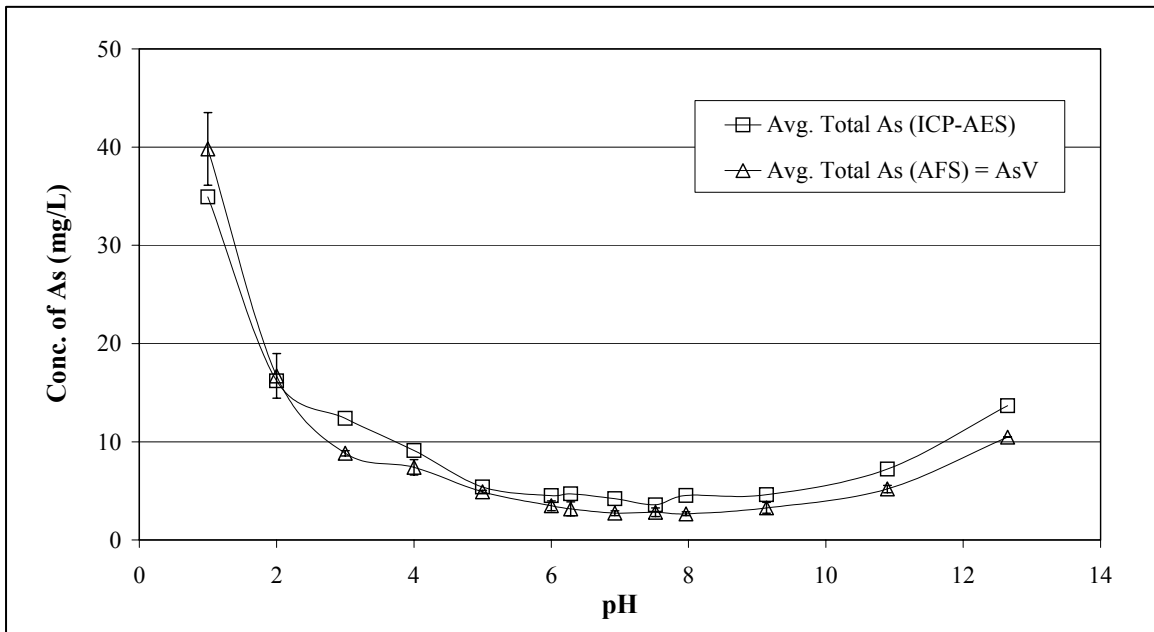


Figure III.1: Leaching of Arsenic from New Wood at Varying pH Values, Total Arsenic as Measured by AFS is in the Form of As(V)

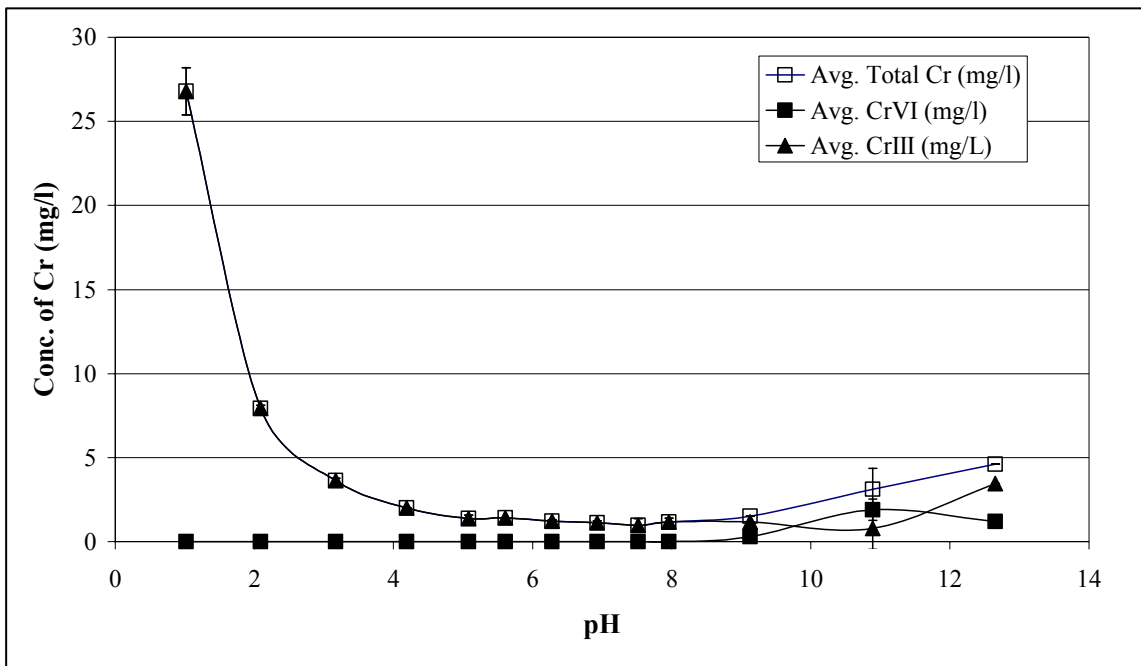


Figure III.2: Leaching of Chromium from New Wood at Varying pH Values

pH	Arsenic							Chromium					
	HPLC – HG - AFS ^c						ICP-AES	ICP-AES			IC	By Difference	
	As(III) Runs 1 & 2 (mg/L)	Std. Dev. (mg/L)	As(V) Runs 1 & 2 (mg/L)	Std. Dev. (mg/L)	Total As Average (mg/L)	Std. Dev. (mg/L)	Total As Avg. (mg/L)	Total As (mg/L)	Total Cr Runs 1 & 2 (mg/L)	Total Cr Average (mg/L)	Std. Dev. (mg/L)	Cr(VI) Average (mg/L)	Cr(III) Average (mg/L)
1.3	NA 2.60	-	NA 25.23	-	NA 27.82	-	27.82	44.46	32.45 31.72	32.09	0.52	BDL	32.09
2.6	2.51 2.84	0.23	1.33 5.25	2.77	3.83 8.08	3.01	5.96	10.03	9.45 10.56	10.01	0.78	BDL	10.01
3.7	2.10 2.64	0.38	6.19 6.25	0.04	8.29 8.89	0.42	8.59	11.54	6.43 5.30	5.87	0.80	BDL	5.87
4.2	2.30 2.46	0.12	6.01 6.97	0.68	8.30 9.43	0.80	8.87	10.77	5.05 5.54	5.30	0.35	BDL	5.30
5.2	2.31 2.56	0.18	2.40 2.70	0.21	4.71 5.26	0.39	4.98	9.64	5.82 5.37	5.60	0.32	BDL	5.60
5.4	1.87 1.98	0.08	3.92 3.98	0.04	5.79 5.96	0.12	5.88	8.21	4.22 5.36	4.79	0.81	BDL	4.79
6.5	2.34 2.71	0.26	4.08 4.37	0.20	6.43 7.08	0.46	6.75	8.73	6.45 6.62	6.54	0.12	BDL	6.54
8.0	1.81 1.46	0.24	4.98 4.46	0.36	6.78 5.93	0.61	6.35	8.07	7.08 5.90	6.49	0.83	BDL	6.49
9.4	0.09 0.05	0.03	5.96 5.83	0.09	6.05 5.88	0.12	5.97	6.68	8.40 7.65	8.03	0.53	0.42	7.61
10.2	0.01 0.01	0.00	7.56 7.37	0.20	7.57 7.39	0.13	7.48	9.96	9.12 8.28	8.70	0.59	1.13	7.57
10.7	0.00 0.00	0.00	9.86 8.33	0.36	9.86 8.33	1.09	9.10	12.04	11.80 11.55	11.68	0.18	2.34	9.34
11.9	0.00 0.00	0.00	10.03 8.61	0.09	10.03 8.61	1.00	9.32	13.82	13.60 11.92	12.76	1.19	4.03	8.73
12.8	0.00 NA	-	26.48 NA	-	26.48 NA	-	26.48	25.23	20.86 19.25	20.06	1.14	5.92	14.14

^aBelow Detection Limit

^bNot Analyzed

^c MMAA and DMAA were not detected

Table III.3: Leaching of Arsenic and Chromium from Weathered Wood at Varying pH Values

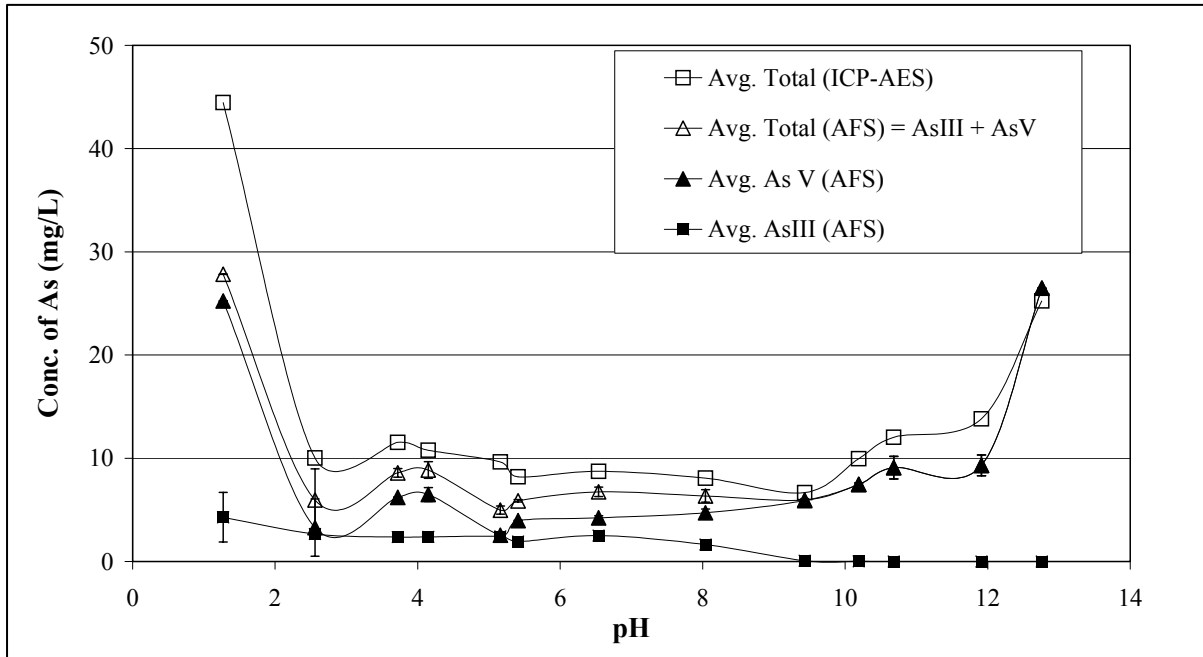


Figure III.3: Leaching of Arsenic from Weathered Wood at Different pH Values

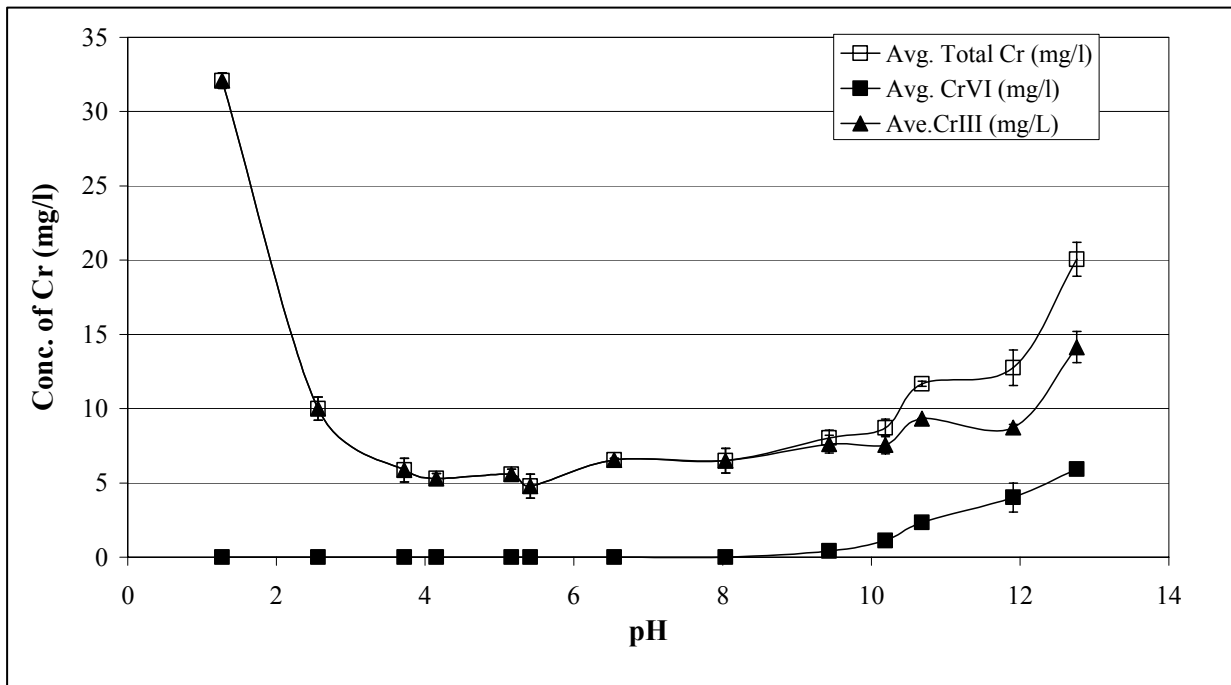


Figure III.4: Leaching of Chromium from Weathered Wood at Different pH Values

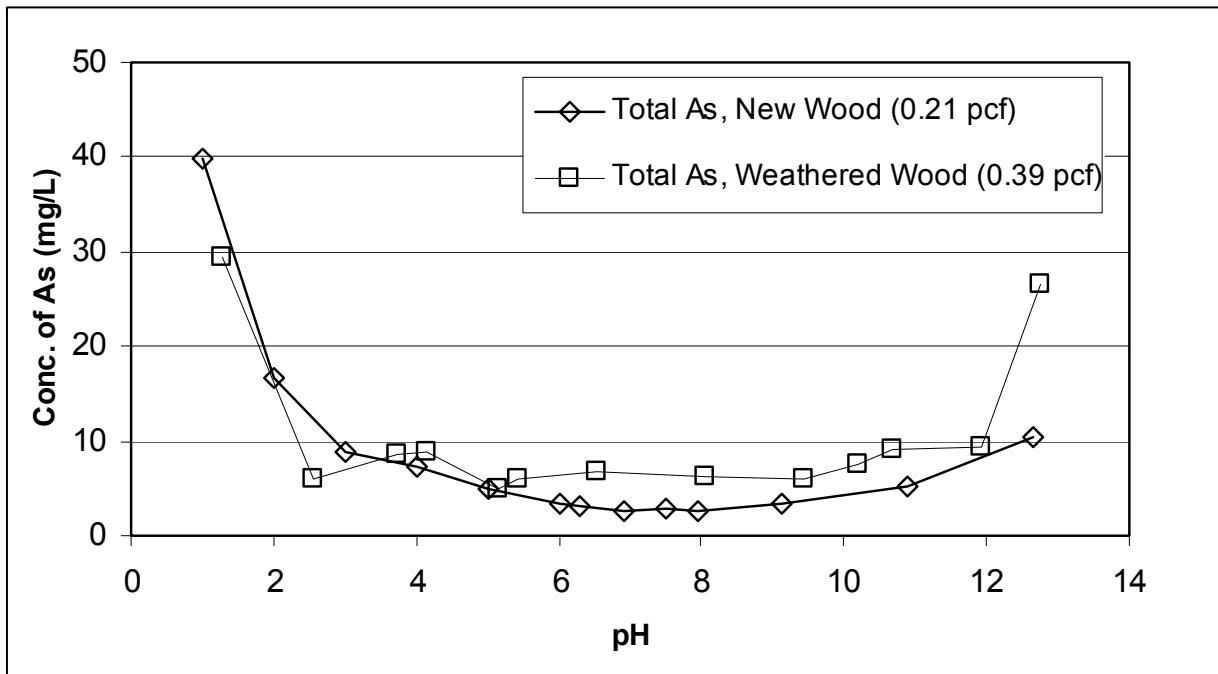


Figure III.5: Total Arsenic Concentrations for New and Weathered CCA-treated Wood Across the pH Range (HPLC-HG-AFS Analysis Method)

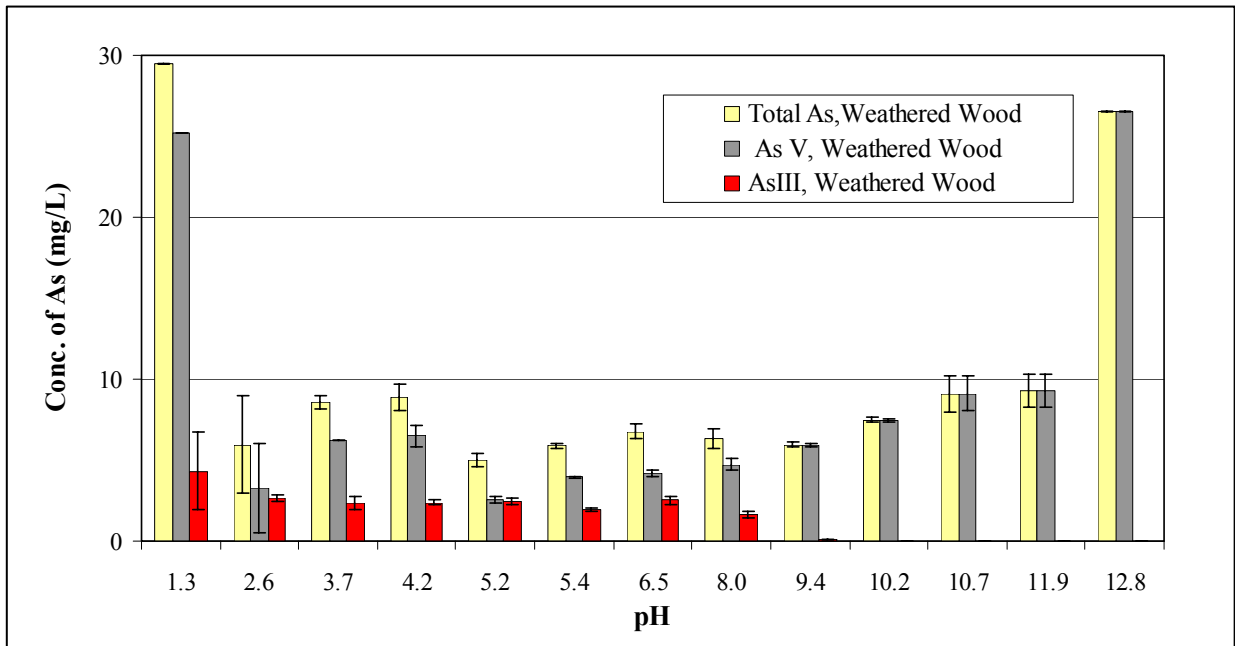


Figure III.6: Distribution of Arsenic Among As(V) and As(III) Across the pH Range for Weathered Wood

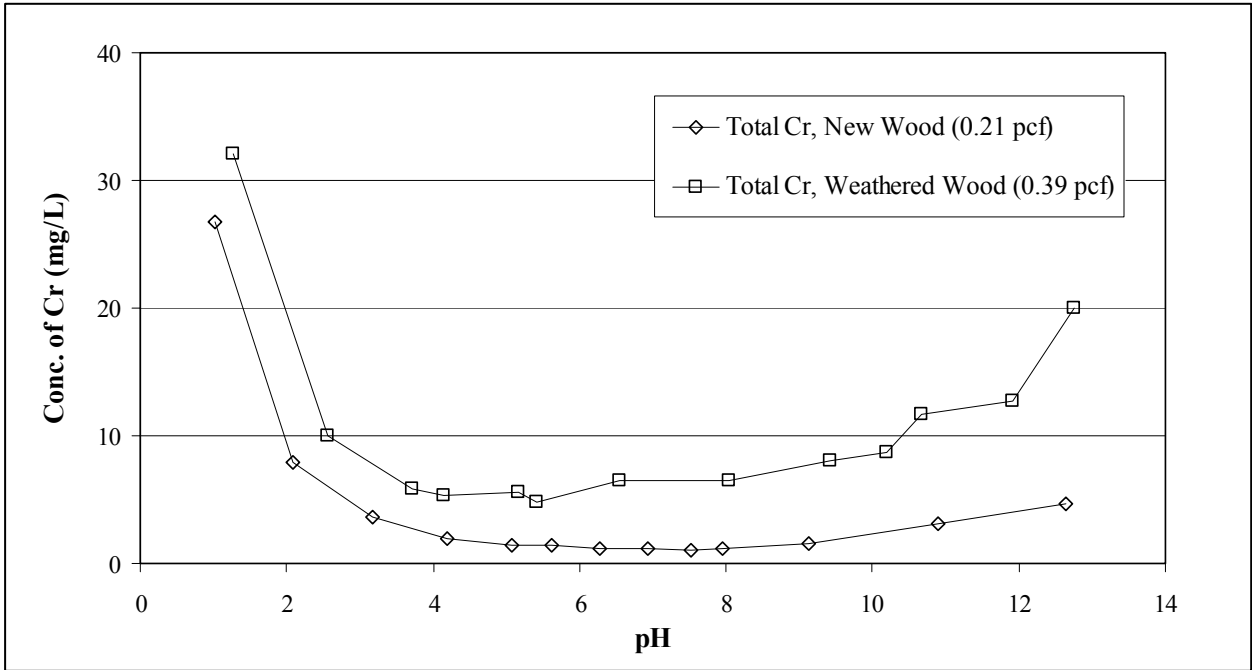


Figure III.7: Total Chromium Concentrations for New and Weathered CCA-treated Wood Across the pH Range

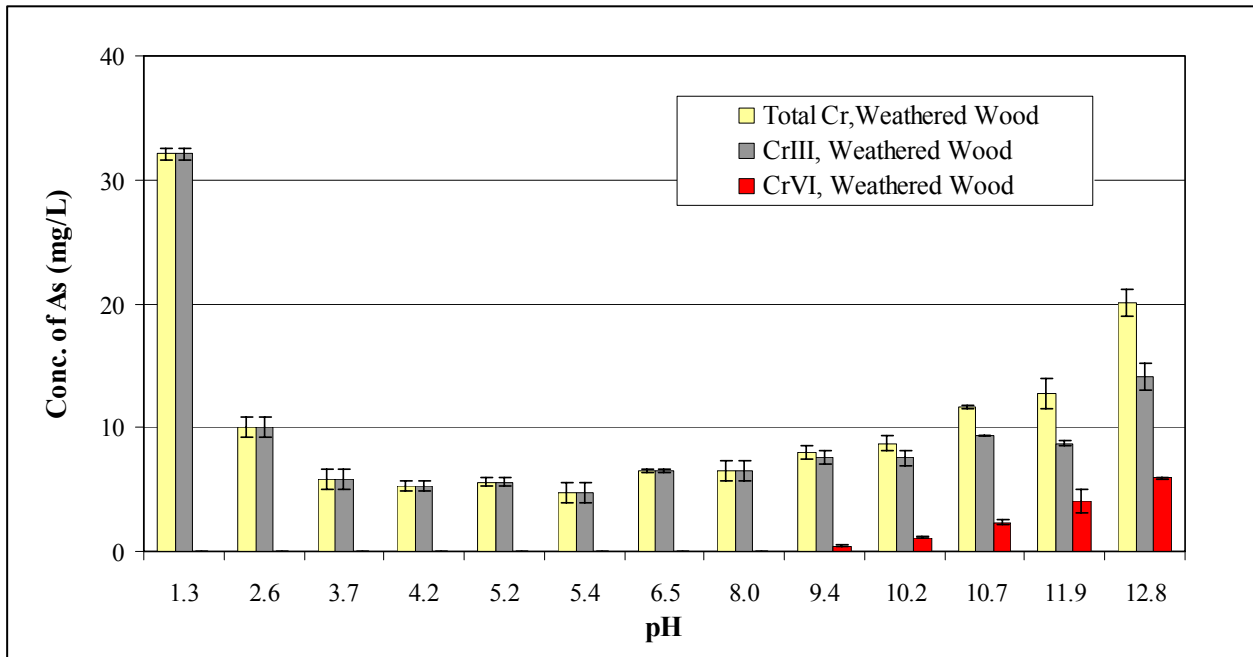


Figure III.8: Distribution of Chromium Among Cr(III) and Cr(VI) Across the pH Range for Weathered Wood

**CHAPTER IV,
RESULTS FROM TCLP AND SPLP TESTS CONDUCTED ON
UNBURNED CCA-TREATED WOOD AND CCA-TREATED WOOD ASH**

This page left intentionally blank.

CHAPTER IV, RESULTS FROM TCLP AND SPLP TESTS CONDUCTED ON UNBURNED CCA-TREATED WOOD AND CCA-TREATED WOOD ASH

Arsenic and chromium species were quantified for leachates generated from CCA-treated wood and CCA-treated wood ash subjected to the U.S. EPA standard SPLP and TCLP tests. The samples utilized for this set of experiments which include weathered wood and unweathered wood samples of various retention levels are described in Section IV.1. Methods used for SPLP and TCLP analysis are described in Section IV.2. Results from the unburned wood are presented first (Section IV.3), followed by the results from the CCA-treated wood ash (Section IV.4). A comparison between the unburned wood and ash results are provided in Section IV.5. It is important to mention that the research team has published SPLP and TCLP results on the *ash* samples used in this study (Solo-Gabriele et al. 2002). The previous ash study focused on measuring total metals. The current study described below differs in that arsenic and chromium species were analyzed.

IV.1 SAMPLE DESCRIPTIONS AND PRE-PROCESSING

The samples selected for the TCLP and SPLP tests were obtained from the University of Miami sample archive. They included weathered and unweathered wood and ash from these wood samples. A listing of these samples is provided in Table IV.1 below.

Sample Category	Sample ID	Description
Unweathered Wood	Untreated	Untreated Southern Yellow Pine
	0.25 pcf	CCA-treated wood at 0.25 pcf
	0.60 pcf	CCA-treated wood at 0.60 pcf
	2.5 pcf	CCA-treated wood at 2.5 pcf
Weathered Wood	Pole	Utility pole originally treated at 0.60 pcf
	C&D 1	Recycled waste wood from C&D recycling facility #1. Likely a mix of untreated and treated wood.
	C&D 3	Recycled waste wood from C&D recycling facility #3. Likely a mix of untreated and treated wood.
Ash from Unweathered Wood	Untreated-ash	Ash from corresponding sample above.
	0.25 pcf-ash	“ “ “ “ “
	0.60 pcf-ash	“ “ “ “ “
	2.5 pcf-ash	“ “ “ “ “
Ash from Weathered Wood	Pole-ash	“ “ “ “ “
	C&D 1-ash	“ “ “ “ “
	C&D 3-ash	“ “ “ “ “

Table IV.1: Samples Utilized for TCLP and SPLP Analysis

The unweathered samples (untreated wood, 0.25 pcf, 0.6 pcf, and 2.5 pcf) were originally purchased as 2” x 4” x 10 ft, as supplied by Ace Hardware/Shell Lumber located in Miami, Florida. The weathered sample was obtained from a pole barn owned by Florida Power and Light (FPL) Company. The pole barn was located outdoors at the Distribution Environmental facility of FPL located in West Palm Beach, Florida. The weathered wood sample was collected during two trips. One trip was conducted on May 31st, 1998 and the other on June 2nd, 1998. The process of collecting the samples involved selecting an aged CCA-treated utility pole from

the pole barn. The pole chosen during the May 31st sampling trip was dated June 1980; the one chosen during the June 2nd sampling trip was dated October 1980. The age of the weathered pole sample was estimated at 20 years old at the time of this study and there was no obvious evidence of deterioration observed on either utility pole. In addition, two samples, C&D 1 and C&D 3, were collected from separate C&D recycling facilities and consisted of a mixture of untreated and CCA-treated wood waste of varying retention levels.

The CCA-treated wood samples were ashed during an earlier study (Solo-Gabriele et al. 1999) using an industrial furnace (Al-Jon/United Inc.), owned and operated by Florida Power and Light (FPL). Prior to the incineration process, the industrial furnace was swept clean. The samples containing the least amount of the CCA chemical were first incinerated followed by the samples containing progressively higher amounts of CCA. This order was chosen to minimize carry-over of CCA from one sample to the next. Samples were placed in the furnace for approximately 1½ hours which was the time necessary to obtain a fine and powdery ash. Ashing temperatures ranged between 800 to 1200 °F. Upon ashing, the sample was removed from the incinerator and permitted to cool for 45 minutes, after which time it was stored in a labeled pre-acid washed container.

Several different methods were utilized to analyze the metals contained within the original solid samples (Figure IV.1). The unburned wood samples (solid) were analyzed by XRF (outer 6/10") and by ICP-AES (entire cross-section of wood). The wood ash (solid) was analyzed by neutron activation analysis and by ICP-AES. Cr(VI) was also analyzed for ash samples and for sawdust samples collected from the entire cross-section of the wood. A description of the methods used are described in Section II.3.

Results of the solid unburned wood samples indicate that the measured XRF values (outer 6/10") were consistent between Langsdale Forest Products and Hickson Corporation (Table IV.2). The measured retention values of the untreated, 0.25 pcf, 0.6 pcf, 2.5 pcf and the pole samples were characterized by the following retention levels: 0.016 pcf, 0.34 pcf, 0.92 pcf, 3.42 pcf, and 0.89 pcf, respectively. The measured values were higher by 30 to 50% than their rated value as indicated by the retail store, emphasizing the importance of measuring the retention values of the samples prior to solvent-extraction studies. The results from ICP-AES (entire cross-section) were lower than the results from XRF (outer 6/10") as expected (Table IV.3). Data also indicate that the C&D samples contain measurable concentrations of chromium, copper and arsenic. Assuming that the treated wood component within the C&D samples is at an equivalent 0.22 pcf CCA (as measured for the 0.25 pcf sample), the estimated fraction of CCA-treated wood in C&D 1 is 16% and for C&D 3 is 22%.

The fraction of Cr(VI) among total chromium was generally low for the solid sawdust samples (Table IV.3). Cr(VI) represented less than 2% of the total chromium for the 0.6 pcf, 2.5 pcf, and pole samples. It represented 4% of the total chromium for the 0.25 pcf sample. One of the C&D samples (C&D 3) contained a relatively high proportion of Cr(VI) at 7%. Cr(VI) in the other C&D sample (C&D 1) was at about 2.5% of the total chromium.

As part of an earlier study (Solo-Gabriele et al. 1999 and 2002), the ash samples (solid) were sent for neutron activation analysis at two different facilities for analysis (Refer to sub-

section II.3.d). The solid ash samples were further analyzed in duplicate for total metals using ICP-AES and for Cr(VI) as part of the work focusing on chromium speciation (See Section II.3 for details concerning methods). Results (Table IV.4) indicate that the variability for neutron activation analysis was greater than the variability from ICP-AES analysis. For samples with higher retention levels, the results between ICP-AES and neutron activation were reasonably close to one another. However, at the lower retention levels the results from these two different methods were significantly different. Overall the analyses indicate that untreated wood contained lower metals concentrations than treated wood. The 0.25 pcf-ash sample contained on the order of 10,000 to 20,000 mg/kg for each of the metals, Cr, Cu, and As. The 0.60 pcf-ash and the pole-ash sample contained on the order of 30,000 to 50,000 mg/kg of Cr, Cu, and As. The 2.50 pcf-ash sample contained on the order of 100,000 mg/kg for each of the metals. The C&D 1-ash and the C&D 3-ash sample contained on the order of 1,000 to 2000 mg/kg for each metal.

The fraction of Cr(VI) in the wood ash samples was highly variable. Of the total chromium in the 0.6 pcf-ash, 2.5 pcf-ash, and the pole-ash samples, between 3 and 5% was in the form of Cr(VI). Cr(VI) in the 0.25 pcf-ash sample represented 5% of the total chromium. The C&D-ash samples contained the highest fraction of Cr(VI). Cr(VI) in C&D 1-ash represented 54% of the total chromium whereas Cr(VI) in the C&D 3-ash sample represented 24% of the total chromium. Apparently the lower the total chromium concentration in the wood samples, the higher the fraction of Cr(VI) formed in the solid ash during incineration.

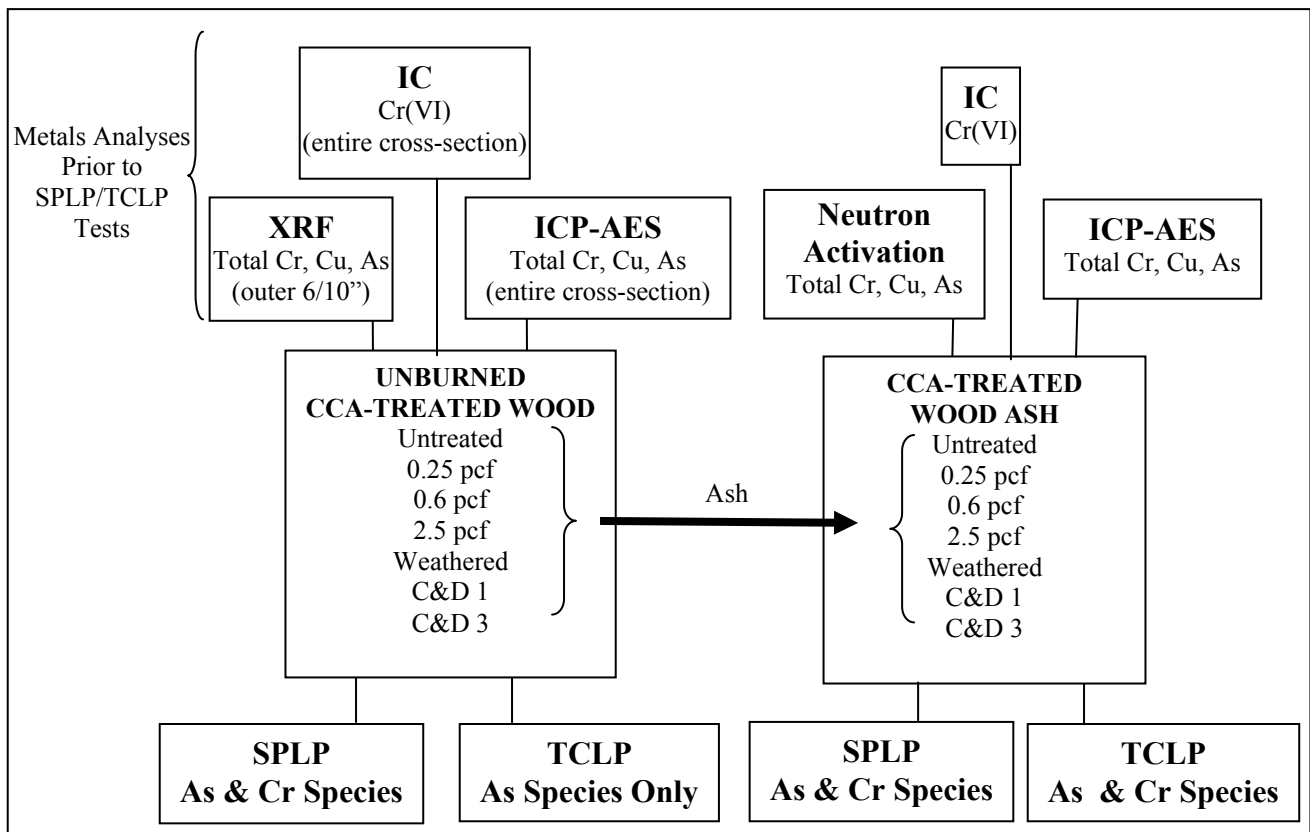


Figure IV.1: Layout of the TCLP and SPLP Experiments

Sample ID	XRF (Outer 6/10")						
	Wood Treatment Plant #1 Analysis (pcf as CCA)	Wood Treatment Plant #2 Analysis, pcf					Average of Analysis by Plant #1 and #2 (pcf as CCA)
		#1	#2	#3	#4	Average	
Untreated	0.006	0.05	0.0	0.05	0.0	0.025	0.016
0.25 pcf	0.352	0.32	0.32	0.33	0.32	0.3225	0.337
0.6 pcf	0.933	0.89	0.9	0.9	0.93	0.905	0.919
2.5 pcf	3.229	3.42	3.77	3.49	3.76	3.61	3.42
Pole	0.92	0.83	0.87	0.84	0.9	0.86	0.890

Table IV.2: Measured Retention Level of the Outer 6/10" of the Unburned Wood Samples Used in TCLP and SPLP Experiments

Sample	IC (Entire Cross-Section)			ICP-AES (Entire Cross-Section)										XRF (Outer 6/10")
	Cr(VI) (mg/kg)	Ave Cr(VI) (mg/kg)	pcf as Cr ^{VI} O ₃ (mg/kg)	Cr (mg/kg)	Ave Cr (mg/kg)	pcf as CrO ₃	Cu (mg/kg)	Ave Cu (mg/kg)	pcf as CuO	As (mg/kg)	Ave As (mg/kg)	pcf as As ₂ O ₅	pcf as CCA	
Untreated	BDL ^b	BDL	BDL	1.2	1.2	0.000	0.7	0.7	0.000	1.0	0.5	0.000	0.000	0.016
	BDL			1.2			0.6			0.0				
	BDL													
0.25 pcf	63.7	71.3	0.00439	1892.6	1800.2	0.111	1157.2	1137.3	0.046	1378.8	1305.4	0.064	0.220	0.337
	61.8			1707.7			1117.4			1232.0				
	88.5													
0.6 pcf	140.1	113.0	0.00695	7005.3	6354.2	0.391	4025.3	3745.9	0.150	5465.0	5057.8	0.248	0.789	0.919
	110.8			5703.2			3466.5			4650.6				
	88.1													
2.5 pcf	307.7	247.9	0.01525	15921.2	15757.0	0.970	9249.6	9275.5	0.372	13473.7	13441.6	0.660	2.00	3.42
	224.3			15592.9			9301.4			13409.5				
	211.6													
Pole	49.7	42.4	0.00261	5256.8	5343.3	0.329	3189.9	3258.1	0.131	3926.1	4038.0	0.198	0.657	0.890
	35.1			5429.8			3326.3			4149.8				
	-													
C&D 1	5.8	6.9	0.00042	206.4	277.9	0.017	121.8	164.4	0.007	146.8	221.2	0.011	0.035	NA ^a
	6.7			349.5			206.9			295.7				
	8.1													
C&D 3	34	29.7	0.00196	435.2	421.3	0.026	231.0	228.2	0.009	272.3	269.8	0.013	0.048	NA
	29.7			407.3			225.4			267.4				
	25.5													

^aNA = Not Analyzed

^bBDL = Below Detection Limit

Table IV.3: Metals Concentrations of Unburned Wood Samples Used in TCLP and SPLP Experiments

Sample Description	IC		Neutron Activation			ICP-AES		
	Cr(VI) (mg/kg)	Cr(VI)/Tot.Cr (%)	Cr (mg/kg)	Cu (mg/kg)	As (mg/kg)	Cr (mg/kg)	Cu (mg/kg)	As (mg/kg)
Untreated, ash	BDL	--	106 (22) ¹	330 (192)	31 (7)	10 (1)	1395 (116)	11 (1)
0.25 pcf, ash	1,090 (214)	5.1	21,300 (7,700)	10,520 (3,800)	11,080 (3,100)	15,715 (2,414)	11,818 (2,046)	11,959 (1,998)
0.60 pcf, ash	1,598 (18)	3.3	49,150 (19,100)	32,950 (11,900)	37,950 (20,500)	40,436 (5,901)	29,318 (5,487)	30,378 (5,238)
2.50 pcf, ash	6,339 (451)	3.8	165,000 (3,000)	98,450 (4,500)	99,300 (5,700)	107,529 (2,044)	95,808 (2,257)	90,414 (2,172)
Pole, ash	2,525 (447)	4.8	52,250 (13,000)	39,250 (15,600)	30,550 (12,100)	52,041 (8,154)	46,587 (3,401)	48,203 (2,260)
C&D 1, ash	595 (27)	54	1,100	1,400	730	2,091 (97)	1,753 (8)	1,957 (31)
C&D 3, ash	843 (94)	24	3,530	1,900	2,250	1,963 (379)	1,738 (315)	1,616 (244)

¹Standard Deviation of the Analysis Given in Parenthesis

Table IV.4: Metals Concentrations of Solid Ash Samples Used in TCLP and SPLP Experiments

IV.2 SAMPLE PROCESSING FOR SPLP AND TCLP ANALYSIS

There were a total of 14 samples (7 unburned and 7 ash) each of which were subjected to a modified solvent-extraction Synthetic Precipitation Leaching Procedure (SPLP) test and Toxicity Characteristic Leaching Procedure (TCLP). All of these samples were analyzed for arsenic and chromium species, with the exception of the 7 unburned wood samples and 3 of the ash samples which were not speciated for chromium. Both the SPLP and the TCLP tests require that the sample be reduced in size and capable of passing through a 9.5 mm (0.375 inch) sieve size before solvent extraction. The unburned wood samples were reduced in size between 5 and 7 mm by a Pulverisette 19, manufactured by Fritsch (Columbo, Ohio) and the ash samples were powder-like from the incineration process and did not require further size reduction.

All samples were carried through a sequence of events as outlined in Figure IV.2. The procedure was the same for both TCLP and SPLP methods. The only difference between the two methods was the solvent utilized. For both the TCLP and SPLP methods, the sequence of analysis began by adding a known volume of solvent to a particular mass of sample such that a 20-to-1 liquid to solid ratio was employed (e.g. 2 liters of solvent to 100 g of sample). The initial pH value of the leaching solution was recorded (Orion Model 720) and the sample/solution mixture was then rotated for a period of 18 ± 2 hours. An extraction fluid blank and a duplicate sample were prepared for each rotational period. The final pH and oxidation reduction potential (ORP) of the leaching solution (Accumet Model 20) were recorded. The leachate sample was filtered through a 0.7 μm borosilicate glass fiber filter.

All samples were run in duplicate and the filtrate split between the University of Miami and the University of Florida teams. Three splits were made for each filtrate with the exception of the TCLP filtrates for unburned wood and 3 of the 7 ash samples where two splits were prepared. The extra split was used for the analysis of Cr(VI) using an IC. Of the remaining two splits, one was used for total arsenic and total chromium analysis using an ICP-AES and the other was used for arsenic speciation using an HPLC-HG-AFS. Thus, arsenic and chromium were speciated for all of the SPLP tests run on both unburned wood and wood ash samples. Arsenic was speciated for all of the TCLP samples; however, chromium was speciated on only 4 of the wood ash samples and none of the unburned wood samples. The University of Miami team conducted the arsenic speciation analysis. The University of Florida team analyzed the filtrate for Cr(VI), and total arsenic and chromium by ICP-AES after an open digestion step. Please refer to Chapter II for more details concerning the laboratory methods used for metals analysis.

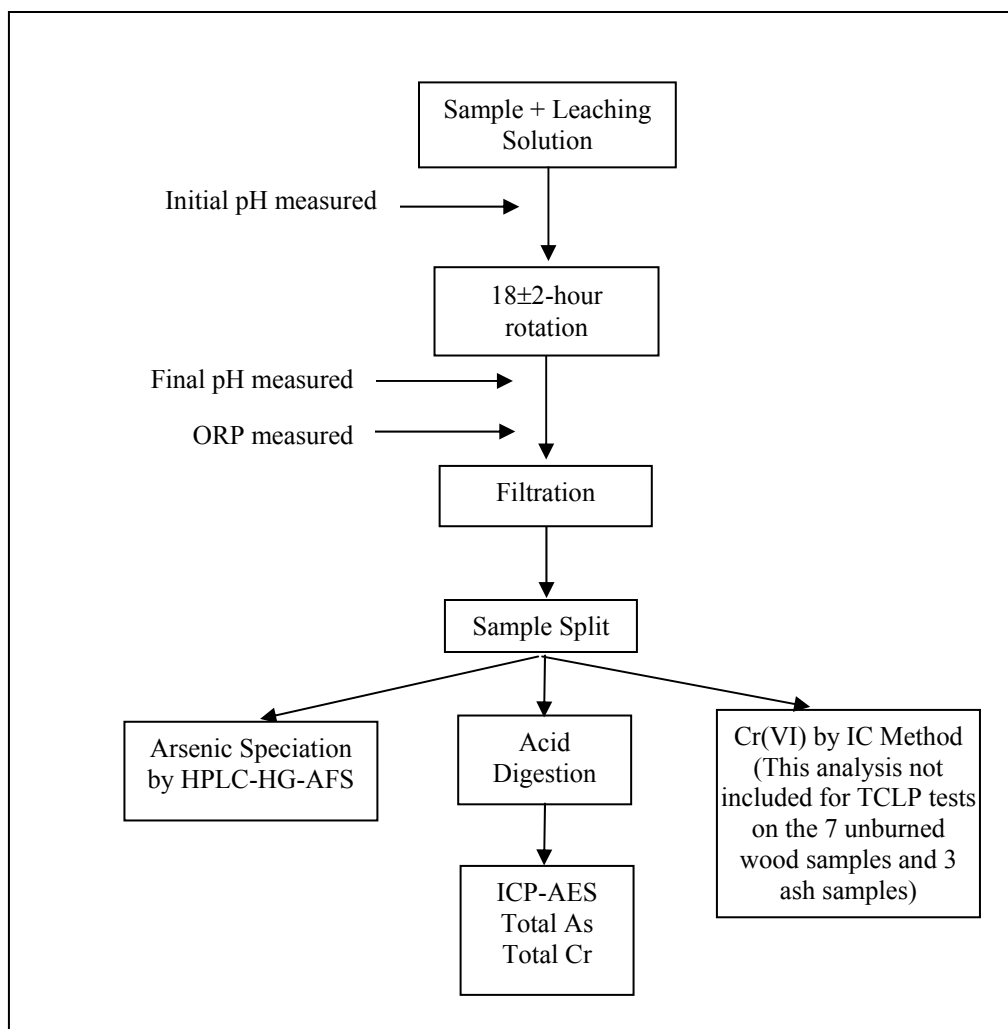


Figure IV.2: Processing Steps for the TCLP/SPLP Experiments

IV.2.a TCLP Extraction Fluid

The TCLP tests consists of using a buffered organic acid solution to extract chemicals from solid wastes. This test was designed to simulate leaching in Municipal Solid Waste (MSW) landfills. The TCLP test prescribes that one of two leaching fluids are to be used depending upon the buffering capacity of the sample. The determination of the appropriate leaching fluid is made by immersing 5 g of sample into 96.5 ml of deionized water and testing the pH. If the pH of the sample is less than 5, then fluid #1 is used. If the pH of the sample is greater than 5, then fluid #2 is used. All of the samples were below a pH of 5, so extraction fluid #1 was used. Extraction fluid #1 was prepared by adding 11.4 mL of glacial acetic acid (CH_3COOH) to approximately 1000 mL of reagent water in a 2-L volumetric flask. This was followed by the addition of 128.6 mL of 1 N sodium hydroxide (NaOH). This mixture was then brought to volume with deionized water water. The resulting pH of this fluid was 4.93 ± 0.05 .

IV.2.b SPLP Extraction Fluid

The SPLP test was designed to simulated leaching due to acid rainfall. East of the Mississippi River, a pH of 4.22 (fluid #1) is used based on the impact of a higher population density and increased industrialization. The SPLP leaching solution was prepared by carefully mixing 60 g of sulfuric acid with 40 g of nitric acid. The SPLP extraction fluid was prepared by adding between 0.4 to 0.5 ml of the sulfuric acid / nitric acid mixture to a 2 L volumetric flask and diluting to volume with deionized water. The resultant pH was 4.22 ± 0.05 .

IV.3 RESULTS FROM UNBURNED CCA-TREATED WOOD

Results from SPLP tests conducted on unburned CCA-treated wood are presented first (sub-section IV.3.a). Results are provided for both arsenic and chromium speciation. Results from TCLP tests, are presented in sub-section IV.3.b. Chromium speciation was not included for the unburned wood samples subjected to TCLP.

IV.3.a Results from the SPLP Test (Arsenic and Chromium)

Arsenic

Total arsenic results between ICP-AES and HPLC-HG-AFS were reasonably close to one another with the results for HPLC-HG-AFS being consistently lower than the results for ICP-AES (Table IV.5 and Figure IV.3). This difference may be due to the presence of “hidden” arsenic that does not form the required hydride during HPLC-HG-AFS analysis. Regardless of these differences, results show that the weathered wood pole leached the highest concentrations of total arsenic, at a concentration of about 10 mg/L. The 0.6 pcf and the 2.5 pcf samples leached similar but lower quantities of total arsenic (at about 7 mg/L). This is unusual as the amount of total arsenic measured in the solid sawdust sample (Table IV.3) for the 2.5 pcf (0.660 pcf as As_2O_5) was more than 3 times greater than the pole sample (0.198 pcf as As_2O_5). The greater leaching observed from the pole sample is due to the greater proportion of As(III) leached from that sample. The conversion of the arsenic towards As(III) is likely a result of the weathering of experienced by the pole sample.

It is also emphasized that elevated concentrations of As(III) in the weathered wood sample were also noted in the pH stat experiments as described in Chapter III. Since the arsenic that is used in the chemical CCA is in the form of As(V), the presence of As(III) in the weathered wood is an intriguing find and can best be explained by some environmental factor(s), presumably biological factor(s), playing a role in the conversion of As(V) to As(III). It is believed that the weathering process of wood results in this conversion thereby promoting the release of the more mobile and more soluble As(III) species.

Chromium

Total chromium levels in the SPLP leachate ranged from 0.1 mg/l to 2.9 mg/l (Figure IV.4). The 0.6 pcf sample leached the highest total chromium. Again, leaching of greater concentrations of chromium from the 0.6 pcf sample versus the 2.5 pcf sample is contrary to the anticipated results, since the retention level of the 2.5 pcf sample is much higher. The pole sample leached less chromium than the 0.6 pcf sample. Hexavalent chromium was not detected

in any of the CCA-treated wood SPLP leachates. Thus the chromium in the leachate was within the trivalent form.

IV.3.b Results from the TCLP Test (Arsenic Analysis Only)

As observed for the SPLP test, the total arsenic leached as measured by ICP-AES and HPLC-HG-AFS were reasonably close to one another with the ICP-AES data higher than the HPLC-HG-AFS results on average. This difference as mentioned earlier could be due to the possible presence of “hidden” arsenic. Furthermore, it is noted that the only species detected were As(V) and As(III), with As(V) predominating. Regardless of these differences, results show that wood characterized by the highest retention levels leached a greater concentration of total arsenic with the 2.5 pcf sample leaching at about 12 mg/L as given by ICP-AES.

The only arsenic species observed from these samples were As(V) and As(III), with As(V) as the predominating species in all the samples evaluated. No organic arsenic species (DMAA and MMAA) were detected. Of interest is the speciation of the pole sample, the C&D 1 sample, and the 0.25 pcf sample, all of which showed a considerable fraction of As(III). For the pole sample, about 40% of the arsenic was found as As(III). For the C&D 1 sample and the 0.25 pcf sample, 14% and 21% of the total arsenic were found as As(III), respectively. The 0.25 pcf and the C&D 1 samples are both characterized by low retention levels and the low total arsenic concentration may contribute to the larger As(III) fraction within the wood sample. The pole, however, is characterized by a high retention level. The retention level of the pole is very close to that of the 0.6 pcf sample but the speciation of both of these samples is very different. The primary difference between the pole and the 0.6 pcf sample is that the pole has undergone weathering whereas the 0.6 pcf was not weathered. This weathering may be the reason for a higher proportion of As(III) found within the pole sample. Also of interest is that the total amount of arsenic leached from the pole is higher on average than the total arsenic leached from the 0.6 pcf sample, although both samples were characterized by very similar retention levels. The higher average total arsenic concentration from the pole sample may be due to the higher proportion of more mobile As(III) in that sample.

It is also noted that the amount of arsenic leaching from unburned untreated, 0.6 pcf, weathered, and the two C&D samples is slightly higher in the SPLP versus TCLP tests. This may be due to the higher lower final pH of the SPLP leaching solution. As observed in the pH Stat experiments, the lower the pH the more arsenic that leaches.

Sample	Initial pH	Final pH	ORP (mV)	AFS			ICP-AES		IC
				As III (mg/L)	As V (mg/L)	Total As ^a (mg/L)	Total As (mg/L)	Total Cr = CrIII (mg/L)	CrVI (mg/L)
Untreated	4.23	4.37	249	BDL ^a	0.025	0.03	0.02	BDL	BDL
	4.23	4.37	249	BDL	0.019	0.02	0.02	BDL	BDL
0.25 pcf	4.23	4.96	283	BDL	3.31	3.31	5.39	1.8	BDL
	4.23	4.96	280	0.73	3.33	4.06	5.48	1.8	BDL
0.6 pcf	4.23	4.64	234	0.45	6.90	7.34	7.05	2.9	BDL
	4.23	4.64	231	BDL	6.14	6.14	7.79	3.2	BDL
Pole	4.23	4.75	222	3.85	6.81	10.65	10.22	1.8	BDL
	4.23	4.75	221	3.11	6.18	9.30	10.86	1.9	BDL
2.5 pcf	4.23	4.70	260	BDL	5.75	5.75	6.65	2.2	BDL
	4.23	4.72	266	BDL	5.71	5.71	6.97	2.2	BDL
C&D 1	4.23	6.64	103	0.10	0.33	0.43	0.52	0.1	BDL
	4.23	6.30	116	0.22	0.26	0.48	0.69	0.1	BDL
C&D 3	4.23	6.50	55	BDL	0.024	0.02	0.20	0.2	BDL
	4.23	6.43	120	BDL	0.031	0.03	0.68	0.4	BDL

^aNo MMAA and DMAA observed, Total Provided is the sum of As(III) and As(V)

^aBDL = Below Detection Limit, Detection limit ~ 0.002 mg/L (2 µg/L)

Table IV.5: SPLP Results for Unburned Wood

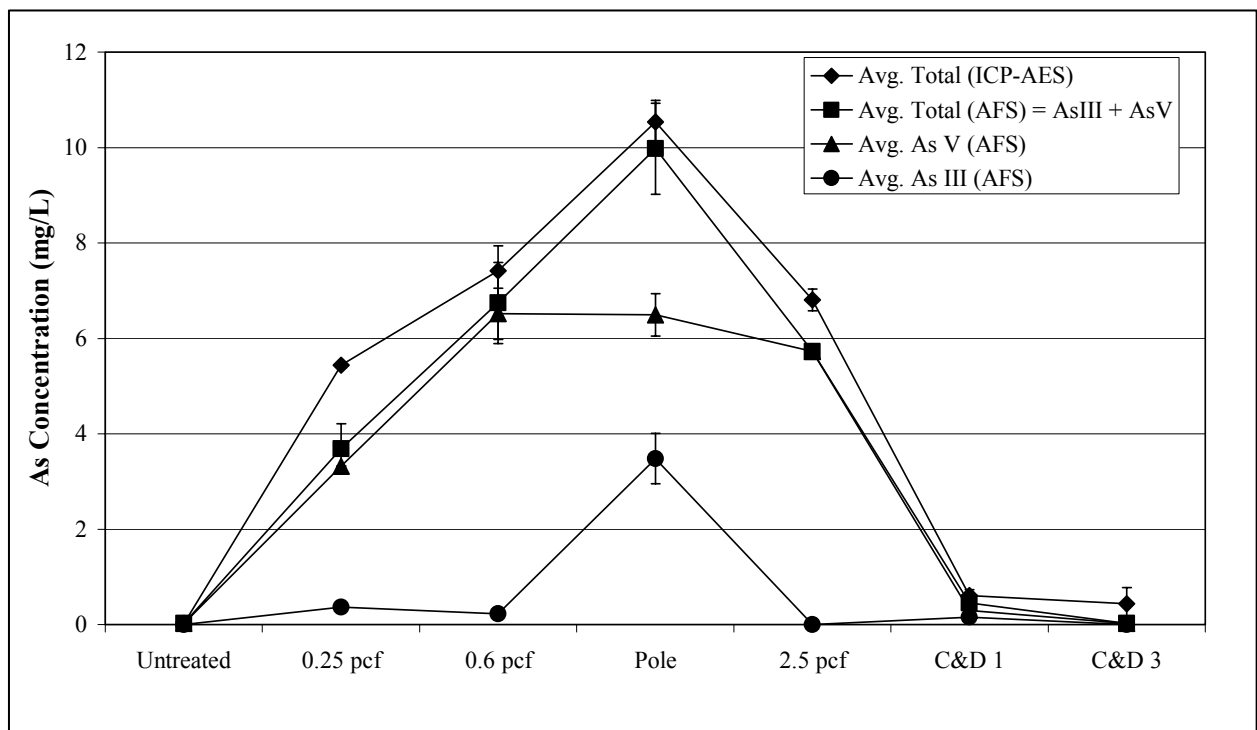


Figure IV.3: Arsenic Species Observed In SPLP Leachates From Unburned Wood Samples

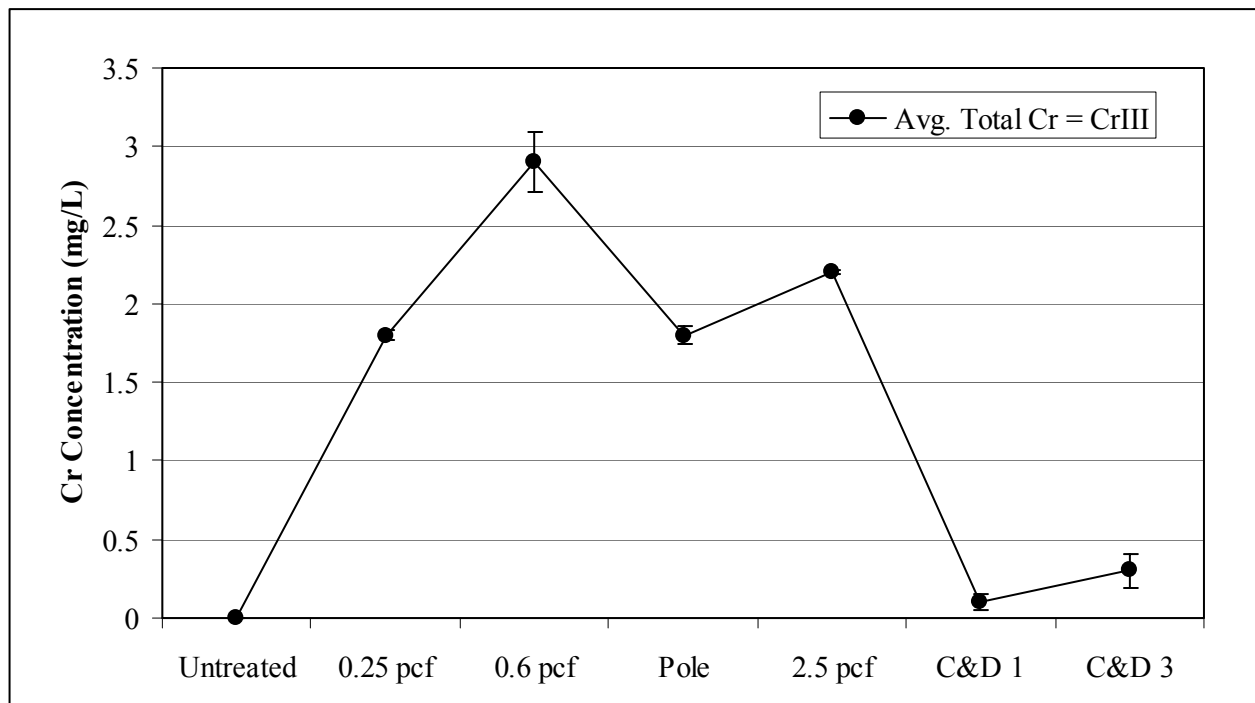


Figure IV.4: Chromium Species Observed In SPLP Leachates From Unburned Wood Samples

Sample ID	Initial pH	Final pH	ORP (mV)	HPLC-HG-AFS			ICP-AES
				As III (mg/L)	As V (mg/L)	Total As ^a (mg/L)	Total As (mg/L)
Untreated	4.96	4.99	231	BDL ^c	0.018	0.02	0.01
	4.96	4.98	230	BDL	0.016	0.02	NA ^b
0.25 pcf	4.96	4.99	274	0.97	4.022	4.02	5.27
	4.93	4.83	278	0.70	3.14	3.84	4.98
0.6 pcf	4.93	4.97	231	0.23	6.03	6.26	7.79
	4.93	4.95	230	BDL	4.50	4.50	7.65
Pole	4.93	4.94	221	4.20	5.41	9.60	9.13
	4.93	4.94	219	2.72	4.22	6.93	NA
2.5 pcf	4.93	4.97	523	0.094	9.38	9.47	11.45
	4.93	4.96	252	0.016	8.55	8.57	12.06
C&D 1	4.93	5.21	219	0.11	0.83	0.94	0.91
	4.98	5.14	232	0.24	1.36	1.60	1.15
C&D 3	4.93	5.14	303	BDL	0.14	0.14	0.28
	4.93	5.16	301	BDL	0.21	0.21	0.32

^aNo MMAA and DMAA observed, Total Provided is the sum of As(III) and As(V)

^bNA = Not Analyzed

^cBDL = Below Detection Limit, Detection limit ~ 0.002 mg/L (2 µg/L)

Table IV.6: TCLP Results for Unburned Wood

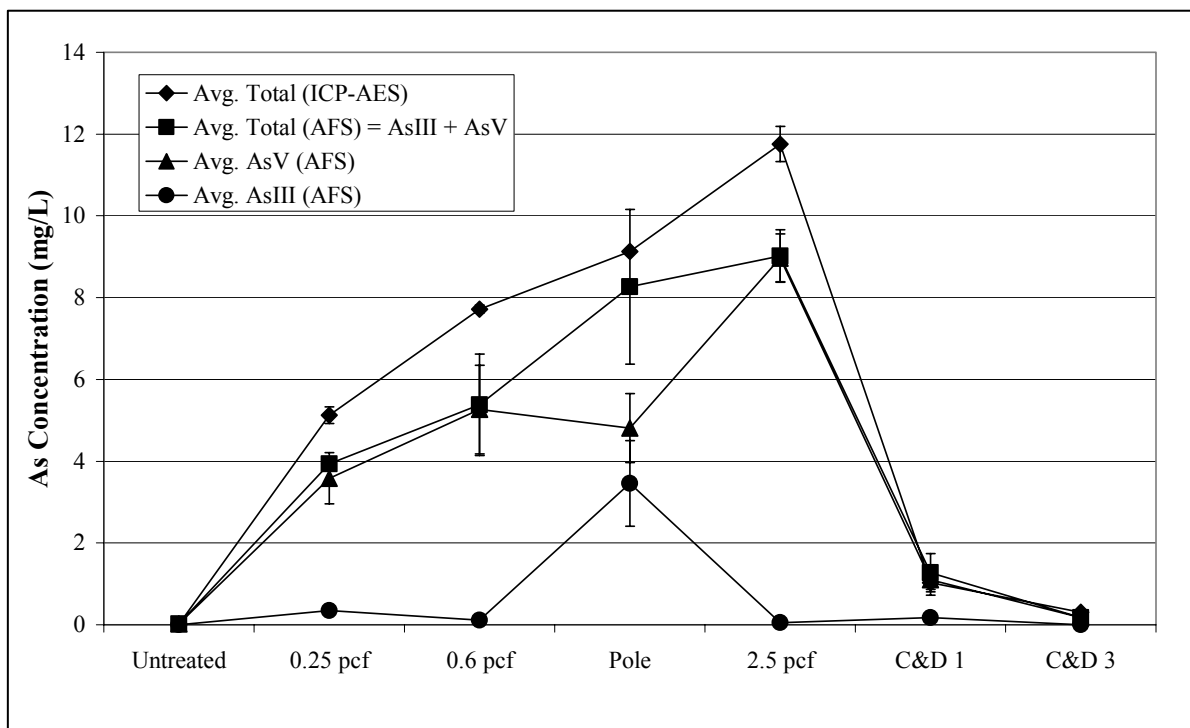


Figure IV.5: Arsenic Species Observed In TCLP Leachates From Unburned Wood Samples

IV.4 RESULTS FROM CCA-TREATED WOOD ASH

Results from SPLP tests conducted on CCA-treated wood ash are presented first (sub-section IV.4.a). Results are provided for both arsenic and chromium speciation. Results from TCLP tests, are presented in sub-section IV.3.b. Chromium speciation was included for only 4 of the 7 wood ash samples.

IV.4.a Results from the SPLP Test (Arsenic and Chromium)

Arsenic

The total arsenic concentrations between the HPLC-HG-AFS and the ICP-AES methods were reasonably close to one another with the results from the HPLC-HG-AFS slightly lower than the results from the ICP-AES (Table IV.7 and Figure IV.6). The highest leachate concentration (between 320 to 370 mg/L) was observed for the 2.5 pcf-ash sample as expected, given that it was characterized by the highest concentration of arsenic within the solid ash. The second highest leachate was measured from the 0.6 pcf-ash sample. This was followed by the pole-ash sample.

The only species observed in these samples was As(V) and As(III), with As(V) predominating. The organic species (MMAA and DMAA) were below detection limits. For this set of samples it is of interest to note that the greatest fraction of As(III) was observed among the 2.5 pcf-ash sample (30%) and the second greatest fraction was observed for the 0.6 pcf-ash sample (10%). The amount of total arsenic leached appears to be dependent upon the presence of As(III) in these samples.

Chromium

The concentrations of total chromium in the SPLP leachates ranged from 0.01 mg/L to 55 mg/L. Cr(VI) was consistently found in samples where total chromium was detected, and most of the total chromium (94 to 100%) existed as Cr(VI) in SPLP leachate from the wood ash. Insignificant levels of Cr(III) were detected in the leachates.

Of interest is the finding that chromium was detected in the leachate from the 0.25 pcf-ash sample, the pole-ash sample, and the C&D-ash samples. This observation was initially surprising, in particular for the C&D samples, since these samples contained the lowest retention levels for chromium in the solid ash samples (Table IV.4). Although the C&D-ash samples had the lowest concentrations of total chromium within the solid ash samples, final pH of the leaching solution for these samples was high between 10.3 and 10.7. Furthermore, it is of interest to note that the fraction of Cr(VI) to the total chromium concentration was the highest (24 to 54%) for the C&D samples. The high pH coupled with the relatively high fraction of Cr(VI) for these samples results in an enhanced leaching of chromium. Similarly, the 0.25 pcf-ash and pole-ash samples also leached more chromium than the 0.6 pcf-ash and the 2.5 pcf-ash samples. This difference again is due to the elevated pH of the leaching solution for the 0.25 pcf-ash and the pole-ash samples relative to the samples with higher retention levels. Furthermore, the fractions of Cr(VI) in the 0.25 pcf-ash and pole-ash samples were also higher (5.1 and 4.8% respectively) than the 0.6 pcf (3.3%) and the 2.5 pcf (3.8%) samples. Apparently pH and the fraction of chromium as Cr(VI) plays a role in the leaching of chromium from these

samples. The higher the pH and the larger the original fraction of Cr(VI) in the solid sample the greater the amount of chromium leached from the sample. In the case of chromium, the lower the concentration of chromium in the solid samples, the higher the Cr(VI) fraction in the solid sample and the higher the pH of the final SPLP solution. The impact of pH alone is illustrated in Figure IV.8 where increases in chromium concentrations in SPLP leachates were observed for SPLP leachates with high pH values, regardless of the initial retention level of the chromium within the solid ash sample. The pH of the ash samples is likely influenced by the amount of CCA in the original wood sample. The CCA chemical is an acidic solution of arsenic acid and chromic acid and as a result the greater the amount of CCA within the wood sample, the lower the pH expected in the leachate solutions. This pH effect resulted in the leaching of greater quantities of chromium for samples containing lower retention levels of CCA.

Sample	Initial pH	Final pH	ORP (mV)	AFS			ICP-AES	ICP-AES	IC	By Difference
				As III (mg/L)	As V (mg/L)	Total As ^a (mg/L)	Total As (mg/L)	Total Cr (mg/L)	Cr VI (mg/L)	Cr III Average (mg/L)
Untreated	4.21	7.7	263	BDL ^b	0.023	0.02	0.02	BDL	BDL	BDL
	4.21	7.63	260	BDL	0.024	0.02	0.03	BDL	BDL	
0.25 pcf	4.21	7.76	260	0.260	52.60	52.86	58.46	28.4	27.3	BDL
	4.21	7.92	255	BDL	59.48	59.48	63.20	25.3 28.2	30.6	
0.6 pcf	4.21	6.50	261	15.84	161.65	177.49	168.00	BDL	BDL	BDL
	4.21	6.60	255	21.78	159.60	181.38	187.40	BDL	BDL	
Pole	4.21	7.44	227	4.43	133.91	138.33	134.70	8.5	10.1	0.53
	4.21	7.50	228	1.02	116.47	117.49	123.80	8.8 15.0	10.4	
2.5 pcf	4.21	4.85	312	88.64	231.11	319.74	354.00	0.0	BDL	0.10
	4.21	4.59	316	106.67	222.66	329.34	374.20	0.2	BDL	
C&D 1	4.21	10.32	150	BDL	0.294	0.29	0.44	16.8	19.8	BDL
	4.21	10.42	147	BDL	0.304	0.30	0.45	15.9 25.5	19.2	
C&D 3	4.21	10.75	135	BDL	2.60	2.60	2.85	38.5	45.7	BDL
	4.21	10.68	135	BDL	1.53	1.53	2.15	31.8 55.0	38.1	

^aNo MMAA and DMAA observed, Total Provided is the sum of As(III) and As(V)

^bBDL = Below Detection Limit, Detection limit ~ 0.002 mg/L (2 µg/L)

Table IV.7: SPLP Results for CCA-Treated Wood Ash

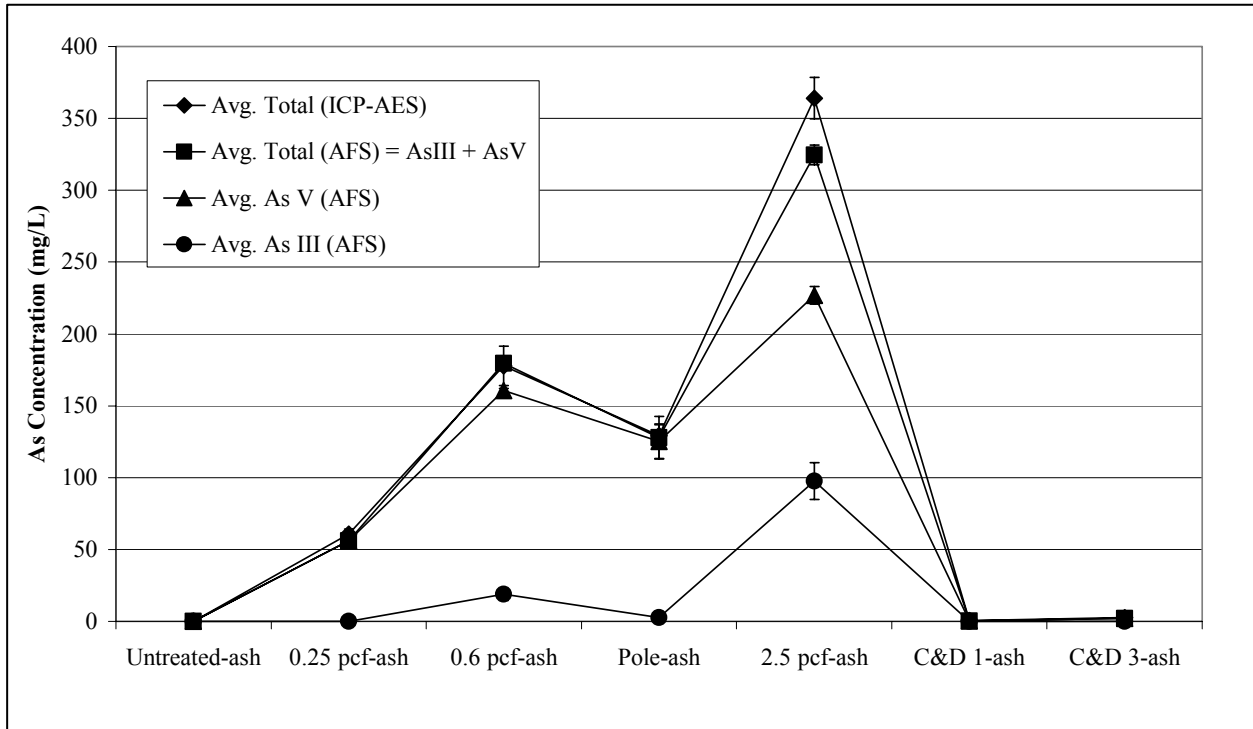


Figure IV.6: Arsenic Species Observed In SPLP Leachates From CCA-Treated Wood Ash

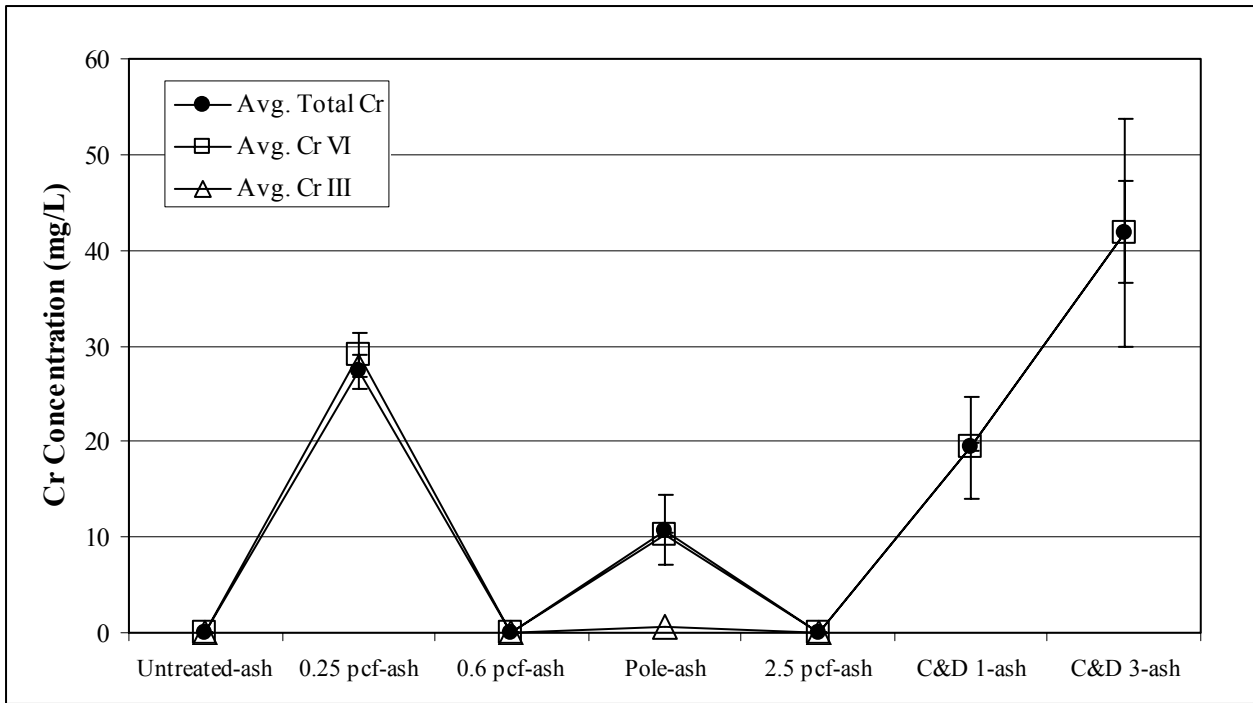


Figure IV.7: Chromium Species Observed In SPLP Leachates From CCA-Treated Wood Ash

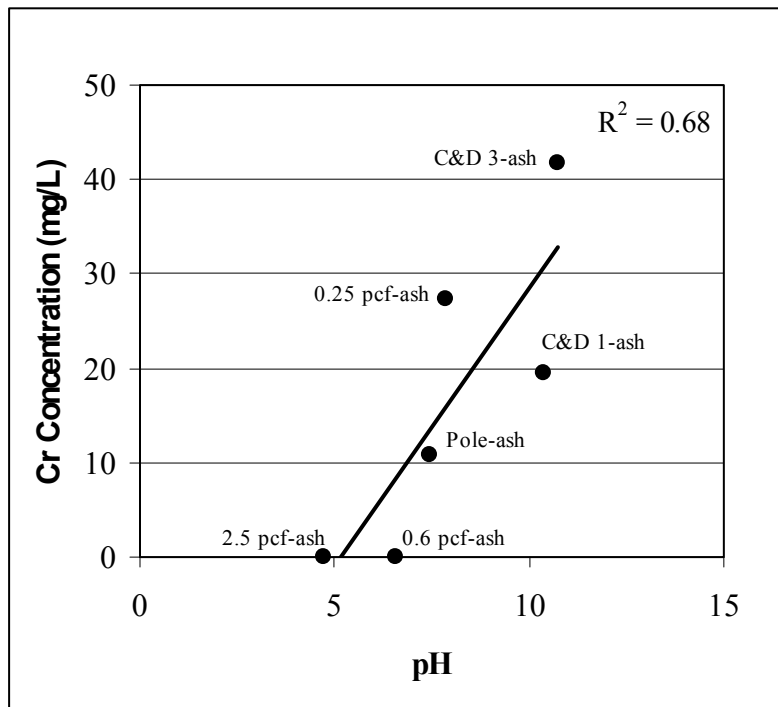


Figure IV.8: Chromium Concentration Versus Final pH of Leaching Solution for SPLP Leachates From CCA-Treated Wood Ash

IV.4.a Results from the TCLP Test (Arsenic and Chromium Analyses)

All ash samples in this study were subjected to the TCLP test and all were evaluated for arsenic species. A selected set of the ash samples was also analyzed for chromium species. The ash samples selected from chromium speciation included untreated-ash, 0.25 pcf-ash, 0.6 pcf-ash, and 2.5 pcf-ash.

Arsenic

Results from the TCLP tests on the ash samples were similar to the results from the SPLP tests. Again the total concentration measurements matched up reasonably well between the HPLC-HG-AFG and the ICP-AES analysis methods, with the results from HPLC-HG-AFS slightly lower than the results from ICP-AES (Table IV.8 and Figure IV.9). The highest total arsenic concentrations were observed to leach from the 2.5 pcf-ash sample (roughly 385 mg/L). The next highest concentration corresponded to the 0.6 pcf-ash and pole-ash sample.

The only species detected in the TCLP leachates were As(V) and As(III), with As(V) predominating. No DMAA nor MMAA were detected. As observed for the SPLP leachates, the 2.5 pcf-ash sample was characterized by the largest concentration of As(III) and the 0.6 pcf-ash sample was characterized by the second largest As(III) concentration. The relatively high arsenic concentrations leached from these samples is likely due to the presence of As(III).

Chromium

As observed for the SPLP, the TCLP tests on the 4 ash samples (untreated-ash, 0.25 pcf-ash, 0.6 pcf-ash, and 2.5 pcf-ash) indicate that the 0.25 pcf-ash sample resulted in the highest concentration of chromium leached (Figure IV.10). All of the chromium leached from the 0.25 pcf-ash sample was in the hexavalent form. Again, as discussed earlier this observation is contrary to what would be expected given that the chromium concentration in the solid 0.25 pcf-ash sample was less than the chromium concentration in the solid 0.6 pcf-ash and the 2.5 pcf-ash samples. The increased leaching by the 0.25 pcf-ash sample is likely associated with the higher proportion of Cr(VI) among total chromium (5.1%) versus the proportions observed among the 0.6 pcf-ash and 2.5 pcf-ash samples (3.3 and 3.8%, respectively) and the relatively high pH of the 0.25 pcf-ash sample (pH = 6.2) relative to the other samples (pH < 5.6). Although these pH values are in the acidic region apparently they still impact the leachability of Cr(VI) which generally dominates chromium speciation in alkaline environments as shown in the pH Stat experiments discussed in Chapter III.

The amount of chromium leached from the TCLP test (6 mg/L for the 0.25 pcf-ash sample) was considerably less than the amount leached from the SPLP test (30 mg/L for the 0.25 pcf-ash sample). This difference is likely due to the differences in final pH. The final pH for the the 0.25 pcf-ash TCLP sample was lower at 6.2 versus the final pH for the 0.25 pcf-ash SPLP samples (pH = 7.8). Since Cr(VI) leaching is enhanced at higher pH values, the elevated pH in the SPLP samples promotes the leaching of Cr(VI).

Sample	Initial pH	Final pH	ORP (mV)	AFS			ICP-AES		IC
				As III (mg/L)	As V (mg/L)	Total As ^a (mg/L) AFS	Total As (mg/L)	Total Cr (mg/L)	Cr(VI) (mg/L)
Untreated	4.96	6.21	NA ^b	BDL ^c	0.077	0.08	BDL	BDL	BDL
	4.96	NA	NA	NA	NA	NA	BDL		
0.25 pcf	4.96	6.31	268	BDL	133.87	133.87	138.00	6.1	6.4
	4.96	6.17	275	0.16	118.52	118.69	129.10		
0.6 pcf	4.96	5.52	306	18.94	151.13	170.06	220.60	BDL	BDL
	4.96	5.52	301	25.95	183.20	209.15	213.40		
Pole	4.96	5.90	265	6.27	227.42	233.69	219.40	NA	NA
	4.96	5.91	268	5.30	198.27	203.57	229.00		
2.5 pcf	4.96	5.11	304	109.38	245.10	354.48	380.34	BDL	BDL
	4.96	NA	301	124.56	235.21	359.77	391.00		
C&D 1	4.96	7.91	220	0.003	7.69	7.69	8.86	NA	NA
	4.96	8.00	220	BDL	7.23	7.23	9.53		
C&D 3	4.96	8.36	211	BDL	8.20	8.20	11.02	NA	NA
	4.96	8.40	210	0.0096	7.67	7.68	11.29		

^aNo MMAA and DMAA observed, Total Provided is the sum of As(III) and As(V)

^bNA = Not Analyzed

^cBDL = Below Detection Limit, Detection limit ~ 0.002 mg/L (2 µg/L)

Table IV.8: TCLP Results for CCA-Treated Wood Ash

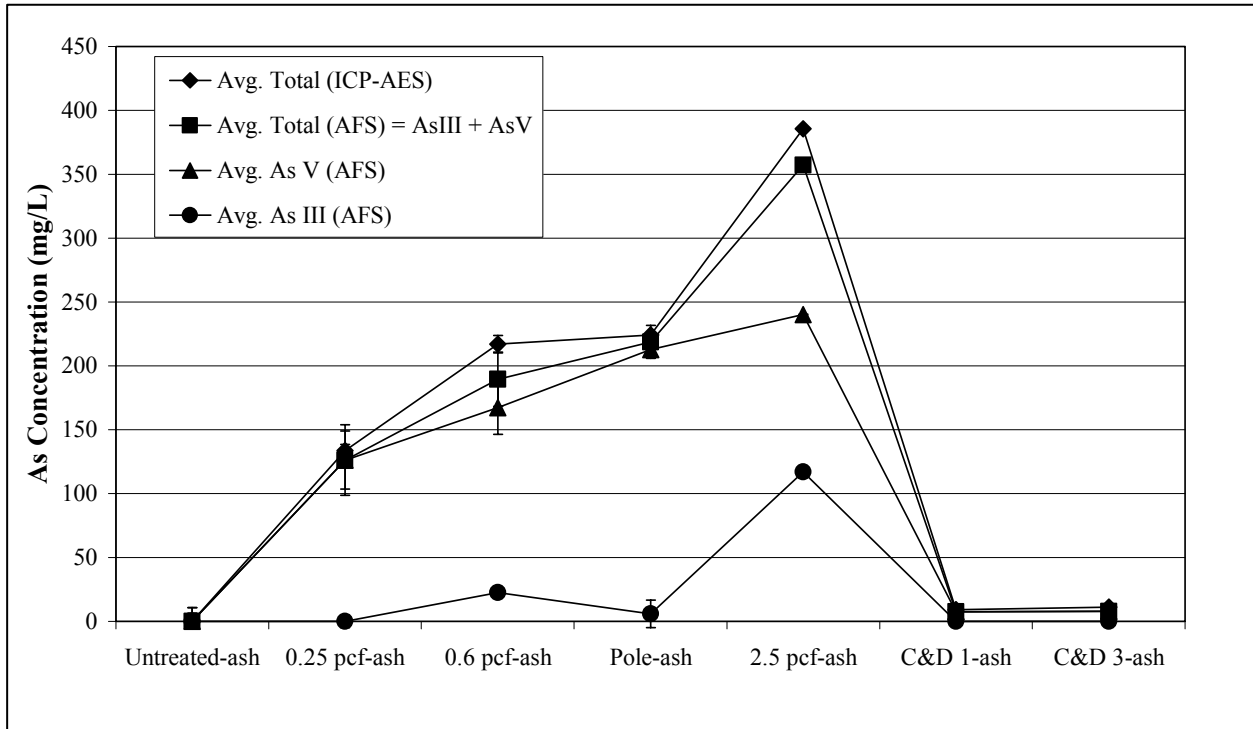


Figure IV.9: Arsenic Species Observed In TCLP Leachates From CCA-Treated Wood Ash

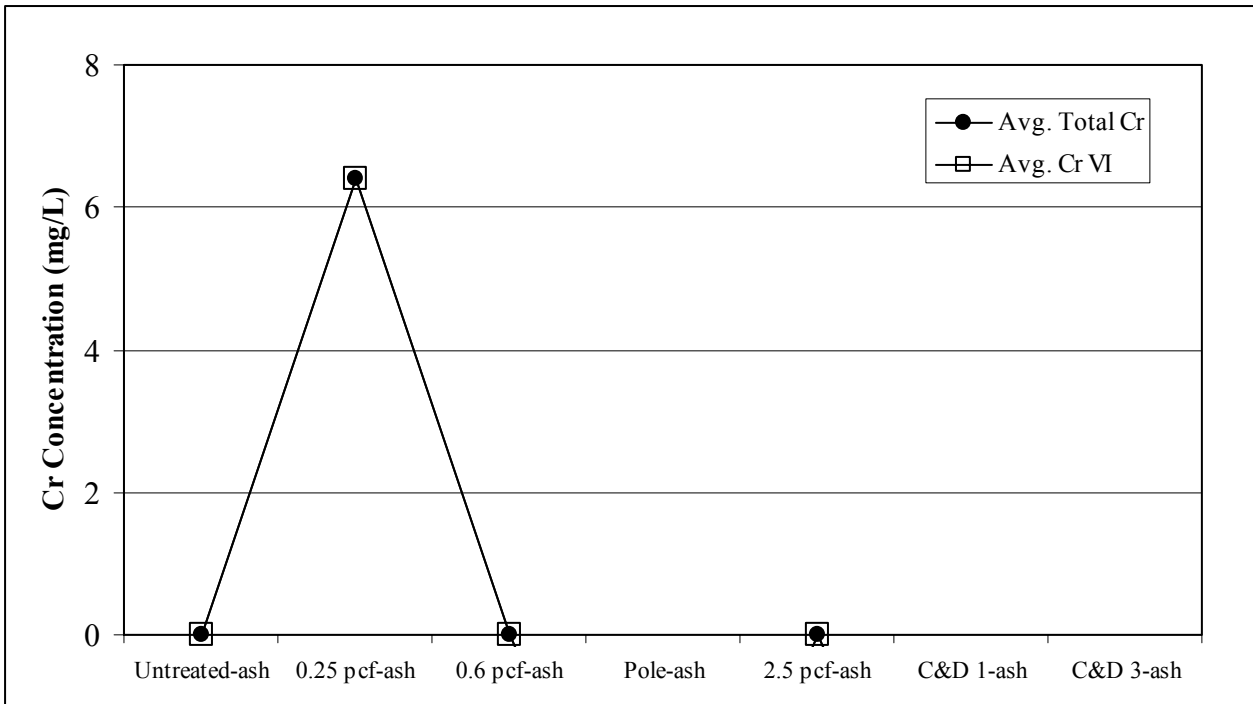


Figure IV.10: Chromium Species Observed In TCLP Leachates From CCA-Treated Wood Ash

IV.5 COMPARISON BETWEEN SPLP AND TCLP TESTS AND BETWEEN UNBURNED CCA-TREATED WOOD AND CCA-TREATED WOOD ASH

Arsenic

The most obvious difference between the unburned wood and the ash samples are the concentrations of arsenic leaching from the samples (Figures IV.11 and IV.12). The concentrations leaching from the ash samples averaged in the hundreds of mg/L whereas the unburned wood samples leached in the tens of mg/L. This is not surprising as incineration decreases the sample volume thereby concentrating the metals and increases the surface area of the particles resulting in greater amounts of metals leaching.

For the unburned wood samples, the weathered pole sample contained elevated concentrations of As(III) for both TCLP and SPLP tests. Other samples had relatively lower concentrations of As(III). The proportion of As(III) for the 0.25 pcf, 0.6 pcf, and the 2.5 pcf samples remained relatively low and consistent between TCLP and SPLP tests.

For the ash samples the relative distribution between As(V) and As(III) remained fairly consistent between TCLP and SPLP tests. In this case, the 2.5 pcf sample resulted in the greatest concentration of As(III) in the leachate for both TCLP and SPLP tests. Since As(III) was not observed in high concentrations within the unburned 2.5 pcf sample, results suggest that the incineration process caused the conversion of As(V) to As(III) in the 2.5 pcf wood.

Chromium

The total chromium concentrations leached from the unburned wood were on the order of 1's of mg/L whereas the amount leached from the wood ash was on the order of 10's mg/L (Figures IV.13 and IV.14). There were two distinguishing features between the leachates from unburned wood and the leachates from the ash. The first was speciation. In the unburned wood, Cr(III) predominated. In the ash, Cr(VI) predominated. This change in speciation is likely a result of the combustion process. The second distinguishing feature is that wood samples with higher retention levels as a whole leached more chromium than those samples containing less chromium for the unburned wood. For the ash, the opposite trend was observed. Samples containing low retention levels in the solid ash, leached greater quantities of chromium. The enhanced leaching of these samples is likely associated with pH. The higher the pH of the leaching solution the greater the quantity of arsenic leached for the ash samples. The pH of the ash samples is likely influenced by the presence of the CCA chemical. The CCA chemical is generally acidic in nature and so wood samples containing a higher retention level typically have lower pH levels in the resultant ash. Samples with low retention levels typically have higher pH levels in the resultant ash which then enhances the formation of Cr(VI) during the combustion process and the subsequent leaching of chromium. It is also of interest to note that the differences in pH between samples were much larger for the ash samples than for the unburned wood samples. Thus the "pH effect" was observed for the ash samples due to the larger pH differences.

Also of interest are the results for the 0.25 pcf-ash sample which showed elevated chromium concentrations within both the TCLP and SPLP leachates. For this sample, the concentration of Cr(VI) in the SPLP leachate was greater than the concentration of Cr(VI) in the

TCLP leachate. This difference is likely due to the different final pH values of each leaching solution. The final pH of the 0.25 pcf-ash leachate from the TCLP extraction was 6.2 whereas the pH from the SPLP extraction was 7.8. As observed from the pH Stat experiment described in Chapter III, leaching of Cr(VI) is enhanced at high pH levels and the elevated pH observed within the SPLP test likely resulted in the greater quantities of Cr(VI) leached. The elevated pH for the SPLP leachate is likely due to the limited buffering capacity of the SPLP solution relative to the TCLP solution.

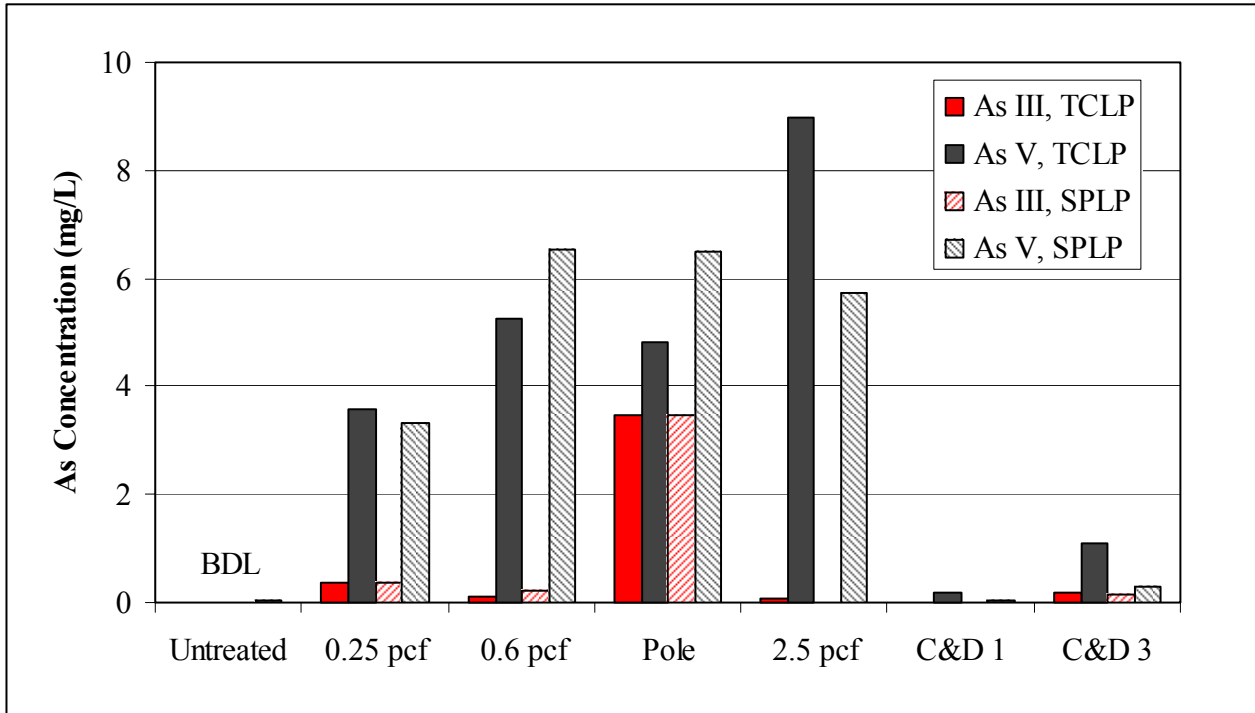


Figure IV.11: Comparison of Arsenic Species in Unburned Wood Between between the TCLP and SPLP Tests

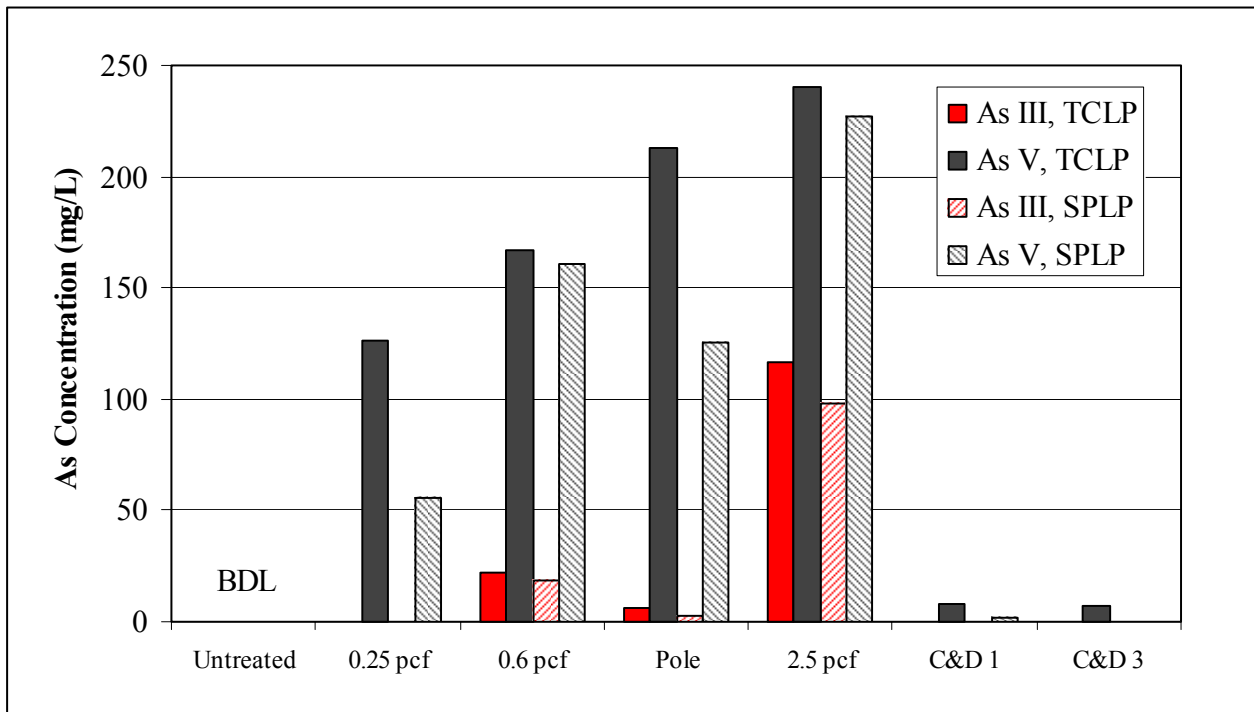


Figure IV.12: Comparison of Arsenic Species in CCA-Treated Wood Ash Between between the TCLP and SPLP Tests

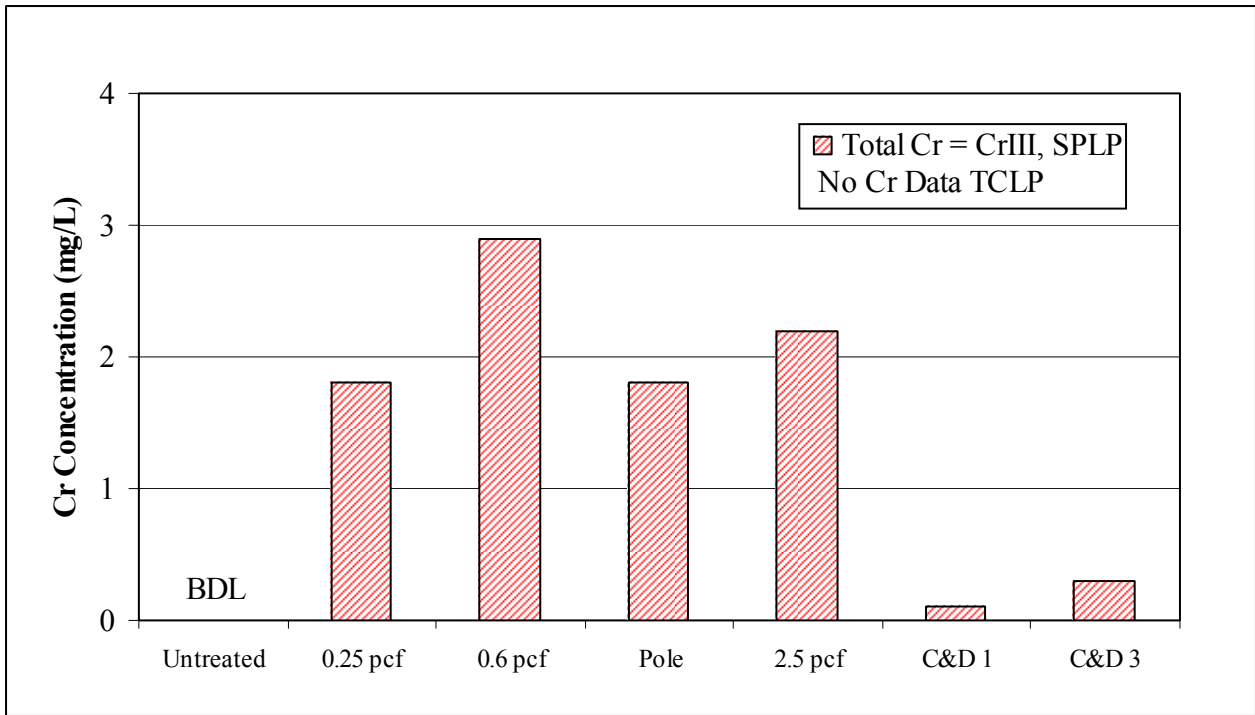


Figure IV.13: Chromium Concentrations in Unburned Wood As Observed During the SPLP Test

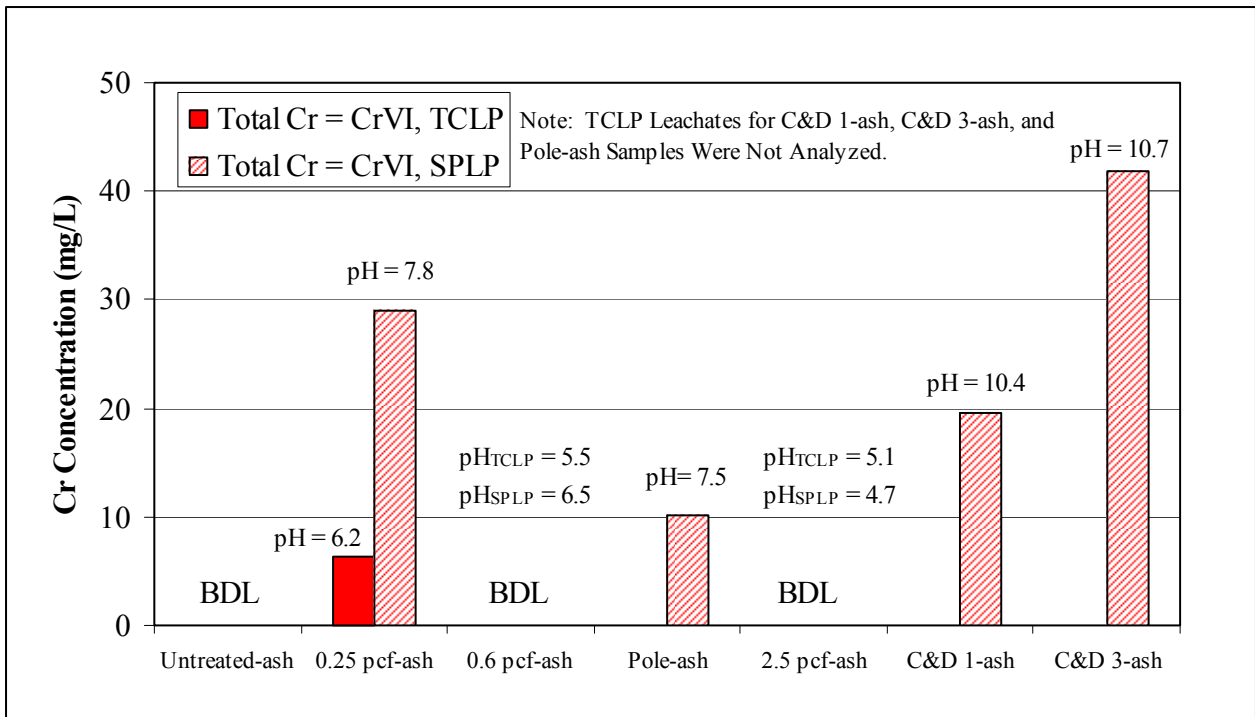


Figure IV.14: Comparison of Cr(VI) Concentrations in CCA-Treated Wood Ash Between between the TCLP and SPLP Tests

This page left intentionally blank.

**CHAPTER V,
LYSIMETER STUDY**

This page left intentionally blank.

CHAPTER V, LYSIMETER STUDY

Leachate collected from a series of lysimeters were analyzed for total arsenic and the major arsenic species, As(III), As(V), MMAA, and DMAA. The lysimeters were constructed (Section V.1) and operated (Section V.2) to simulate the conditions in landfills and to study the leachability of CCA-treated wood under these conditions. Results from these lysimeters are described in Section V.3.

V.1 LYSIMETER CONSTRUCTION

A total of six 22-foot high lysimeters made of 1-ft diameter PVC columns were constructed at the Alachua County Solid Waste Landfill in Alachua, Florida. Two lysimeters simulate wood monofills, two simulate C&D debris landfills, and two simulate MSW landfills. Each set of two lysimeters were identical except that the wood component in one is untreated and the other is CCA-treated. Thus an untreated control was maintained within each set of two to quantify the impacts from the CCA component within each type of waste. The amount of wood placed into each lysimeter is summarized in Table V.1. The wood monofill lysimeters contain the greatest amount of wood (100%), the C&D debris lysimeters contain the second most (33.7%), and the MSW lysimeters contain the least amount of added wood at 2%. Since the MSW lysimeters were made with Refuse Derived Fuel (RDF), the MSW lysimeters may contain some wood in addition to the 2% that was added. The new and weathered wood utilized in each of the lysimeters were the same as those used in the pH Stat experiment (See Chapter III). Please see Chapter III for a more thorough description of the retention levels of these wood samples.

Lysimeter Number	Lysimeter Type	Density ^a (kg/m ³)	Amount of As Added ^b (g)	Proportion of Wood Contained Inside (by weight)
1	Monofill	353	0	100% Untreated Wood
2	Monofill	324	241	50% New CCA-Treated Wood, 50% Weathered CCA-Treated Wood
3	C&D Debris	345	0	33.7% Untreated Wood
4	C&D Debris	359	25.5	23.5% Untreated Wood, 5.1% New CCA-Treated Wood, 5.1% Weathered CCA-Treated Wood
5	MSW	294	0	2% Untreated Wood
6	MSW	293	4.0	1% New CCA-Treated Wood, 1% Weathered CCA-treated wood

^aIn place density of waste in each lysimeter.

^bAs added as part of CCA-treated wood component only.

Table V.1: Summary of Wood Types Contained Within Each Lysimeter

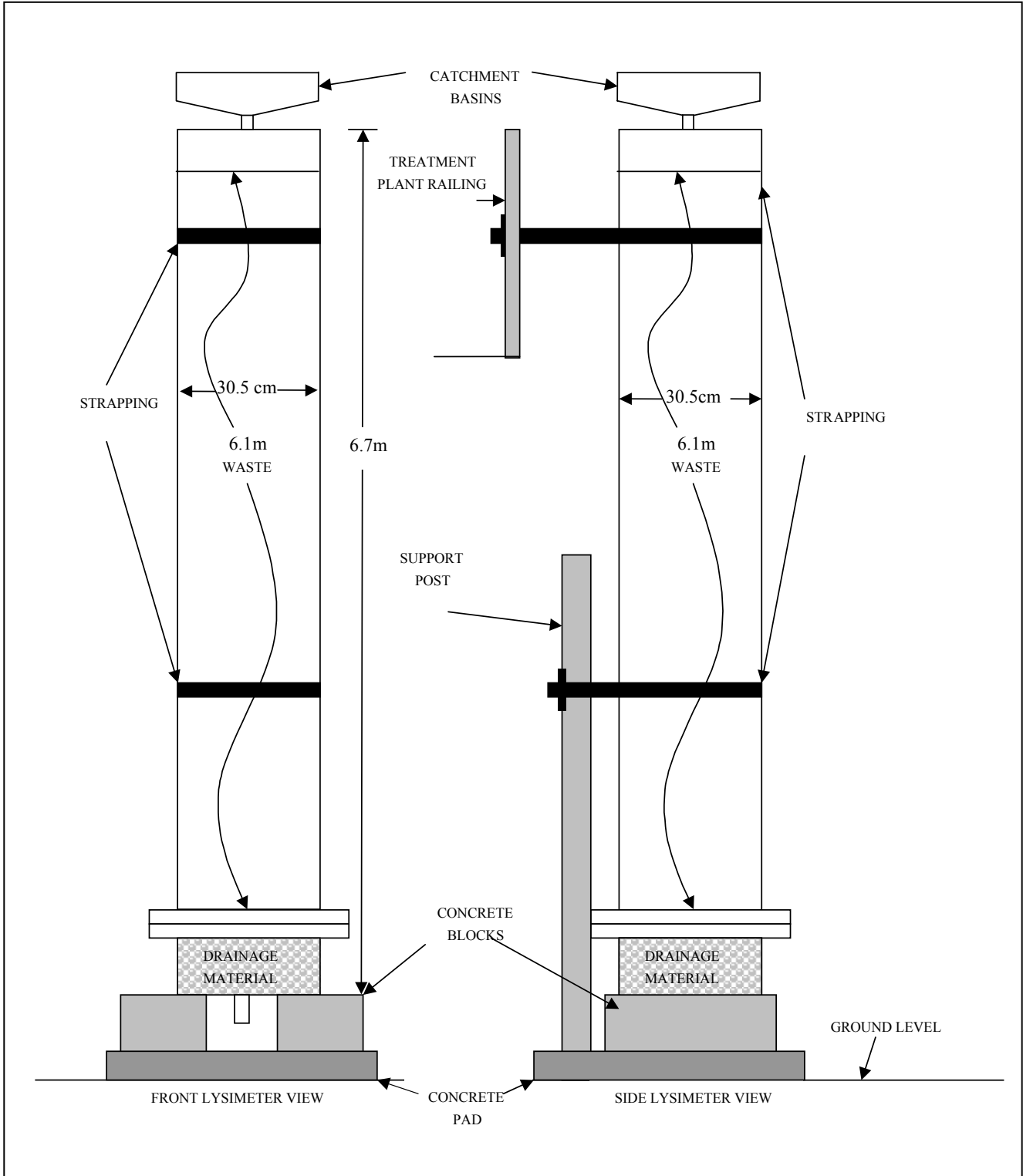


Figure V.1: Schematic of Lysimeter

The lysimeters were placed 2 feet apart on center and were supported by a concrete pad and posts located behind each lysimeter. Each lysimeter sat on cement blocks strapped to the post with steel straps (Figure V.1). They were constructed from the bottom up, as follows (Table V.2).

Description of Layers
6-inch washed 1" gravel
Stainless steel screen
6-inch washed 1" gravel
20 feet of simulated waste
Stainless steel screen
Cap with distribution system
Upside down cap to catch precipitation

Table V.2: Layers of Each Lysimeter

Each lysimeter was filled with 20 feet of waste that was reduced in size to 2 inch by 2 inch pieces whenever possible. A measured amount of the appropriate components (Tables V.3 to V.5) were added to a 5-gallon bucket, thoroughly mixed, and transferred to the appropriate lysimeter. Once the waste was transferred, a tamping device was used to compact the waste.

The wood monofill lysimeters represent a possible scenario for disposal of CCA-treated wood where CCA-treated wood is disposed in a separate dedicated area of a landfill for isolation and possible “mining” at a later time when technology becomes economically feasible for the recovery of metals. These lysimeters (lysimeters 1 and 2) will provide information on the leaching for this scenario which also simulates the leaching of the wood with no other materials present to interact with it. Prior studies have found that the fraction of construction wood (composed of new CCA-treated wood) and demolition wood (composed of weathered CCA-treated wood) can vary considerably within a waste pile depending upon the source of the waste (Solo-Gabriele et al. 1999 and 2001). Given the large variability, a 50:50 construction to demolition waste ratio by weight was chosen to represent the proportion of construction and demolition CCA-treated wood within the waste stream.

The proportions of materials within the C&D lysimeters are consistent with Jang, 2000, who evaluated the typical components of C&D waste. The percentage of CCA-treated wood within the C&D lysimeters (lysimeters 3 and 4) was based upon field studies in Florida that found in 1996 that the average composition of 12 recycled wood waste piles in Florida contained 6% CCA-treated wood by weight (Tolaymat et al. 2001). A study conducted during 1999 at 3 facilities found a range of 9 and 10% at two facilities that actively sorted out CCA-treated wood and 30% at the one facility visited that did not practice sorting (Solo-Gabriele et al., 2000). A subsequent study in 2001 found 22% CCA-treated wood at one facility studied in considerable detail (Solo-Gabriele et al., 2001). Projections have estimated that up to 50% of the wood waste stream could be CCA-treated wood (Townsend et al. 2001). Given these observations a CCA-treated wood fraction corresponding to 30% of the wood (which is equivalent to 10% of C&D as a whole) was chosen and considered consistent with prior work. Of the 10%, ½ of this was assumed to be in the form of new CCA-treated wood (representing construction debris) and ½ was assumed to be in the form of weathered CCA-treated wood (representing demolition debris).

The bulk of the MSW lysimeters (lysimeters 5 and 6) contain refuse derived fuel (RDF) collected from the Palm Beach County Solid Waste Authority (SWA) RDF plant. This plant processes 2,032 metric tons per day of MSW into RDF. The processed MSW is size-reduced and homogeneously mixed. Two trips were made to SWA to collect RDF from the storage building. The first trip was in May 2001 and the second in September of 2001. Both times RDF was collected in 160-Liter garbage cans directly from the storage room. An organic food waste constituent represented by dog food was added to the MSW at 9% to provide an adequate biodegradable fraction. The CCA-treated wood percentage in the MSW lysimeters is less than the percentage in the C&D lysimeters. The total fraction of wood within MSW is estimated at 6.1% by the US EPA, 2000. Of this quantity, 32% was assumed to be in the form of CCA-treated wood. Thus 2% of the MSW by weight (32% x 6.1%) was considered to represent CCA-treated wood. The 2% is the same amount as used in a study of pentachlorophenol-treated wood co-disposed with MSW in lysimeters (Pohland et al. 1998). Although MSW would contain a fraction of wood, 2% wood was added to the waste to control this fraction for the possible presence/absence of CCA-treated wood.

Monofill Component	Source	% Composition by Mass	
		Lysimeter 1	Lysimeter 2
Untreated Southern Yellow Pine (SYP), 2" x 6"	Donation from Great Southern	100	0
New CCA-Treated SYP, 2" x 4"	Home improvement store	0	50
Weathered CCA-treated Wood, 2"x 4"	Kidspace demolition, Gainesville, FL	0	50

Table V.3: Composition of Wood Monofill Lysimeters

C&D Component	Source	% Composition by Mass	
		Lysimeter 3	Lysimeter 4
Untreated Southern Yellow Pine (SYP), 2" x 6"	Donation from Great Southern	33.7	23.5
New CCA-Treated SYP, 2" x 4"	Home improvement store	0	5.1
Weathered CCA-Treated Wood, 2"x4"	Kidspace demolition, Gainesville, FL	0	5.1
Drywall	Home improvement store	12.4	12.4
Concrete	Concrete recycling center	29.3	29.3
Copper wire	Home improvement store	0.6	0.6
Steel sheet	Home improvement store	0.6	0.6
Aluminum	Home improvement store	0.6	0.6
Steel bar (1/2" rebar)	Home improvement store	0.6	0.6
Roofing (shingle roll)	Home improvement store	13.7	13.7
Insulation (R11, fiberglass)	Home improvement store	0.6	0.6
Cardboard (Dry)	Recycling facility	8.0	8.0

Table V.4: Composition of C&D Lysimeters

MSW Component	Source	% Composition by Mass	
		Lysimeter 5	Lysimeter 6
Untreated Southern Yellow Pine (SYP), 2" x 6"	Donation from Great Southern	2	0
New CCA-Treated SYP, 2" x 4"	Home improvement store	0	1
Weathered CCA-treated Wood, 2"x 4"	Kidspace demolition, Gainesville, FL	0	1
Dog Food (Purina Dog Chow)	Pet Warehouse	9	9
Municipal Solid Waste (processed)	West Palm Beach Solid Waste Authority	89	89

Table V.5: Composition of MSW Lysimeters

V.2 OPERATION AND MONITORING OF LYSIMETERS

Operation of the lysimeters involved the periodic addition of deionized water (sub-section V.2.a) and collection and analysis of leachate samples (sub-section V.2.b).

V.2.a Precipitation and Deionized Water Addition

Natural precipitation is allowed to infiltrate all of the lysimeters. Due to the limited quantity of leachate produced, water within all 6 lysimeters has been supplemented by the addition of deionized water.

The wood monofill lysimeters began operation on August 28, 2001. The lysimeters received 129 cm of natural rainfall between August 28, 2001 and February 10, 2003. An additional 192 and 152 centimeters of deionized water were input from August 28, 2001 through February 10, 2003 into lysimeters 1 and 2, respectively. Leachate was generated from lysimeter 2 first on September 28, 2001. Leachate was not generated from Lysimeter 1 until August 6, 2002.

The C&D lysimeters began operation on August 28, 2001. These lysimeters were exposed to the same amount of natural precipitation (129 cm) as the monofill lysimeters, and were supplemented with 238 cm of deionized water between August 28, 2001 through February 10, 2003. Leachate was generated from both lysimeters at the same time beginning on June 25, 2002.

The MSW lysimeters were completed and began operation on September 27, 2001. These lysimeters have been exposed to 117 centimeters of natural precipitation between September 27, 2001 and February 10, 2003. An additional 23 cm of deionized water have been added to each MSW lysimeter from September 27, 2001 through February 10, 2003. Leachate was initially generated from Lysimeter 5 on June 27, 2002 and from Lysimeter 6 on July 17, 2002.

V.2.b Sample Collection and Analysis

The lysimeters were sampled twice monthly. General water quality parameters, including pH, dissolved oxygen (DO), conductivity, oxidation-reduction potential (ORP), and temperature were taken in the field every time leachate was sampled. Leachate was collected in 20-Liter containers to homogenize the sample before splitting it up into proper containers for preservation and analysis. The samples were stored in a walk-in cooler at 4 degrees C. Upon sample collection, one sample split was sent overnight to the University of Miami in a shipping cooler with ice. These samples were then analyzed for arsenic species at FIU using HPLC-ICP-MS as described in sub-section II.1.b. Another sample split was digested and analyzed for total arsenic, chromium, and copper by ICP-AES at the University of Florida (See sub-section II.1.c). Samples for all 6 lysimeters have been analyzed for general water quality parameters and metals up through the February 10, 2003 sampling date. Only the arsenic data are discussed herein. A

table of some of the results to date, including chromium, copper, and some physico-chemical data, are provided in Appendix C.

V.3 RESULTS

Cumulative quantities of total arsenic increase with time for the lysimeters that contain an added CCA-treated wood fraction (Figure V.2 as computed from Tables V.7 and V.9). For the wood monofills, the lysimeter without treated wood (lysimeter 1) has released less than 1 mg of arsenic, whereas the lysimeter containing CCA-treated wood (lysimeter 2) has released about 1,400 mg during the 456 Days it has been in operation. For the C&D debris lysimeters the untreated wood control (lysimeter 3) released less than 4 mg of arsenic whereas the C&D lysimeter containing CCA-treated wood (lysimeter 4) released roughly 115 mg during the 318 days in operation. The MSW lysimeter containing the added CCA-treated wood (lysimeter 6) released 90 mg of arsenic whereas the MSW lysimeter containing the added untreated wood released 17 mg of arsenic (lysimeter 5). Of interest is that the lysimeters containing the highest proportion of CCA-treated wood leached the most arsenic with the quantities leached proceeding from lysimeter 2 to 4 to 6. Also of interest is that the untreated wood control lysimeters leached measureable amounts of arsenic. The MSW untreated wood control (lysimeter 5) leached a quantity of arsenic equal to about 1/4 of the amount leached by the MSW lysimeter with the added treated wood (lysimeter 6), indicating that the MSW contains an additional arsenic source. The source of this arsenic is unknown.

Arsenic speciation for each lysimeter is illustrated in Figures V.3 to V.8. These plots provide a comparison between the cumulative quantities of arsenic leached as measured between ICP-AES and HPLC-ICP-MS. In some cases the values match up well between these two analytical methods (lysimeters 1 and 5) and in two other cases results from the HPLC-ICP-MS are higher than results using ICP-AES (lysimeters 3 and 6) and in two other cases the results using ICP-AES were higher (lysimeters 2 and 4). The average arsenic concentrations from each lysimeter are nevertheless fairly consistent between each analytical method (Table V.6), with the concentration of total arsenic in lysimeter 2 within the 20 to 30 mg/L range. Total arsenic concentrations from lysimeter 4 were on the order of 1 to 2 mg/L and from lysimeter 6 at about 0.9 mg/L. The average total arsenic concentrations from the control lysimeters (lysimeters 1, 3, and 5) were less than 0.2 mg/L.

Lysimeter	Lysimeter Type	Total As (mg/L)	
		HPLC-ICP-MS	ICP-AES
1	Monofill, Untreated Wood	0.02	0.02
2	Monofill, CCA-treated Wood	23.7	30.8
3	C&D Debris, Untreated Wood Only	0.03	0.02
4	C&D Debris With CCA-Treated Wood	1.21	1.98
5	MSW with Untreated Wood Added	0.20	0.16
6	MSW with CCA-Treated Wood Added	0.85	0.87

Table V.6: Average Total Arsenic Concentrations From Each Lysimeter

The most intriguing feature of the speciation data (Figures V.3 to V.8) is the observation that DMAA is the dominant arsenic species for the control lysimeters (lysimeters 1, 3, and 5). In

other words, for the lysimeters containing untreated wood and as a consequence low concentrations of total arsenic, the form of arsenic leached is the less toxic DMAA form. For the lysimeters containing the added CCA-treated wood, the predominant form of arsenic leached is either As(V) for lysimeters 2 and 4 or As(III) for lysimeter 6. The leaching of As(V) from the lysimeters containing added CCA-treated wood is consistent with the predominant form of arsenic (As(V)) within the original wood samples. No DMAA nor MMAA were detected in the CCA monofill lysimeter (lysimeter 2). The methylated forms (DMAA and MMAA) were observed at concentrations less than As(V) for the C&D and MSW lysimeters that contain added CCA-treated wood (lysimeters 4 and 6). Assuming that arsenic exists in treated wood is As(V), it appears that this form of arsenic is converted to As(III) within MSW. The MSW lysimeters were characterized by the lowest average ORP value (-592 mV on average for lysimeter 6) as compared to the lysimeters 1 through 4 which were characterized by ORP values greater than -500 mV. This difference in ORP along with the difference in the composition of the MSW waste may be the reason for the predominance of As(III). Overall, the results from the lysimeters suggest that lower levels and less toxic forms of arsenic are leached from the lysimeters containing only untreated wood, whereas the lysimeters that contain added CCA-treated wood leach higher concentrations of arsenic with the more toxic As(V) and As(III) forms predominating.

Date Collected	Lysimeter 1 (Untreated Wood)						Lysimeter 2 (CCA-Treated Wood)					
	HPLC-ICP-MS					ICP-AES	HPLC-ICP-MS					ICP-AES
	As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)	As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)
Sep. 28, 01							NS ^c					3.78
Jan. 28, 02							Trace ^b	4.85	Trace	ND ^a	4.85	5.31
Apr. 2, 02							0.075	4.29	0.12	ND	4.48	6.25
May 16, 02							NS					6.55
Jun. 12, 02							Trace	3.50	ND	ND	3.50	14.75
Jun. 25, 02							0.58	3.61	ND	ND	4.19	32.03
Jul. 17, 02							8.33	24.93	ND	ND	33.26	37.11
Aug. 6, 02	Trace ^b	ND ^a	Trace	0.009	0.013	0.012	40.78	2.15	ND	ND	42.93	48.84
Aug. 21, 02	Trace	ND	Trace	ND	Trace	NS	ND	23.60	ND	ND	23.60	26.79
Sep. 6t, 02	0.015	0.01	Trace	ND	>0.025	NS	28.07	2.26	ND	ND	30.33	28.21
Sep. 25, 02	NS ^c					NS	ND	28.12	ND	ND	28.12	31.55
Oct. 14, 02	Trace	ND	0.007	ND	>0.012	0.016	6.42	16.59	ND	ND	23.01	29.44
Oct. 30, 02	0.008	0.005	0.009	ND	0.021	0.021	19.71	22.03	Trace	ND	>41.74	45.46
Nov. 18, 02	Trace	0.006	0.010	Trace	>0.018	0.030	Trace	24.08	Trace	ND	>24.08	33.45
Dec. 2, 02	Trace	ND	0.008	ND	>0.011	0.017	Trace	23.11	Trace	ND	>23.11	35.90
Dec. 20, 02	Trace	0.017	0.012	ND	>0.032	0.016	0.67	24.09	ND	ND	24.76	32.48
Jan. 7, 03	0.019	0.024	ND	ND	0.043	0.023	ND	39.97	ND	ND	39.97	55.39
Jan 27, 03	0.005	0.009	ND	ND	0.014	0.012	2.61	24.07	ND	ND	26.68	29.40
Feb. 10, 03	NS					0.016	NS					42.41
Mar. 10, 03	0.006	0.007	0.013	ND	0.027	0.036	18.06	37.63	ND	ND	55.69	64.59
Mar. 25, 03	Trace	0.005	0.015	ND	>0.023	0.030	0.46	38.52	ND	ND	38.98	65.80
Apr. 21, 03	Trace	ND	0.019	ND	>0.023	0.022	ND	33.28	ND	ND		49.02
May 9, 03	Trace	0.007	0.0086	Trace	>0.011	0.024	Trace	27.44	ND	ND		41.11

^aND = Not Detected

^bTrace = <0.005 mg/L

^cNS = No Sample Available

Table V.7: Arsenic Results for Lysimeters 1 & 2 (Monofills)

Date Collected	Lysimeter 3 (C&D, Untreated Wood Only)						Lysimeter 4 (C&D with CCA-Treated Wood)					
	HPLC-ICP-MS					ICP-AES	HPLC-ICP-MS					ICP-AES
	As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)	As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)
Jun.25, 02	ND ^a	ND	ND	ND	ND	NS	0.664	0.766	Trace ^b	Trace	>1.430	NS
Jul.17, 02	NS ^c					NS	Trace	0.272	Trace	Trace	>0.272	NS
Aug.6, 02	0.004	0.013	0.007	0.006	0.031	0.018	0.0288	0.258	0.062	0.046	0.40	1.09
Aug.21,02	0.01	0.024	0.013	0.012	0.059	NS	ND ^a	0.186	0.735	0.232	1.15	NS
Sep.6, 02	Trace ^b	Trace	0.013	0.012	>0.024	0.027	Trace	0.168	0.402	0.251	0.821	1.24
Sep.25, 02	Trace	Trace	0.011	0.019	>0.042	0.028	0.122	0.060	0.385	1.28	1.844	2.22
Oct.14, 02	0.007	0.008	0.012	0.007	0.034	0.026	0.0448	0.372	0.314	0.245	0.976	1.73
Oct.30, 02	0.005	0.005	0.001	0.017	0.028	0.021	0.005	0.0045	0.0013	0.0168	0.028	1.54
Nov.18,02	0.007	Trace	0.01	0.0064	>0.023	0.019	0.2728	0.281	0.370	0.650	1.57	1.34
Dec.2, 02	0.004	ND	0.008	ND	0.012	0.012	0.0802	0.237	0.286	0.156	0.760	1.17
Dec.20,02	0.007	ND	0.015	ND	0.022	0.017	0.0949	0.395	0.488	0.209	1.19	1.51
Jan 7, 03	0.020	ND	0.038	ND	0.057	0.020	0.1447	0.539	0.428	0.135	1.25	2.46
Jan 27, 03	0.006	ND	0.012	ND	0.019	0.013	0.221	0.392	0.355	0.253	1.22	2.41
Feb.10, 03	NS					0.013	NS ^c					3.09
Feb.23, 03	NS					0.017	NS					3.99
Mar.10,03	0.006	0.018	0.012	ND	0.019	0.018	0.0939	1.29	0.441	0.329	2.16	3.01
Mar.25,03	0.007	0.016	0.014	0.006	0.020	0.016	0.0995	0.672	0.408	0.546	1.73	2.31
Apr.21,03	0.012	0.020	0.017	0.003	0.030	0.020	0.051	0.864	0.562	1.02	2.48	3.00
May 9, 03		0.030				0.030	0.0698	0.254	0.176	0.808	1.31	2.70

^aND = Not Detected

^bTrace = <0.005 mg/L

^cNS = No Sample Available

Table V.8: Arsenic Results for Lysimeters 3 & 4 (Simulated C&D)

Date Collected	Lysimeter 5 (MSW, Untreated Wood Added)						Lysimeter 6 (MWS, withCCA-Treated Wood)					
	HPLC-ICP-MS					ICP-AES	HPLC-ICP-MS					ICP-AES
	As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)	Total Cr (mg/L)	Total Cu (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)
Jun.25, 02	0.741	ND ^a	Trace ^b	ND	>0.741	0.200						
Jul.17, 02	ND	ND	ND	ND	ND	0.083	3.780	0.405	ND	ND		3.751
Aug.6, 02	Trace	ND	0.230	ND	0.230	0.116	2.071	0.261	ND	ND	2.332	2.429
Aug.21,02	Trace	ND	Trace	Trace	Trace	0.124	0.474	0.173	Trace	ND	> 0.647	0.793
Sep. 6, 02	0.036	0.013	0.143	ND	>0.192	0.148	0.296	0.105	0.137	ND	0.537	NS
Sep. 25 02	0.028	Trace	0.150	ND	>0.187	0.198	0.300	0.111	0.052	ND	0.463	0.793
Oct.14, 02	Trace	0.011	Trace	Trace	>0.011	0.251	0.211	-	0.172	ND	0.383	0.549
Oct.30, 02	Trace	0.022	0.194	ND	0.216	0.290	0.090	0.010	0.570	0.077	0.747	0.801
Nov.18,02	Trace	ND	0.168	ND	>0.168	0.235	0.074	0.096	0.389	0.043	0.602	0.541
Dec. 2, 02	0.008	ND	0.108	ND	0.116	0.187	0.074	0.080	0.212	0.063	0.428	0.446
Dec.20,02	0.018	ND	0.129	ND	0.147	0.130	0.104	0.127	0.361	0.101	0.693	0.374
Jan. 7, 03	0.093	ND	0.227	ND	0.320	0.140	0.188	0.312	0.438	0.206	1.144	0.232
Jan.27, 03	0.039	ND	0.095	ND	0.134	0.138	0.199	0.472	0.390	0.240	1.301	0.324
Feb.10, 03	NS					0.135						0.249
Mar.10,03	0.01	-	0.073	ND	0.083	0.115	0.096	0.168	0.187	0.071		0.407
Mar.25 03	0.01	Trace	0.180	ND	0.19	0.113	0.027	0.354	0.282	0.147	0.810	0.781
Apr.21,03	Trace	-	0.120	ND	>0.120	0.104	0.024	0.379	0.106	0.226	0.734	0.787
May 9, 03	0.018	-	0.099	ND	0.117	0.114	0.162	0.637	0.104	0.134	1.037	0.655

^aND = Not Detected

^bTrace = <0.005 mg/L

^cNS = No Sample Available

Table V.9: Arsenic Results for Lysimeters 5 & 6 (MSW)

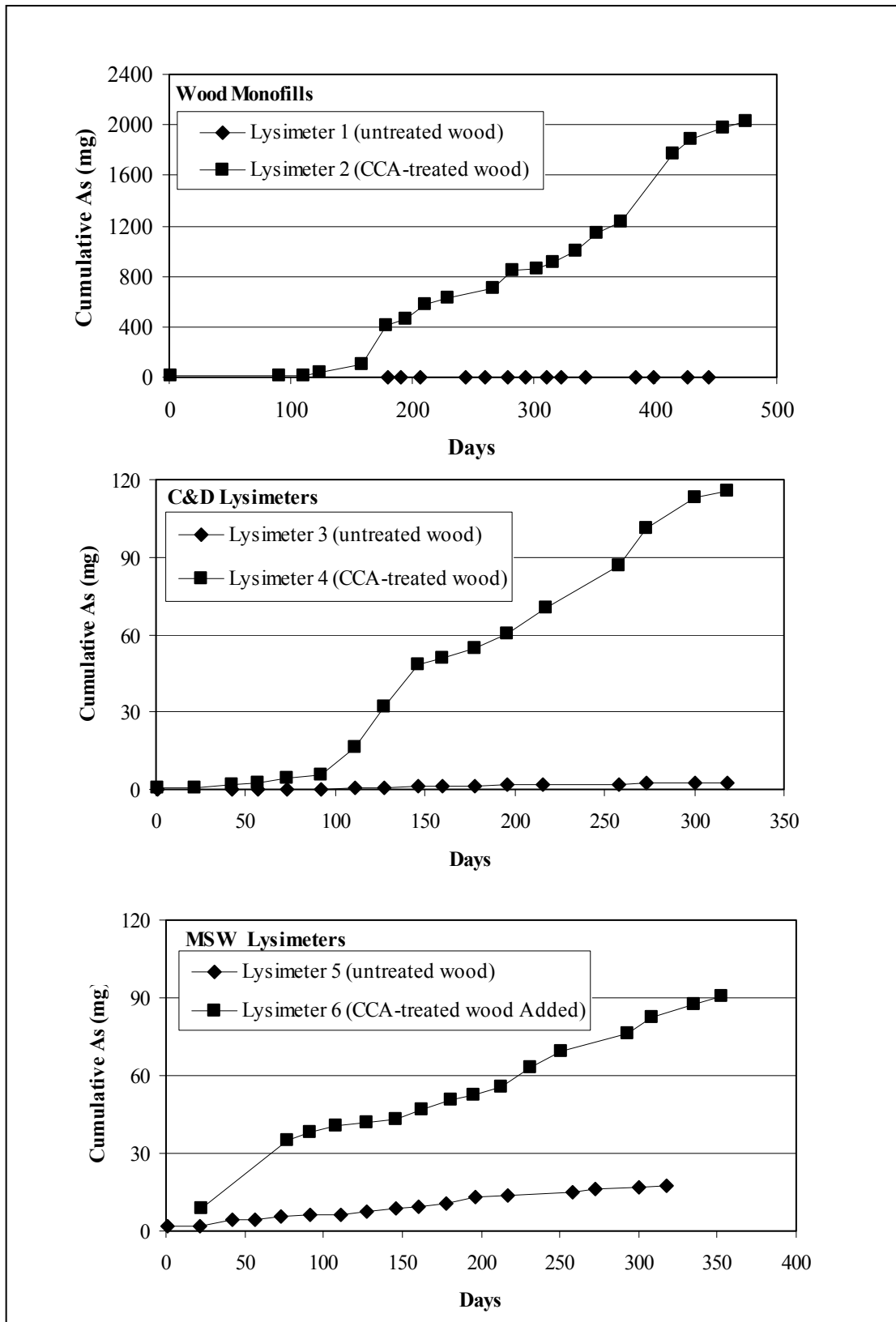


Figure V.2: Comparison to Cumulative Total Arsenic Between Each Set of Lysimeters Using Data from HPLC-ICP-MS Analysis

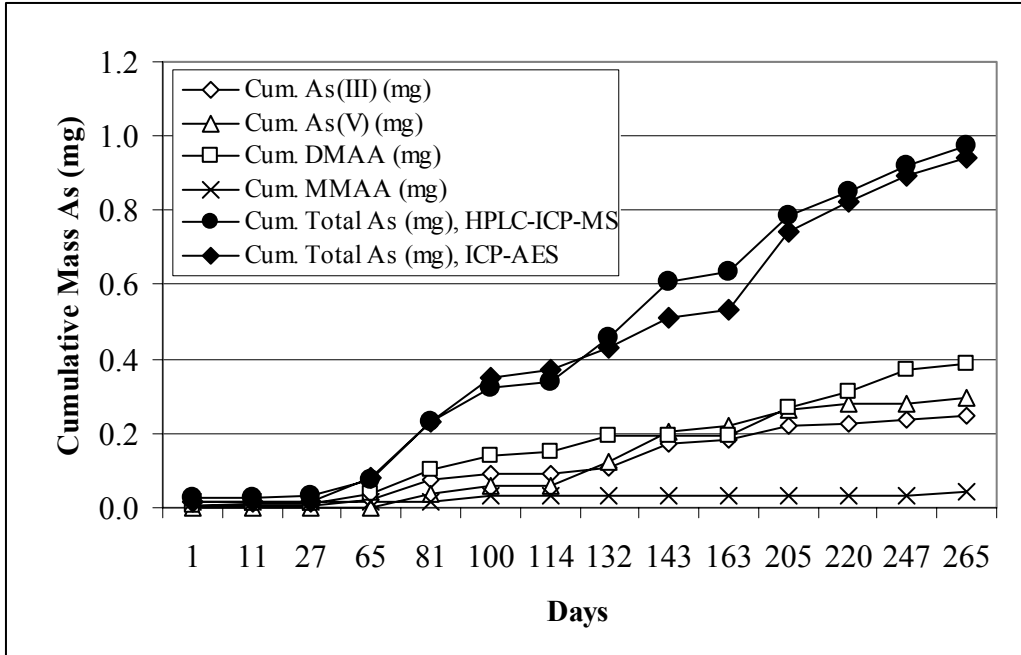


Figure V.3: Cumulative Quantities of Various Arsenic Species from Lysimeter 1

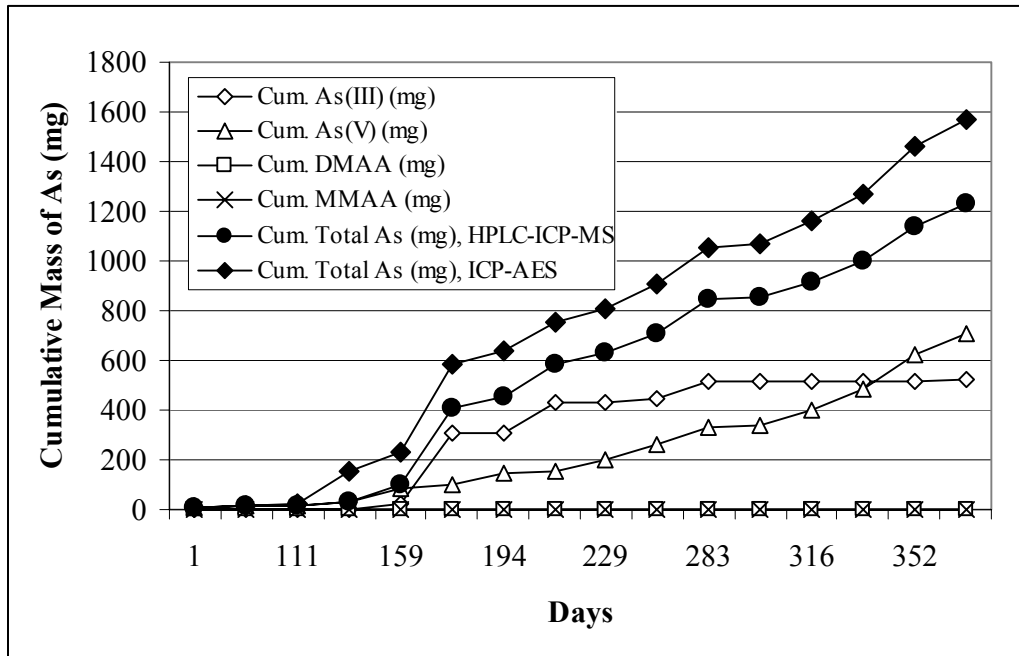


Figure V.4: Cumulative Quantities of Various Arsenic Species from Lysimeter 2

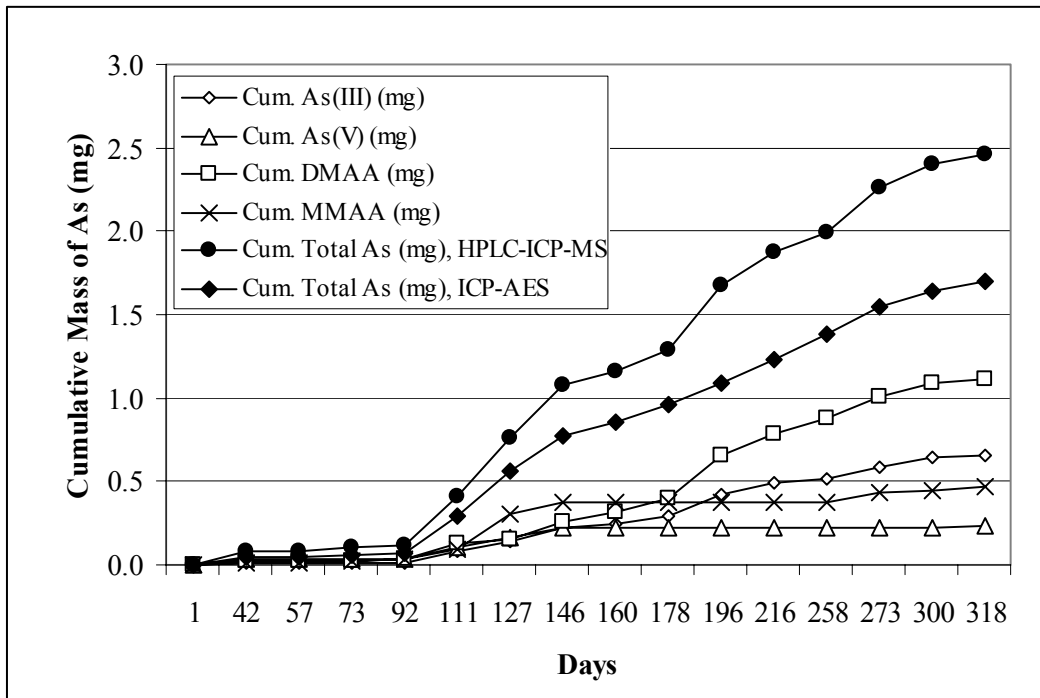


Figure V.5: Cumulative Quantities of Various Arsenic Species from Lysimeter 3

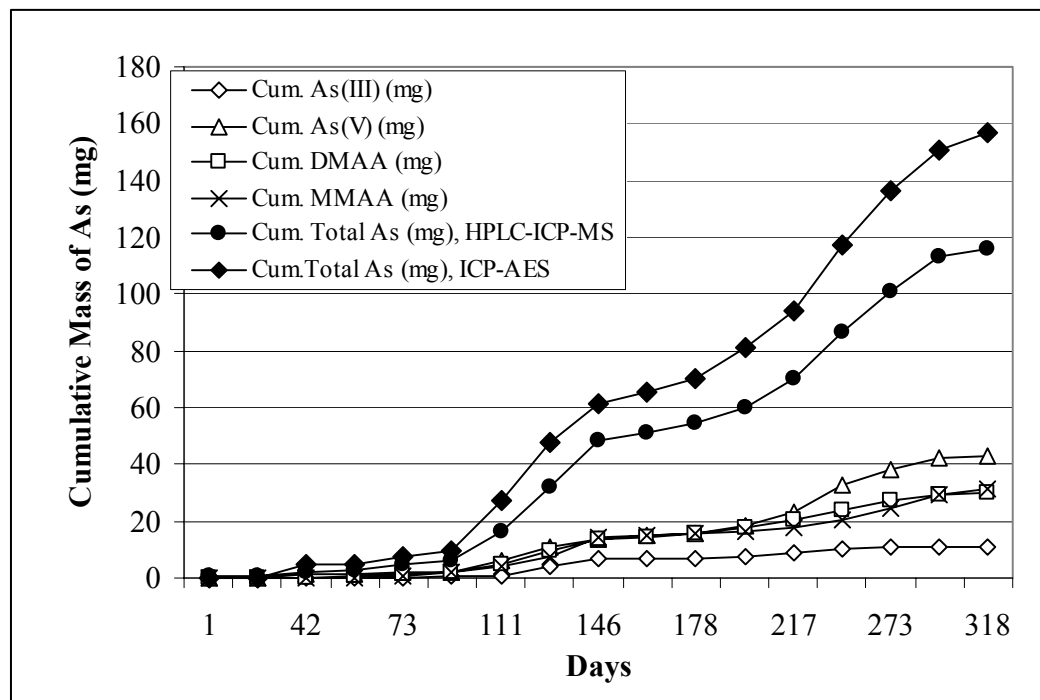


Figure V.6: Cumulative Quantities of Various Arsenic Species from Lysimeter 4

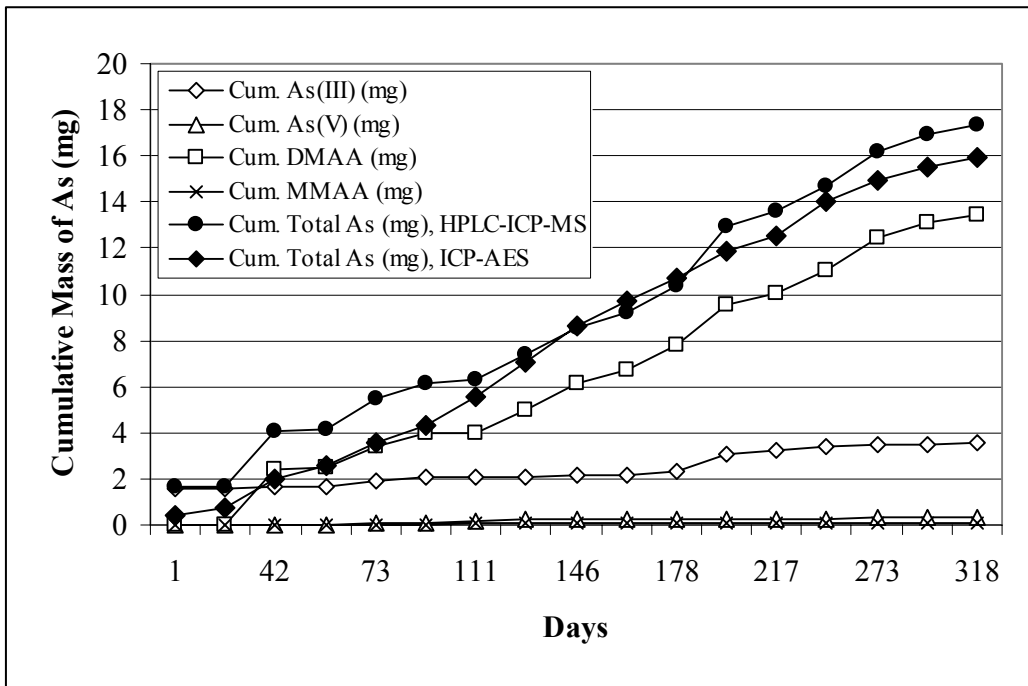


Figure V.7: Cumulative Quantities of Various Arsenic Species from Lysimeter 5

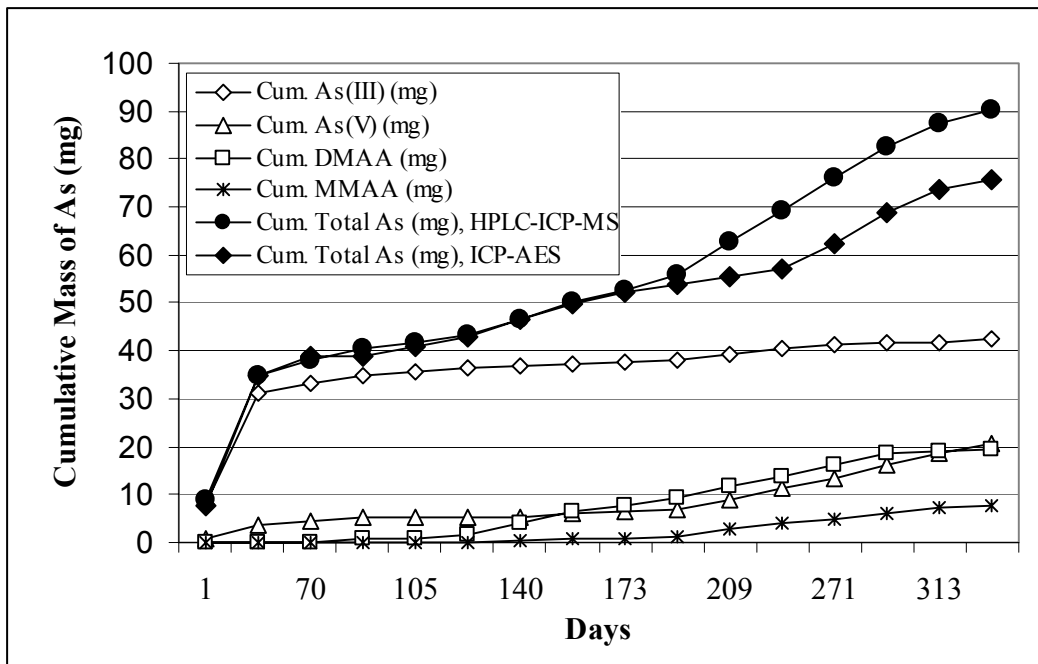


Figure V.8: Cumulative Quantities of Various Arsenic Species from Lysimeter 6

This page left intentionally blank.

**CHAPTER VI,
ANALYSIS OF GROUNDWATER NEAR C&D DEBRIS DISPOSAL
FACILITIES**

This page left intentionally blank.

CHAPTER VI, ANALYSIS OF GROUNDWATER NEAR C&D DEBRIS DISPOSAL FACILITIES

This chapter focuses on arsenic speciation analysis of groundwater collected in the vicinity of Construction and Demolition (C&D) debris disposal sites within the State of Florida. The motivation for this work was due to concern about the lack of liners at these sites and the co-disposal of CCA-treated wood which could possibly contaminate groundwater in the vicinity of these sites. The intent of this effort was to determine whether or not arsenic concentrations in groundwaters near these sites were in fact elevated above background levels and, if elevated, what were the arsenic species of the samples. It was believed that arsenic speciation of the groundwater samples would shed some light on the ultimate source of the arsenic and would be useful in evaluating the relative toxicity of those groundwater samples. A considerable amount of work early during the study was associated with obtaining permission to collect the samples. A summary of these preliminary efforts are described in sub-section VI.1. Furthermore, early efforts also focused on the use of ion exchange cartridges in an effort to preserve arsenic speciation immediately upon sampling. Laboratory work with the ion exchange cartridges indicated that they did not function properly in maintaining the arsenic species, and this effort was therefore abandoned. A description of the work with the cartridges is described in Appendix A. After these preliminary efforts, a new strategy was established for collecting the required samples (sub-section VI.2). This new strategy resulted in the collection of the originally targeted groundwater samples and the results for these groundwater samples are described in sub-section VI.3.

VI.1 PRELIMINARY EFFORTS

Preliminary efforts for this study focused on getting voluntary permission to sample groundwater at the C&D facilities. This was the initial approach that was requested by the Florida Department of Environmental Protection (FDEP). Groundwater data from C&D disposal facilities were obtained through Richard Tedder of the FDEP on March 20, 2001. A spreadsheet was provided by Richard Tedder that provided C&D site data collected between January 1998 and December 2000. Out of 832 samples, 125 had arsenic concentrations greater than the detection limit, 593 did not detect arsenic, and the remaining 114 samples were not analyzed for arsenic. The 125 detects were observed at 30 different C&D sites throughout the State. Of these 30 facilities, 26 facilities had at least one groundwater sample with an arsenic concentration greater than 10 ug/L. The 10 ug/L threshold corresponds to the new drinking water limit for arsenic.

The 26 C&D sites with at least one groundwater sample with an arsenic concentration greater than 10 ug/L were thus targeted for sampling. The Florida Department of Environmental Protection originally requested that the research team contact each of the targeted C&D sites and ask that they volunteer to provide a sample. Each of the facilities was contacted by telephone and in some cases by fax. Contact was made with either a facility owner or operator. In some cases, owners/operators would indicate that they did not want to participate. In other cases, owners/operators indicated that they needed to consider the request further, but in all of these

cases the owners/operators did not respond to further inquiries and therefore permission was never granted for sample collection in this first attempt to contact the landfill owners and operators.

VI.2 NEW STRATEGY

As a result of the difficulty in getting voluntary participation, the research team re-approached the Florida Department of Environmental Protection for assistance in getting permission to collect the groundwater samples. During this second effort, the Florida Department of Environmental Protection, Tallahassee, contacted the District Offices asking for assistance with obtaining the samples. In many instances the District Offices informed the landfill owners/operators of the study by letters, telephone, and email. The research team then followed up with subsequent correspondence and arranged for sample collection. Participation among the C&D sites was much improved with this new strategy. Of the 26 sites targeted for sample collection, 21 participated in the study. The 5 that did not participate were under enforcement action with either the FDEP or local regulatory agencies, and as a consequence cooperation would have required legal action which was beyond the mandate of this research project.

Sample collection at the participating 21 sites was to coincide with the site's regular sampling schedule for FDEP compliance purposes. Prior to sample collection at the site, the research team would establish a "sampling coordinator" for the C&D debris disposal facility which would be the individual who collects the sample on behalf of the facility. The sample coordinators were typically the consultants hired by the facility and in the case of the Northwest District, the FDEP District Office personnel. Once a sampling coordinator and a sampling date were established, the research team would then request a diagram of the site which included the location of the monitoring wells. A minimum of 1 background well was identified for sample collection. In the cases where two geologic layers existed below the site, two background samples, one from each geologic layer, were targeted for sample collection. In addition to the background samples, wells downgradient of the facilities were identified for sample collection. A minimum of two downgradient wells were to be sampled. For sites overlying two geologic layers at least one sample was to be collected from each geologic layer. The down-gradient monitoring wells were either compliance and /or detection monitoring wells, depending upon the availability at each facility. Once the sample locations were established, a Fedex a sampling box was shipped to each sampling coordinator one to two weeks prior to the sample collection date. The sampling box consisted of a styrofoam cooler which contained pre-labeled sampling bottles, freezer packs, a sample collection log sheet, a pre-paid Fedex label for over-night return shipment, and detailed instructions for sample collection. Once the box was sent, the research team followed-up with the sampling coordinator to assure receipt of the box and to reconfirm sample collection procedures. The day after the scheduled sampling date the research team would call the sampling coordinator to confirm the shipping date for the samples. About a month after the sample collection date, the research team would recontact the sampling coordinator to obtain the results from the samples analyzed on behalf of the C&D facility for FDEP compliance purposes. The results provided by the sampling coordinator were analyzed for total arsenic concentrations by an independent commercial lab as contracted by the C&D facility owner.

In order to develop sampling instructions, three facilities were sampled by a member of the research team early during the study. During these visits the research team member “tagged along” with the sampling coordinator for the facility to observe their sampling procedures. During these visits, the sampling coordinators followed standard procedures for sample collection as specified by the Florida Department of Environmental Protection which include limits on purge rate and requirements for monitoring temperature, turbidity, conductivity, and dissolved oxygen. As a result of these visits, sample collection sheets and instructions for the sampling coordinators were fine tuned in order to make sample collection procedures clearer and easier to follow (See Appendix B for Sample Collection Log Sheet). Subsequently all samples were collected by the sampling coordinator without a member of the research team present.

During this sample collection effort, groundwater samples were collected from 21 C&D debris facilities from 16 counties in Florida. A total of 71 samples were collected, 23 were from background wells and 48 were from compliance or detection wells. One facility was not able to provide a background sample and three facilities provided two sets of background samples. In some cases, more than two downgradient samples were provided.

Arsenic speciation for all groundwater samples were analyzed by HPLC-ICP-MS. See sub-section II.1.b for more details concerning this analysis method. Total arsenic was analyzed independently by commercial labs for FDEP compliance purposes on behalf of the C&D facilities.

VI.3 RESULTS

Results are presented for both the background wells (sub-section VI.3.a) and for the compliance/detection wells (sub-section VI.3.b). A comparison between background wells and compliance wells is provided towards the end of sub-section VI.3.b.

VI.3.a Background Wells

The total arsenic concentration (calculated by summing the individual arsenic species concentrations obtained by HPLC-ICP-MS) was compared with the results from the commercial laboratories (Figure VI.1 and Table VI.1). Results indicate that there were no detectable levels of arsenic in 14 of the 23 background wells. Only 7 samples were above the 5 ug/L detection limit of the HPLC-ICP-MS system. The highest concentration measured for total arsenic was 67 ug/L. Most of the arsenic in this sample was in the form of As(V) with smaller quantities of As(III) and DMAA. The overall average total arsenic concentration computed for the background wells was 7 ug/L (where samples below the detection limit were set to a value of 0 ug/L). For background wells testing positive for arsenic, the majority of the arsenic was present at As(V). Smaller quantities of As(III) and DMAA were detected for some of the positive samples. MMAA was not detected in any of the background samples.

The results between HPLC-ICP-MS and the commercial laboratories were fairly consistent. The one sample that was significantly elevated above detection limits was measured as 67 ug/L using HPLC-ICP-MS and at 77 ug/L by the commercial lab. These values are reasonably close given that two separate samples (not splits) were analyzed and considering the

possible differences in analytical procedures used. All the other samples were very close to the detection limits of the commercial laboratories which were reported to range between 5 and 10 ug/L.

VI.3.b Detection/Compliance Wells

Of the 48 detection/compliance samples, 21 were found to contain total arsenic concentrations greater than the 5 ug/L detection limit of the HPLC-ICP-MS system (Table VI.2). The average among all of the wells (where the below detects were set to 0) was 10 ug/L. The maximum concentration measured by HPLC-ICP-MS was 57 ug/L as observed for well #64.

The results from HPLC-ICP-MS and the commercial laboratories were fairly consistent (Figure VI.2). Most samples were either at or near the detection limits. For samples that were significantly above the detection limits, results were found to be consistently elevated between the two sets of samples. This is shown for well #3, 5, 22, and 24. Wells 64 and 65 were also found to be significantly above background levels by both HPLC-ICP-MS and the commercial laboratories; however, in this case, the commercial laboratory measured concentrations much higher than the concentrations measured by HPLC-ICP-MS. Overall, the results are consistent in that when one method indicates that concentrations are significantly above background, the other method confirms this result.

The arsenic species of those samples that were above background levels are shown in Figure VI.3. Groundwater at only three separate C&D facilities were found to contain arsenic concentrations significantly above 20 ug/L. For one of these facilities (corresponding to well numbers 1, 3, 4, and 5) the background sample for that well was also characterized by an elevated arsenic concentration (60 ug/L). A background sample was not available for the second C&D facility characterized by elevated arsenic concentrations (corresponding to well numbers 22, 23, and 24). The background concentration was low (<10 ug/L) for the third facility characterized by elevated arsenic concentrations. Interestingly, the facility with the elevated background concentration contained arsenic in the organic forms as both DMAA and MMAA. Groundwater at the other two facilities did not have measureable levels of organic species. Perhaps the presence of arsenic in the background well impacted the speciation of the arsenic observed in the detection/compliance wells for the first landfill. The differences observed in speciation between the facilities are worth further exploration.

Well #	HPLC-ICP-MS					Commercial Lab
	As(III) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	As(V) (mg/L)	Total As (mg/L)	Total As (mg/L)
2	0.002	<0.005	ND	0.060	0.067	0.077
6	ND ^a	ND	ND	ND	ND	<0.01
8	<0.005	ND	ND	ND	<0.005	<0.01
10	<0.005	ND	ND	<0.005	0.010	BDL ^b
13	<0.005	<0.005	ND	<0.005	0.015	<0.005
16	ND	ND	ND	ND	ND	<0.005
27	ND	ND	ND	ND	ND	0.010
28	ND	ND	ND	ND	ND	0.018
31	ND	ND	ND	ND	ND	BDL
33	ND	ND	ND	ND	ND	BDL
37	<0.005	<0.005	ND	<0.005	0.015	<0.005
38	ND	ND	ND	ND	ND	<0.005
41	ND	ND	ND	ND	ND	<0.005
44	ND	ND	ND	0.010	0.010	<0.005
47	<0.005	ND	ND	<0.005	0.010	BDL
50	ND	ND	ND	<0.005	<0.005	<0.005
53	ND	ND	ND	ND	ND	BDL
54	ND	ND	ND	ND	ND	BDL
57	0.007	ND	ND	0.011	0.018	0.010
60	ND	ND	ND	ND	ND	<0.01
63	ND	ND	ND	ND	ND	<0.001
66	ND	ND	ND	ND	ND	<0.005
69	ND	ND	ND	ND	ND	<0.005

^aND = Not Detected by HPLC-ICP-MS

^bBDL = Below Detection Limit (Detection Limits of Commercial Laboratories Between 0.005 and 0.010 mg/L)

Table VI.1: Groundwater Data for Background Wells at C&D Facilities

Well #	HPLC-ICP-MS					Commercial Lab
	As(III) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	As(V) (mg/L)	Total As (mg/L)	Total As (mg/L)
1	<0.005	<0.005	<0.005	ND ^a	0.015	0.018
3	0.012	0.008	0.008	0.014	0.042	0.039
4	0.003	ND ^a	<0.005	<0.005	0.013	<0.01
5	0.008	0.008	0.010	0.018	0.044	<0.054
7	<0.005	ND	ND	ND	<0.005	<0.01
9	<0.005	<0.005	<0.005	ND	0.015	<0.01
11	<0.005	<0.005	ND	ND	0.010	BDL ^b
12	<0.005	ND	ND	ND	<0.005	BDL
14	0.004	ND	<0.005	ND	0.008	0.007
15	0.003	<0.005	0.004	0.006	0.017	<0.005
17	ND	ND	<0.005	ND	<0.005	<0.005
18	<0.005	ND	<0.005	ND	0.010	<0.005
19	ND	ND	<0.005	ND	<0.005	<0.005
20	ND	ND	<0.005	ND	<0.005	<0.005
21	<0.005	ND	<0.005	ND	0.010	<0.005
22	0.029	<0.005	ND	ND	0.034	0.029
23	<0.005	ND	<0.005	ND	0.010	<0.01
24	0.026	<0.005	ND	ND	0.031	0.054
25	ND	ND	ND	ND	ND	0.010
26	ND	ND	ND	ND	ND	0.010
29	<0.005	ND	<0.005	ND	0.010	0.010
30	<0.005	ND	<0.005	ND	0.010	0.010
32	ND	ND	ND	ND	ND	BDL
34	ND	ND	ND	ND	ND	BDL
35	<0.005	ND	<0.005	<0.005	0.015	<0.005
36	<0.005	ND	<0.005	ND	0.010	<0.005
39	<0.005	ND	ND	ND	<0.005	<0.005
40	<0.005	ND	ND	ND	<0.005	0.006
42	ND	ND	ND	ND	ND	<0.005
43	<0.005	ND	ND	ND	<0.005	0.009
45	<0.005	ND	ND	ND	<0.005	<0.005
46	ND	ND	ND	ND	ND	<0.005
48	ND	ND	ND	ND	ND	BDL
49	ND	<0.005	ND	ND	<0.005	BDL
51	ND	ND	ND	ND	ND	<0.005
52	ND	ND	ND	ND	ND	<0.005
55	ND	ND	ND	ND	ND	BDL
56	ND	ND	ND	ND	ND	BDL
58	ND	ND	ND	ND	ND	<0.01
59	<0.005	<0.005	ND	ND	0.010	0.010
61	<0.005	ND	ND	ND	<0.005	<0.1
62	0.006	ND	ND	ND	0.006	0.017
64	0.016	0.041	ND	ND	0.057	0.091
65	0.016	0.024	ND	ND	0.040	0.180
67	ND	ND	ND	ND	ND	<0.005
68	ND	ND	ND	ND	ND	<0.005
70	ND	ND	ND	ND	ND	<0.005
71	ND	ND	ND	ND	ND	<0.005

^aND = Not Detected by HPLC-ICP-MS

^bBDL = Below Detection Limit (Detection Limits of Commercial Laboratories Between 0.005 and 0.010 mg/L)

Table VI.1: Groundwater Data for Detection/Compliance Wells at C&D Facilities

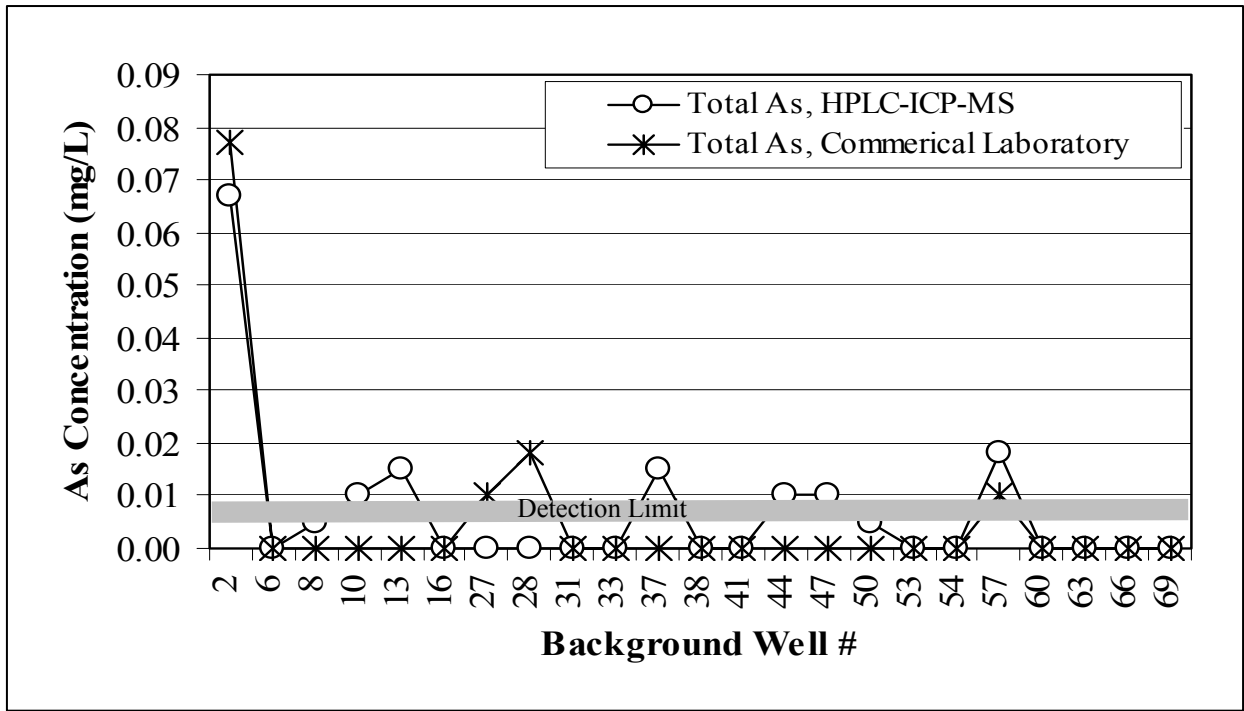


Figure VI.1: Total Arsenic for Background Wells as Measured by HPLC-ICP-MS and Independent Commercial Laboratories

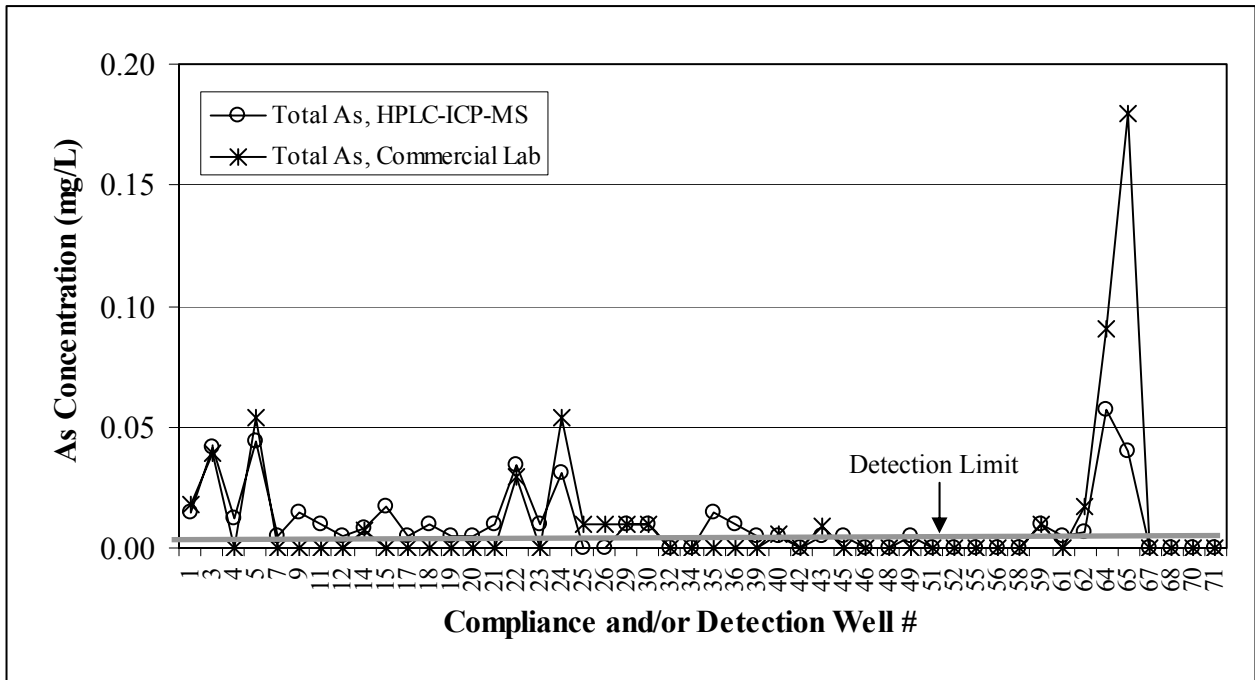


Figure VI.2: Total Arsenic for Compliance/Detection Wells as Measured by HPLC-ICP-MS and Independent Commercial Laboratories

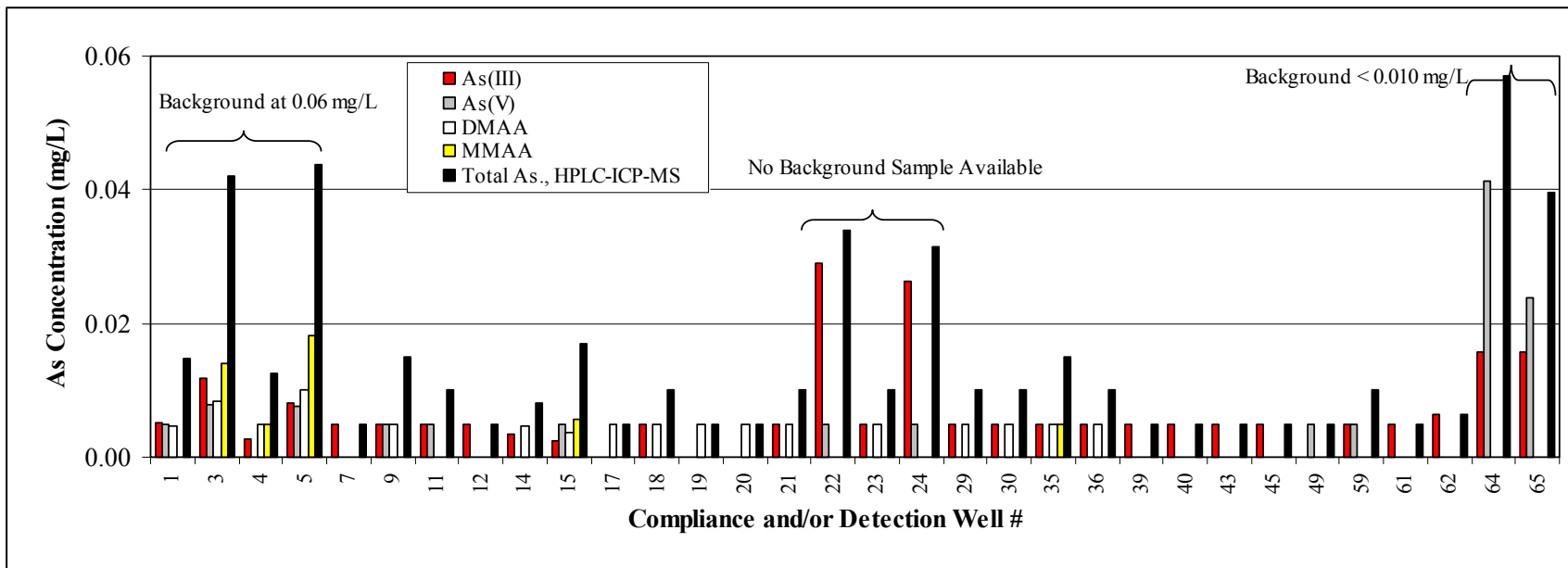


Figure VI.3: Arsenic Species of Compliance/Detection Wells that Tested Above Detection Limits

**CHAPTER VII,
SUMMARY, CONCLUSIONS, AND RECOMMENDATIONS**

This page left intentionally blank.

CHAPTER VII, SUMMARY, CONCLUSIONS, RECOMMENDATIONS, AND ACKNOWLEDGMENTS

VII.1 SUMMARY AND CONCLUSIONS

This study focused on evaluating leachates from CCA-treated wood for arsenic and chromium species. Experiments ranged from very controlled small-scale laboratory experiments such as the “pH Stat” experiment, to laboratory experiments designed to simulate particular field conditions (SPLP and TCLP tests on unburned wood and wood ash), to large scale field experiments (lysimeter study), to environmental sampling of groundwater in the vicinity of C&D debris disposal facilities. The intent of these tasks was to quantify the total quantity metals released under different environmental conditions and to obtain some insight concerning the speciation of these releases. Samples evaluated in this study were speciated for arsenic as As(V), As(III), DMAA, and MMAA. Chromium speciation focused on evaluating the relative distribution of total chromium between Cr(III) and Cr(VI).

Methods

A considerable effort in this study was associated with the development of methods for analysis. Analyses were conducted on solid wood samples and on leachates from these wood samples using a series of different analytical techniques. Solid wood samples were analyzed for total metals (As, Cr, and Cu) and for hexavalent Cr. Techniques utilized for total metals included XRF analysis and acid digestion followed by ICP-AES. In the case of CCA-treated wood ash, the samples were also subjected to neutron activation analysis. For Cr(VI) analysis the solid samples were subjected to an alkaline digestion followed ion chromatography. Liquid leachate samples were analyzed for arsenic species using either HPLC-HG-AFS or HPLC-ICP-MS. Hexavalent chromium was quantified using an ion chromatographic method followed by total chromium analysis. Cr(III) was determined by difference. In a fashion similar to the solid samples, the liquid leachate samples were analyzed for total metals (As, Cr, and Cu) using an acid digestion followed by ICP-AES.

pH Stat

The “pH stat” experiment focused on evaluating the distribution of different arsenic and chromium species with changes in pH. Samples used in this experiment were subjected to an analysis procedure identical to the EPA standard TCLP test, except that a different solvent was used. The solvent consisted of weak mineral acids mixed in various proportions to provide a range of different pH values. Two types of CCA-treated wood were evaluated, new CCA-treated wood at a measured retention level of 0.19 pcf (for sawdust collected from the entire wood cross-section) and weathered CCA-treated wood with a corresponding retention level of 0.31 pcf. Results indicate that leaching of arsenic and chromium is enhanced at the pH extremes. Leaching within the near neutral was fairly constant with total arsenic concentrations in the 4 to 5 mg/L range and total chromium leaching in the 1 to 2 mg/L range. The weathered wood sample leached greater quantities of arsenic and chromium within the near neutral pH range than new wood. The enhanced leaching of weathered wood may be due to the higher retention level and/or due to the age of the wood. Of interest is the finding that As(III) was observed to leach

only from the weathered wood sample between a pH of 1 to 7. Cr(VI) was observed in both new and weathered wood at pH values greater than 9.

SPLP and TCLP Experiments

The SPLP and TCLP experiments simulate leaching due to rainfall and landfill conditions, respectively. Samples evaluated in this portion of the study included unburned wood and wood ash. The unburned wood included a set of unweathered wood samples at various rated retention levels (untreated wood, 0.25 pcf, 0.60 pcf, and 2.5 pcf wood) and a set of weathered wood samples which included an 18 year old utility pole and samples of recycled wood from 2 different C&D facilities. Results for unburned wood indicated that the weathered pole sample consistently leached a significant fraction of arsenic as As(III) in both the TCLP and SPLP tests. The unweathered samples leached much smaller quantities of As(III). Chromium leached from these samples as Cr(III). No Cr(VI) was detected in the leachates from the unburned wood samples. Total chromium concentrations leached from these samples were consistently below 3 mg/L. The maximum amount of total arsenic leached from the unburned wood samples was roughly 10 mg/L. Leachates from the 0.6 pcf, 2.5 pcf, and pole samples exceeded 5 mg/L total arsenic and the leachate from the 0.25 pcf sample was near 5 mg/L.

One distinguishing feature of the ash evaluated in this study was the high metals concentrations released from these samples as compared to the unburned samples. Concentrations on the order of 100's mg/L for arsenic and 10's mg/L for chromium were observed. Another distinguishing feature of these samples was the speciation as compared to the unburned wood. In this case, the samples with the highest concentrations of total arsenic in the solid phase (e.g. the 2.5 pcf-ash sample) were characterized by the greatest releases of total arsenic and As(III). Chromium speciation was very peculiar. Chromium was leached from the ash almost entirely as Cr(VI) as opposed to leachates from the unburned wood which were characterized by solely Cr(III). The leaching of chromium from the ash samples was found to be strongly dependent upon pH of the leaching solution. The higher the pH the greater the quantity of chromium as Cr(VI) leached. The pH effect is likely influenced by the retention level of the wood. Wood samples with high retention levels (e.g. 2.5 pcf) had lower pH values in the leachates from the ash samples. Wood samples with low retention levels (e.g. 0.25 pcf and the C&D samples) had ash leachates characterized by high pH values. Given that the CCA solution is acidic, the greater the quantity of chemical in the wood the lower the pH values of the resulting leachate. As a consequence, samples characterized by lower retention levels (e.g. higher pH values) were characterized by greater quantities of chromium leached. This resulted in the peculiar data where ash samples containing lower concentrations of total chromium in the solid phase, leached greater quantities of chromium.

Lysimeters

Six lysimeters, 1 foot in diameter and 22 feet tall, were operated for a period of approximately 18 months. Two lysimeters simulate wood monofills, two simulate C&D landfills, and two simulate MSW landfills. Each set of two lysimeters were identical except that the wood component in one was untreated and the other was CCA-treated. Thus an untreated control was maintained within each set to quantify the impacts from the CCA component within each type of waste. Speciation was conducted only for arsenic within this task. Results showed that the quantities of arsenic leached from the lysimeters containing CCA-treated wood were significantly higher than the quantities leached from the lysimeters containing solely untreated

wood. The average concentration of total arsenic from the monofill, C&D, and MSW lysimeters containing CCA-treated wood was 29, 1.8, and 0.9 mg/L, respectively. The concentrations leached from the control lysimeters was less than 0.2 mg/L. The cumulative quantities of arsenic leached was on the order of 1,400 mg, 120 mg, and 85 mg for the monofill, C&D, and MSW lysimeters containing CCA-treated wood, respectively. The control lysimeters containing predominantly untreated wood leached less than 18 mg of total arsenic. Of interest is that the organic arsenic species, DMAA, predominated the speciation of arsenic from the untreated control lysimeters. As(V) predominated the speciation of the monofill and C&D lysimeters containing CCA-treated wood. As(III) predominated the speciation of the MSW lysimeter with added CCA-treated wood.

Groundwater Sampling

Groundwater sampling in the vicinity of 21 unlined C&D debris disposal facilities was undertaken in an effort to determine whether or not arsenic is elevated at these facilities beyond background concentrations. The presumption is that CCA-treated wood has been disposed at these facilities and that the arsenic from the CCA-treated wood may be starting to impact groundwater at the monitoring wells located at the site. Of the 48 samples collected from compliance/detection wells, 21 were found to contain total arsenic concentrations greater than the 5 ug/L detection limit. Of these samples, 6 were characterized by concentrations greater than 20 ug/L. These 6 samples came from 3 separate facilities. For these samples it was difficult to determine from the data collected whether or not the arsenic observed in the wells was coming from the C&D debris disposal facilities given that the background arsenic concentration from one of the facilities was elevated and no background sample was available from the second facility. Of interest is that the organic arsenic species (DMAA and MMAA) were the predominant arsenic species in groundwater from the one C&D facility with elevated background concentrations. The predominant arsenic species in groundwater at the other two facilities were As(III) and As(V). This difference in speciation was interesting and suggests perhaps a difference in source.

Overall

Results of this study suggest that arsenic that leaches from CCA-treated wood leaches primarily as either As(V) or As(III). Chromium predominantly leaches as Cr(III). If the wood is burned, arsenic speciation of the leachates are consistent with that of the unburned wood with As(V) and As(III) predominating, but chromium speciation of the leachates converts almost exclusively to Cr(VI). The degree of Cr(VI) leaching from ash is highly dependent upon the pH of the ash leachate. The pH effect is likely due to the CCA chemical itself which is acidic, so samples with high pH are characterized by low CCA retention levels and as a consequence are also characterized by a greater amount of chromium leaching. Results of this study also showed that more As(III) leaches from weathered wood than from unweathered wood. The conversion of arsenic from As(V) to As(III) with weathering may enhance the leaching of arsenic from treated wood as it weathers. Furthermore, results also suggest that arsenic that leaches from untreated wood is predominately in the less toxic organic form (DMAA), whereas arsenic that leaches from CCA-treated wood is in the more toxic As(V) and As(III) forms. Consistent with this observation are the results from the groundwater sampling effort which found that arsenic as As(V) and As(III) in groundwater from C&D debris disposal facilities with low background levels of arsenic, whereas the organic species predominated (DMAA and MMAA) in

groundwaters where high background levels were observed. These differences in speciation may indicate a different source.

Results of this study confirm that CCA-treated wood and CCA-treated wood ash exceed the 5 mg/L regulatory level for total arsenic leaching as given by the TCLP test. Given these observations, CCA-treated wood ash should be classified as a hazardous waste. CCA-treated wood would be classified as a hazardous waste if the regulatory exemption were not provided for this material. Furthermore, it is of interest to note that the CCA monofill lysimeter leached arsenic in quantities much greater than the 5 mg/L regulatory limit. If CCA-treated wood were thus disposed in monofills, the leachate would be considered a hazardous waste thereby increasing the costs for this particular disposal scenario. The elevated total arsenic concentrations in the monofill leachate would thus be a deterrent to this form of disposal.

VII.2 RECOMMENDATIONS

This study did not provide data concerning the speciation of leachates from CCA-treated wood in service. Such data would be helpful in evaluating whether or not runoff from existing CCA-treated structures represents a possible health problem. It is also of interest to evaluate the speciation of chromium and arsenic leachates as they travel through different soils. Evaluating the degree to which different soils are capable of binding the metals would be useful in evaluating potential groundwater impacts from leachates from CCA-treated wood. This study did not speciate arsenic within the solid phase. It would be of interest to develop methods for such analysis.

The observation that the organic species arsenic (DMAA) was observed to dominate speciation from the untreated lysimeter versus the dominance of As(III) and As(V) from the CCA-treated wood lysimeter was a very intriguing find. It would be of interest to conduct further analysis to confirm this observation.

The finding that weathered CCA-treated wood releases significant quantities of arsenic was also an interesting observation. It would be helpful to conduct experiments with additional weathered and unweathered wood samples to reconfirm this observation. Once reconfirmed, research should focus on the mechanisms of arsenic conversion during weathering. Such mechanisms would be helpful in developing strategies for the removal of arsenic from contaminated wood.

It would be of interest to evaluate the mechanisms that cause the change in chromium speciation from Cr(III) to Cr(VI) when the wood is burned. Results suggest that decreasing the pH of the wood ash sample would limit the leaching of Cr(VI) regardless of the amount of chromium initially in the sample. Perhaps a new disposal technology for chromium contaminated waste can take advantage of the pH effect by adding a chemical prior to combustion which lowers the pH of the result ash, thereby limiting the leaching of chromium.

VII.3 ACKNOWLEDGMENTS

Funding for this project was received from the Florida Center for Solid and Hazardous Waste Management, the Florida Department of Environmental Protection, and the National Institutes of Environmental Health Sciences (Grant No. S11ES11181-03). The authors gratefully acknowledge the project's technical awareness group (TAG) and TAG meeting participants for their guidance and feedback. A list of technical awareness group (TAG) members along with a list of TAG meeting attendees are provided in Appendix D.

The research team gratefully acknowledges the assistance received from the FDEP in promoting participation among the C&D facility owners for this project. Richard Tedder was an incredible help in getting the permissions initiated. Without his assistance, the C&D groundwater sampling effort would not have occurred. The research team also gratefully acknowledges the assistance received from the FDEP district offices. We gratefully acknowledge the assistance received from Mary Nogas and Sally Heuer of the Northeast District; James Bradner, Saadia Qureshi, and Laxamee Levin of the Central District; Susan Pelz of the Southwest District; Phil Barbaccia of the South District; OJ Carlo of the Southeast District; and John Hickey of Miami-Dade DERM. We especially thank the participation of the Northwest District FDEP Office which served as our intermediary with the C&D facilities within that area. The effort within the Northwest District was led by Charlie Reyes with the assistance of Jack McNulty, David Grimes, Larry Ritchie, and Rick Prusa. The research team would also like to thank the cooperation of the numerous consultants who hosted our “tag alongs” or who collected the samples on behalf of the research team. It is emphasized that the C&D facility consultants were extremely cooperative and helpful and in many cases went much beyond our expectations in providing us with assistance. (The names of these consultants are not included here in order to maintain the confidentiality of the facilities that provided samples.) The research team would also like to thank Alachua County for permission to install the lysimeters at their landfill site. The team also thanks Great Southern Wood Preservation for providing the untreated wood used in the lysimeters and thank Palm Beach County SWA for provision of the RDF used in the MSW lysimeters. The following students also assisted with various aspects of this project and we are also appreciative of their assistance: Gary Jacobi, Sanna Gaspard, Tomoyuki Shibata, Sheena Szuri, Myron Georgiadis, Zhangrong Chen, and Thabet Tolaymat.

The web page developed for this project (www.ccaresearch.org) was maintained through the Florida Center for Solid and Hazardous Waste Management (FCSHWM). The dedicated staff from the FCSHWM also handled numerous information requests associated with this project.

This page left intentionally blank.

REFERENCES

- American Wood Preservers' Association, 1999. *American Wood Preservers' Association Book of Standards*. American Wood Preservers' Association, Grandbury, TX.
- American Wood Preservers' Institute, 1999. *The 1998 Wood Preserving Industry Production Statistical Report*. American Wood Preservers' Institute, Fairfax, Virginia.
- Ball, J. W., and Nordstrom, D.K., 1998. "Critical evaluation and selection of standard state thermodynamic properties for chromium metal and its aqueous ions, hydrolysis species, oxides, and hydroxides." *Journal of Chemical Engineering and Data*, (43): 895-918.
- Barceloux, D. G., 1999. "Chromium." *Clinical Toxicology* 37(2): 173-194.
- Barnhart, J., 1997. "Occurrence, uses, and properties of chromium." *Regulatory Toxicology and Pharmacology* (26): S3-S7.
- Benramdane, L, Bressolle. F. and Vallon, J.J., 1999. "Arsenic speciation in humans and Food Products: a review." *Journal of Chromatographic Science*, 37:330-344.
- Cooper, P.A., 1991. "Leaching of CCA from treated wood; pH effects." *Forest Products Journal*, 41:1;30-32.
- Del Razo, L.M., Styblo, M., Cullen, W.R., and Cullen, D.J., 2001. "Determination of trivalent methylated arsenicals in biological matrices." *Toxicology and Applied Pharmacology*, 174, 282-293.
- Eary, L.E., and Rai, D., 1987. "Kinetics of chromium(III) oxidation to chromium(VI) by reaction with manganese dioxide." *Environmental Science and Technology*, (21): 1187-1193.
- Francesconi, K.A. and Edmonds, J.S., 1994. "Determination of arsenic species in marine environmental samples." In: *Arsenic in the Environment. Part I: Cycling and Characterization* edited by Jerome O. Nriagu. John Wiley and Sons, Inc., New York.
- James, B. R., 1996. "The challenge of remediating chromium-contaminated soil." *Environmental Science and Technology*, 30(6): 248A-251A.
- Jang, Y.C., 2000. *A Study of Construction and Demolition Waste Leachate from Laboratory Landfill-Simulators*. PhD dissertation, University of Florida, Gainesville, FL.
- Katz, S. A., and Salem, H., 1993. "The toxicology of chromium with respect to its chemical speciation: a review." *Journal of Applied Toxicology*, 13(3): 217-224.
- Kim, J. G., Dixon, J.B., Chusuei, C.C., and Deng, Y, 2002. "Oxidation of chromium(III) to (VI) by manganese oxides." *Soil Science Society American Journal*, (66): 306-315.

Korte, N.E. and Fernando, Q., 1991. A review of arsenic (III) in groundwater. *Critical Reviews in Environmental Control*, 21, 1-40.

Le, X.C., Yalcin, S., and Ma, M., 2000. "Speciation of submicrogram per liter levels of arsenic in water: on-site species separation integrated with sample collection." *Environmental Science Technology*, 34:2342-2347.

Naqvi, S. M., Vaishnavi, C. and Singh, H., 1994. "Toxicity and metabolism of arsenic in vertebrates." In: *Arsenic in the Environment. Part II: Human Health and Ecosystem Effects*, edited by Jerome O. Nriagu. John Wiley and Sons, Inc., New York.

Pantsar-Kallio, M. and Manninen, P.K.G., 1997. "Speciation of mobile arsenic in soil samples as a function of pH." *The Science of the Total Environment*, 204:193-200.

Pohland, F.G., Karadagli, F., Kim, J.C., and Battaglia, F.P., 1998. "Landfill codisposal of pentachlorophenol (PCP)-treated waste wood with municipal solid waste," *Water Science Technology*, 38(2): 169-175.

Rai, D., Eary, L.E., and Zachara, J.M., 1989. "Environmental chemistry of chromium." *The Science of the Total Environment*, (86): 15-23.

Schnoor, J.L., 1996. *Environmental Modeling. Fate and Transport of Pollutants in Water, Air, and Soil*. John Wiley & Sons. New York, NY.

Seiler, H.G., Sigel, A., and Sigel, H., 1994. *Handbook on Metals in Clinical and Analytical Chemistry*. Marcel Dekker, New York, New York.

Solo-Gabriele, H., Townsend, T., Calitu, V., Messik, B., and Kormienko, M., 1999. *Disposal of CCA-Treated Wood: An Evaluation of Existing and Alternative Management Options*. Florida Center for Solid and Hazardous Waste Management, Gainesville, FL.

Solo-Gabriele, H., Townsend, T., Kormienko, M., Gary, K., Stook, K., Tolaymat, T., 2000. *Alternative Chemicals and Improved Disposal-End Management Practices for CCA-Treated Wood*. Florida Center for Solid and Hazardous Waste Management, Gainesville, FL.

Solo-Gabriele, H.M., Townsend, T., Hahn, D, Hosein, N., Jacobi, G., Jambeck, J., Moskal, T., Iida, K., 2001. *On-Line Sorting Technologies for CCA-Treated Wood*. Florida Department of Environmental Protection, Innovative Recycling Grants Program, Tallahassee, FL.

Solo-Gabriele, H.M., Townsend, T.G., Messick, B., Calitu, V., 2002. Characteristics of chromated copper arsenate-Treated Wood Ash. *Journal of Hazardous Materials*, B89: 213-232.

Squibb, K.S. and Fowler, B.A., 1983. "The toxicity of arsenic and its compounds." In B.A. Fowler (Ed.), *Biological and Environmental Effects of Arsenic*. Elsevier, Amsterdam, 233-263.

Tolaymat, T.M., Townsend, T.G., and Solo-Gabriele, H., 2000. "Chromated Copper Arsenate Treated Wood in Recovered Wood at Construction and Demolition Waste Recycling Facilities." *Environmental Engineering Science*, 17(1): 19-28.

Townsend, T.G. Townsend, T., Stook, K., Tolaymat, T., Song, J.K., Solo-Gabriele, H., Hosein, N., Khan, B., 2001. *New Lines of CCA-Treated Wood Research: In-Service and Disposal Issues*. 2001. Florida Center for Solid and Hazardous Waste Management, Gainesville, FL. Report #00-12.

U.S. Environmental Protection Agency, 1996. *Test Methods for Evaluating Solid Waste, SW846, 3rd edition*. Office of Solid Waste and Emergency Response, Washington D.C.

Warner, J.E. and Solomon, K.R., 1990. Acidity as a factor in leaching of copper, chromium and arsenic from CCA-treated dimension lumber. *Environmental Toxicology and Chemistry*, 9:1331-1337.

Yamauchi, H. and Fowler, B.A., 1994. Toxicity and metabolism of inorganic and methylated arsenicals. In: *Arsenic in the Environment. Part II: Human Health and Ecosystem Effects* edited by Jerome O. Nriagu. John Wiley and Sons, Inc., New York.

This page left intentionally blank.

**APPENDIX A,
SEPARATION OF ARSENIC SPECIES BY ION-EXCHANGE
CARTRIDGES**

This page left intentionally blank.

APPENDIX A, SEPARATION OF ARSENIC SPECIES BY ION-EXCHANGE CARTRIDGES

When a solution containing charged ions is passed through a series of cation- and anion-exchange cartridges (Figure A.1), positively and negatively charged ions are removed from the solution, respectively. The cartridges are not arsenic specific and can be used to separate many other elements. Some researchers have recommended using them in the field to separate arsenic species in aqueous environmental samples prior to analysis. Separation of species serves to reduce the presence of interfering ions and lessens the analytical time by eliminating the use of HPLC for separation.

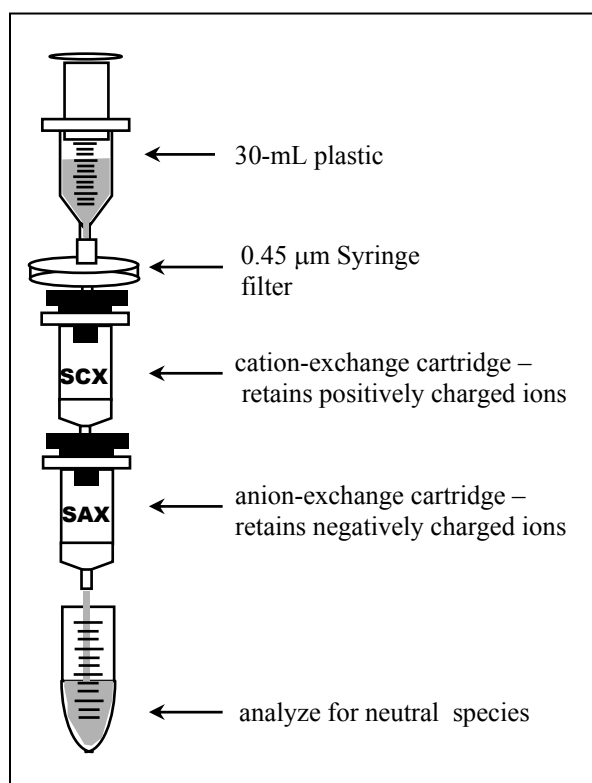


Figure A.1: Ion-exchange Cartridge in Series

Korte and Fernando, 1991, in the article “A Review of Arsenic (III) in Groundwater” show that arsenic species vary in accordance with pH. From Figure A.2, at a pH range of 6 to 8, the pH value of most environmental samples, As(III) is present as a neutral species and the species As(V), MMAA and DMAA exist as negatively-charged ions.

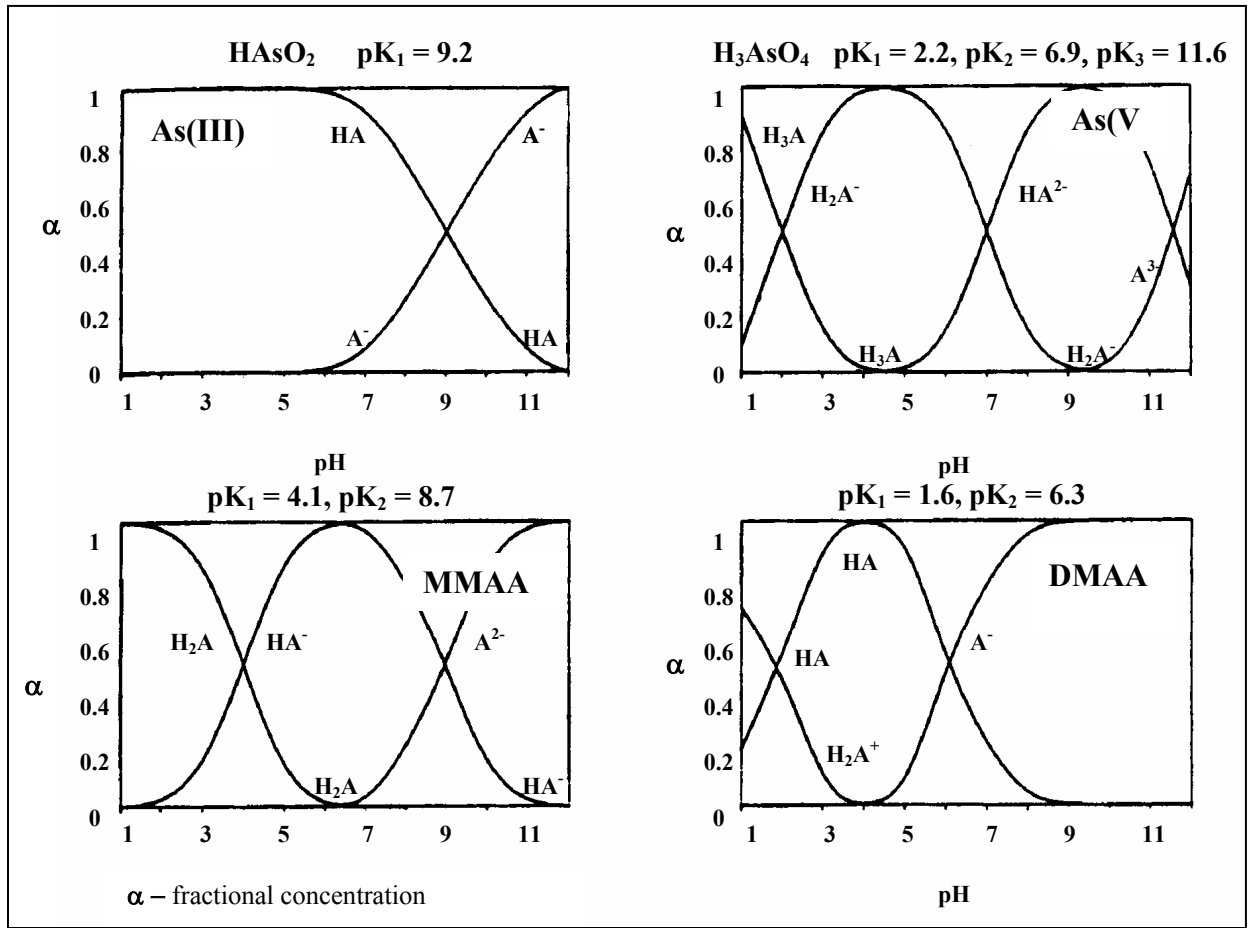


Figure A.2: Fractional Concentrations of Arsenic Species Plotted as a Function of pH (Korte and Fernando, 1991)

Based upon this fact alone, the ion-exchange cartridge system described above can theoretically separate out As(III) successfully but would fail in the separation of As(V), MMAA, and DMAA because these three species would all collect within the anion-exchange cartridge making it difficult to separate. There has been some discrepancy among researchers as to whether DMAA is a positively- or negatively-charged ion at the working pH range. Le et al., 2000, in their article entitled, "Speciation of Submicrogram per Liter Levels of Arsenic in Water: On site Species Separation Integrated with Sample Collection" described how they successfully separated the four arsenic species using the ion-exchange cartridges with the supposition that DMAA was a positively-charged species. By connecting the cartridges in series, they claimed to successfully remove DMAA using the cation-exchange cartridge, As(V) and MMAA using the anion-exchange cartridge and As(III), which was not retained on either cartridge, was retained in solution. Once the species were captured within their respective cartridges, they were eluted with acid and analyzed by AFS. One major drawback of this study is that nowhere in the article do the researchers mention the role pH plays with speciation. Le et al., 2000, treats DMAA as a cation, whereas, Korte et al., 1991, indicates this species as an anion at the working pH.

The task initiated in this study focused on determining the charge of DMAA and to whether the four major arsenic species, As(III), As(V), MMAA, and DMAA can be separated successfully with the use of ion-exchange cartridges.

A.1 METHODS

Resin-based cation-exchange cartridges and silica-based anion-exchange cartridges were purchased from Supelco and PVDF membrane filters (0.45 μm pore size, 13 mm) and 30-mL graduated syringes were obtained from VWR Scientific. The ion-exchange cartridges were preconditioned with 50% methanol and deionized water before use. A standard containing 20 $\mu\text{g/L}$ each of the four species, As(III), As(V), MMAA, and DMAA, was prepared and passed through a cation-exchange and a anion-exchange cartridge (Figures A.3 and A.4). The filtrates were collected after each cartridge and analyzed for arsenic species by HPLC-HG-AFS. The cation-exchange cartridges were eluted with 1.0 M HCl to release any DMAA that may be present, and the anion-exchange cartridges were eluted sequentially with 60 mM acetic acid (for MMAA) and then 1.0 M HCl (for As(V)). The eluent from the cartridges were analyzed for the percent arsenic recovery by HPLC-HG-AFS.

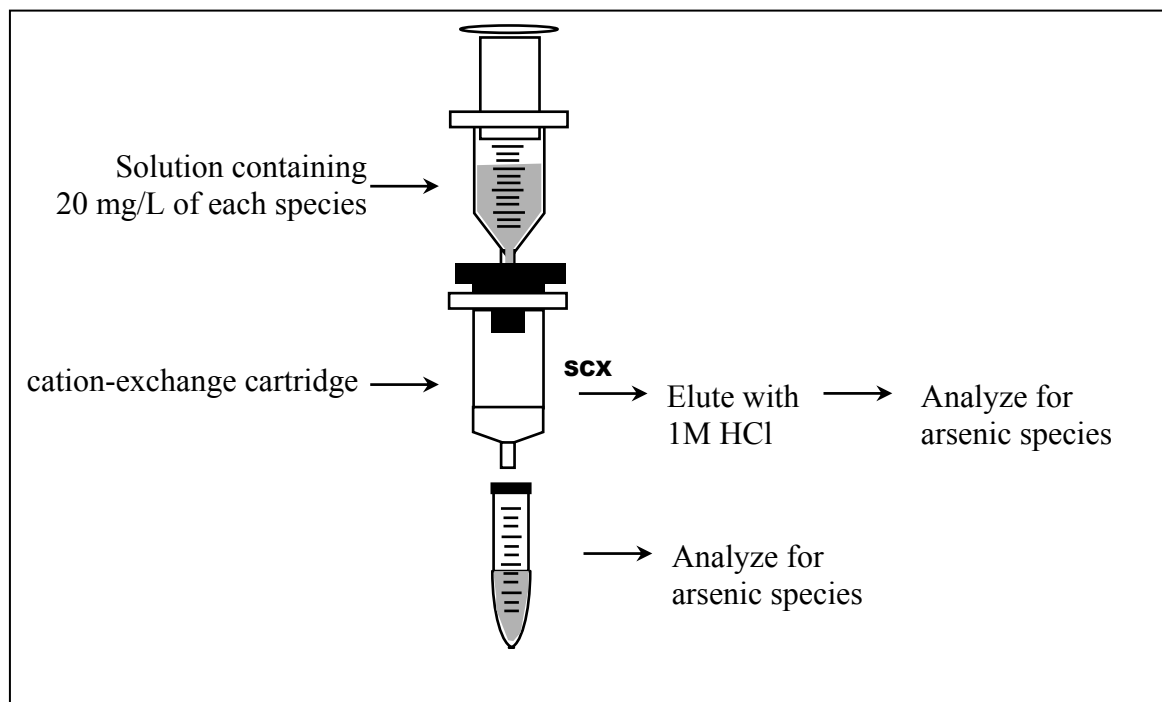


Figure A.3: Outline of the Cation-Exchange Cartridge Experiment

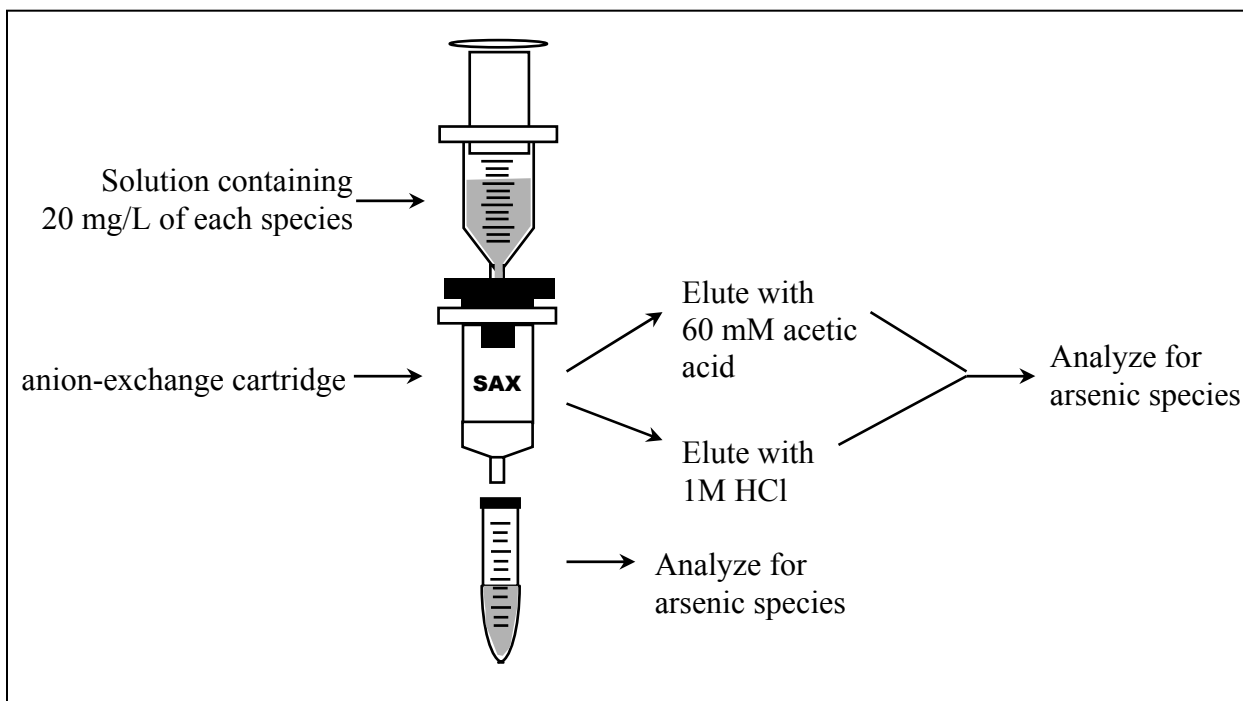


Figure A.4: Outline of the Anion-Exchange Cartridge Experiment

A.2 RESULTS AND DISCUSSION

Arsenic Specie	Filtrate after SCX ^a	Filtrate after SAX ^b	Elute SCX	Elute SAX
As(III)	59%	91%	-	-
As(V)	99%	-	-	97%
MMAA	100%	-	-	98%
DMAA	88%	53%	-	-

^aSCX- cation-exchange, ^bSAX – anion-exchange

Table A.1: Percent Recovery of Arsenic Species from Experiments with Ion-Exchange Cartridges

Both filtrates and eluents were analyzed for all four arsenic species (Table A.1). The filtrate from the cation-exchange cartridge showed predominately As(V), MMAA, and DMAA. If DMAA was a positively-charged specie than there should be no DMAA in this filtrate. The presence of As(V) and MMAA in this filtrate confirms the fact that they are not positively-charged species. Although, As(III) is a neutral specie, only 59% was recovered in the filtrate. There may be some interference with the SCX cartridge resin because according to Figure A.2, As(III) is either a negatively-charged or neutral specie.

When the filtrate from the anion-exchanged cartridge was speciated, once again the results confirmed the negative nature of both As(V) and MMAA. As(III) recovery is almost complete suggesting that it is indeed a neutral specie. DMAA recovery, however, should be close to 100% if it is a positively-charged specie but the results indicate that some of it is negatively-charged.

The eluent from the cation-exchange cartridge was lost, however, the eluent from the anion-exchange cartridge confirms that both As(V) and MMAA are negatively-charged species.

Overall, the results have successfully shown that both As(V) and MMAA are negative species, DMAA shows tendency toward being both anionic and cationic species, and As(III) may be subjected to matrix interference of the cation cartridge. The results of the experiment were inconclusive and use of the cartridges was found to be problematic. The ion-cartridges may not be applicable to all elements, as they were not designed specifically for arsenic. They were therefore dispensed with and not utilized in any of the experimentation described in the main report within this research study.

This page left intentionally blank.

**APPENDIX B,
DATA LOG SHEET FOR GROUNDWATER SAMPLING STUDY**

This page left intentionally blank.

UNIVERSITY OF MIAMI SAMPLING DATA SHEET (UMSDS)

Please send 1) completed UMSDS, 2) map of the landfill layout (indicating sample locations and groundwater flow arrow), and 3) the most recent arsenic data on all samples collected. **Ship as soon as possible. Keep samples on ice or cold.**

CONSTRUCTION & DEMOLITION LANDFILL INFORMATION:

Landfill Name: _____ Contact Person: _____

Address: _____

Phone No.: _____ Fax No.: _____

Email: _____

Type of Waste Accepted at Landfill: _____

Is Wood Collected at Landfill? _____ Is it lined or unlined? _____

Volume collected: 2 liters per site Sampled by: _____

Date collected (m/d/yr) : _____

GROUNDWATER SAMPLES

Sample ID*	pH	Temp. (°C)	ORP (mV)	Conductivity (µS/cm)	DO (mg/L)	Turbidity (ntu)

NOTES:

(Sample appearance (e.g. color) or any information that might affect sample content (e.g. previous heavy rains): _____

PLEASE SHIP SAMPLE AS SOON AS POSSIBLE VIA FEDEX 1-800-463-3339

Add enough ice packing to last travel time.

FEDEX Account No: XXXXX

Tracking No: _____

Ship to: University of Miami, c/o: Bernine Khan - Civil, Architectural & Environmental Engineering, 1251 Memorial Drive, McArthur Bldg, Rm. 325, Coral Gables, FL 33146-0630

ANY QUESTIONS: H. Solo-Gabriele, 305-284-3489, hmsolo@miami.edu, Fax 305-284-3492.

This page left intentionally blank.

**APPENDIX C,
SUPPLEMENTAL DATA FROM LYSIMETER STUDY**

This page left intentionally blank.

Date Collected	Volume Collected (mL)	pH	DO (mg/L)	Temp (°C)	Cond (uS/cm)	ORP (mV)	HPLC-ICP-MS					ICP-AES		
							As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)	Total Cr (mg/L)	Total Cu (mg/L)
Aug. 6, 02	1545	6.18	1.55	25.9	517	-405	Trace ^b	ND ^a	Trace	0.009	0.013	0.012	0.004	0.008
Aug. 21, 02	125	6.28	3.35	25.1	NS	-413	Trace	ND	Trace	ND	Trace	NS	NS	NS
Sep. 6, 02	75	6.32	4.00	27.1	NS	-295	0.015	0.01	Trace	ND	>0.025	NS	NS	NS
Sep. 25, 02	50	6.60	5.44	25.6	NS	-239	NS ^c					NS	NS	NS
Oct. 14, 02	4025	6.04	1.05	22.4	685	-404	Trace	ND	0.007	ND	>0.012	0.016	0.005	0.003
Oct. 30, 02	7175	5.65	1.27	26.8	538	-241	0.008	0.005	0.009	ND	0.021	0.021	0.007	ND
Nov. 18, 02	4075	6.11	1.74	10.5	434	-292	Trace	0.006	0.010	Trace	>0.018	0.030	0.006	0.003
Dec. 2, 02	1275	5.83	1.63	12.3	384	-300	Trace	ND	0.008	ND	>0.011	0.017	0.004	0.012
Dec. 20, 02	3775	5.85	1.89	22.2	220	-255	Trace	0.017	0.012	ND	>0.032	0.016	0.005	0.005
Jan. 7, 03	3450	5.81	1.68	9.8	174	-370	0.019	0.024	ND	ND	0.043	0.023	0.005	0.016
Jan. 27, 03	1850	5.76	4.17	10.2	203	-362	0.005	0.009	ND	ND	0.014	0.012	0.004	0.012
Feb. 10, 03	250	5.99	3.82	19.0	248	-213	NS					0.016	0.005	0.016
Mar. 10, 03	5750	5.15	1.90	20.7	263	-411	0.006	0.007	0.013	ND	0.027	0.036	0.011	0.014
Mar. 25, 03	2800	5.43	1.33	22.9	303	-308	Trace	0.005	0.015	ND	>0.023	0.030	0.011	0.010
Apr. 21, 03	3100	5.61	0.89	27.7	242	-514	Trace	ND	0.019	ND	>0.023	0.022	0.009	0.009
May 9, 03	2150	5.53	1.2	33.1	254	-234	Trace	0.007	0.0086	Trace	>0.011	0.024	0.008	0.007

^aND = Not Detected (Detection limit for ICP-AES: 0.011 mg/L for As; 0.004 mg/L for Cu; 0.003 mg/L for Cr)

^bTrace = <0.005 mg/L

^cNS = No Sample Available

Table C.1: Results for Lysimeter 1 (Monofill no CCA)

Date Collected	Volume Collected (mL)	pH	DO (mg/L)	Temp (°C)	Cond (uS/cm)	ORP (mV)	HPLC-ICP-MS					ICP-AES		
							As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)	Total Cr (mg/L)	Total Cu (mg/L)
Sep. 28, 01	620	6.67				65	NS ^c					3.78	0.705	0.122
Jan. 28, 02	1880	6.24	3.15	23.9	1001	135	Trace ^b	4.85	Trace	ND ^a	4.85	5.31	0.958	0.243
Apr. 2, 02	1330	5.58	3.4	24	747	102	0.075	4.29	0.12	ND	4.48	6.25	0.934	0.273
May 16, 02	2710	6.57	-	-	510	-21	NS					6.55	0.449	0.0634
Jun. 12, 02	392	6.64	2.71	31.1	815	134	Trace	3.50	ND	ND	3.50	14.8	0.568	0.177
Jun. 25, 02	4200	5.63	0.95	29.5	430	76	0.58	3.61	ND	ND	4.19	32.0	3.32	0.446
Jul. 17, 02	2090	5.56	2.75	33.7	413	-301	8.33	24.93	ND	ND	33.3	37.1	4.27	0.488
Aug. 6, 02	7125	5.53	1.54	26	427	-230	40.78	2.15	ND	ND	42.9	48.8	8.82	4.76
Aug. 21, 02	2000	5.37	2.14	24.6	280	-273	ND	23.60	ND	ND	23.6	26.8	4.11	0.893
Sep. 6, 02	4150	5.96	1.37	27.2	287	-240	28.07	2.26	ND	ND	30.3	28.2	4.21	0.869
Sep. 25, 02	1650	6.2	4.16	25.6	357	-299	ND	28.12	ND	ND	28.1	31.6	6.09	0.618
Oct. 14, 02	3540	5.89	1.1	23.4	346	-410	6.42	16.59	ND	ND	23.0	29.4	5.10	0.613
Oct. 30, 02	3200	5.87	1.02	25.8	451	-241	19.71	22.03	Trace	ND	>41.7	45.5	9.29	0.668
Nov. 18, 02	445	5.50	4.06	11.7	514	-344	Trace	24.08	Trace	ND	>24.2	33.5	6.69	1.69
Dec. 2, 02	2650	5.46	1.76	12.5	411	-200	Trace	23.11	Trace	ND	>23.1	35.9	9.64	1.35
Dec. 20, 02	3300	5.52	1.71	20.4	427	-354	0.67	24.09	ND	ND	24.8	32.5	9.36	2.61
Jan. 7, 03	3500	5.50	1.62	10.9	434	-95	ND	39.97	ND	ND	40.0	55.4	13.7	1.57
Jan 27, 03	3550	5.49	1.38	11.4	344	-264	2.61	24.07	ND	ND	26.7	29.4	6.74	1.68
Feb. 10, 03	1225	5.49	3.29	19.1	338	-67	NS					42.4	10.8	6.86
Mar. 10, 03	9675	4.92	1.06	22	442	-383	18.06	37.63	ND	ND	55.69	64.6	14.8	3.01
Mar. 25, 03	2900	5.14	0.94	20.7	416	-310	0.458	38.52	ND	ND	38.98	65.8	16.9	5.05
Apr. 21, 03	2600	4.99	0.8	27.1	374	-455	ND	33.28	ND	ND		49.0	10.6	4.13
May 9, 03	1850	5.35	1.7	33	327	-220	Trace	27.44	ND	ND		41.1	8.72	3.33

^aND = Not Detected (Detection limit for ICP-AES: 0.011 mg/L for As; 0.004 mg/L for Cu; 0.003 mg/L for Cr)

^bTrace = <0.005 mg/L

^cNS = No Sample Available

Table C.2: Results for Lysimeter 2 (Monofill with CCA)

Date Collected	Volume Collected (mL)	pH	DO (mg/L)	Temp (°C)	Cond (uS/cm)	ORP (mV)	HPLC-ICP-MS					ICP-AES		
							As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)	Total Cr (mg/L)	Total Cu (mg/L)
Jun. 25, 02	770	6.47	0.54	29.4	3.5	-238	ND ^a	ND	ND	ND	ND	NS	NS	NS
Jul. 17, 02	60	6.8	2.82	35.2	-	-249	NS ^c					NS	NS	NS
Aug. 6, 02	2510	6.76	0.49	26	3.5	-489	0.004	0.013	0.007	0.006	0.031	0.018	0.015	ND
Aug. 21, 02	150	6.88	5.23	26.3	2.74	-400	0.01	0.024	0.013	0.012	0.059	NS	NS	NS
Sep. 6, 02	700	6.64	0.39	27.1	3.33	-508	Trace ^b	Trace	0.013	0.012	>0.024	0.027	0.017	ND
Sep. 25, 02	250	7.5	0.36	25	3.3	-455	Trace	Trace	0.011	0.019	>0.042	0.028	0.018	ND
Oct. 14, 02	8790	6.84	0.1	22.6	4.19	-502	0.007	0.008	0.012	0.007	0.034	0.026	0.014	ND
Oct. 30, 02	12375	6.92	0.13	26.1	4.52	-518	0.005	0.005	0.001	0.017	0.028	0.021	0.011	ND
Nov. 18, 02	11350	6.96	1.14	11.8	4.11	-575	0.007	Trace	0.01	0.0064	>0.023	0.019	0.008	ND
Dec. 2, 02	6450	6.93	1.07	14.5	3.26	-506	0.004	ND	0.008	ND	0.012	0.012	0.005	ND
Dec. 20, 02	5850	6.9	0.91	19.6	3.89	-514	0.007	ND	0.015	ND	0.022	0.017	0.008	ND
Jan. 7, 03	6775	6.88	1.94	8.4	3.55	-513	0.020	ND	0.038	ND	0.057	0.020	0.009	ND
Jan. 27, 03	10725	6.57	2	10.6	3.18	-430	0.006	ND	0.012	ND	0.019	0.013	0.007	0.038
Feb. 10, 03	8150	6.65	1.79	18	3.31	-475	NS					0.013	0.008	0.018
Feb. 23, 03	9450	6.77	-	18.2	-	-356	NS					0.017	0.011	0.018
Mar. 10, 03	8150	6.58	0.07	22.5	4.15	-540	0.006	ND	0.012	ND	0.019	0.018	0.010	0.006
Mar. 25, 03	10250	6.71	0.06	24.8	3.95	-522	0.007	ND	0.014	0.006	0.020	0.016	0.010	0.006
Apr. 21, 03	4600	6.95	0.3	27.3	2.92	-522	0.012	ND	0.017	0.003	0.030	0.020	0.015	0.026
May 9, 03	2025	6.75	0.11	33.1	3.1	-327						0.030	0.018	0.008

^aND = Not Detected (Detection limit for ICP-AES: 0.011 mg/L for As; 0.004 mg/L for Cu; 0.003 mg/L for Cr)

^bTrace = <0.005 mg/L

^cNS = No Sample Available

Table C.3: Results for Lysimeter 3 (C&D Untreated Wood Only)

Date Collected	Volume Collected (mL)	pH	DO (mg/L)	Temp (°C)	Cond (uS/cm)	ORP (mV)	HPLC-ICP-MS					ICP-AES		
							As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)	Total Cr (mg/L)	Total Cu (mg/L)
Jun. 25, 02	300	6.73	0.74	29	4.3	-450	0.664	0.766	Trace ^b	Trace	>1.43	NS	NS	NS
Jul. 17, 02	100	6.74	2.54	35.2	5.48	-244	Trace	0.272	Trace	Trace	>0.272	NS	NS	NS
Aug. 6, 02	4330	6.83	0.4	26.4	4.6	-496	0.0288	0.258	0.0622	0.0464	0.40	1.09	0.3388	0.0732
Aug. 21, 02	300	6.79	0.38	26.9	3.84	-557	ND ^a	0.186	0.735	0.232	1.15	NS	NS	NS
Sep. 6, 02	2525	6.68	0.4	28.4	3.97	-464	Trace	0.168	0.402	0.251	0.821	1.24	0.5532	ND
Sep. 25, 02	650	7.32	0.84	24.7	3.54	-475	0.122	0.060	0.385	1.28	1.84	2.22	1.674	ND
Oct. 14, 02	10575	6.91	0.08	22.9	4.17	-589	0.0448	0.372	0.314	0.245	0.976	1.73	1.415	ND
Oct. 30, 02	13100	6.88	0.1	25.6	4.25	-659	0.005	0.0045	0.0013	0.0168	0.028	1.54	1.707	ND
Nov. 18, 02	10325	6.98	1.07	12.7	3.60	-479	0.273	0.281	0.370	0.650	1.57	1.34	1.55	
Dec. 2, 02	3525	6.93	1.37	14.4	3.26	-448	0.0802	0.237	0.286	0.156	0.760	1.17	1.263	0.0099
Dec. 20, 02	2800	6.9	1.39	20.2	4.13	-454	0.0949	0.395	0.488	0.209	1.19	1.51	1.251	ND
Jan 7, 03	4600	6.87	1.81	8.4	3.73	-457	0.145	0.539	0.428	0.135	1.25	2.46	1.585	0.0567
Jan 27, 03	5300	6.64	1.21	9.2	3.43	-484	0.221	0.392	0.355	0.253	1.22	2.41	1.478	0.0273
Feb.10, 03	5125	6.85	1.29	17.3	3.83	-285	NS ^c					3.09	1.602	0.0505
Feb.23, 03	9250	6.73		17.8	-	-527	NS					3.99	2.115	0.0340
Mar.10, 03	7650	6.48	0.08	21.1	3.81	-574	0.0939	1.29	0.441	0.329	2.16	3.01	1.882	0.0153
Mar.25, 03	8350	6.83	0.43	24.3	3.37	-625	0.0995	0.672	0.408	0.546	1.73	2.31	1.377	0.0190
Apr.21, 03	4750	6.88	0.81	27.6	2.78	-672	0.051	0.864	0.562	1.01	2.48	3.00	1.056	0.0084
May 9, 03	2250	6.76	0.52	33.1	2.83	-468	0.0698	0.254	0.176	0.808	1.31	2.70	1.106	0.0086

^aND = Not Detected (Detection limit for ICP-AES: 0.011 mg/L for As; 0.004 mg/L for Cu; 0.003 mg/L for Cr)

^bTrace = <0.005 mg/L

^cNS = No Sample Available

Table C.4: Results for Lysimeter 4 (C&D With CCA-Treated Wood)

Date Collected	Volume Collected (mL)	pH	DO (mg/L)	Temp (°C)	Cond (uS/cm)	ORP (mV)	HPLC-ICP-MS					ICP-AES		
							As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)	Total Cr (mg/L)	Total Cu (mg/L)
Jun. 25, 02	2175	4.76	0.66	25.7	27.1	-126	0.741	ND ^a	Trace ^b	ND	>0.741	0.200	0.538	ND
Jul. 17, 02	3940	5.10	3.15	34.8	33.3	-504	ND	ND	ND	ND	ND	0.083	0.264	ND
Aug. 6, 02	10505	6.28	0.55	27.2	36.7	-550	Trace	ND	0.230	ND	0.230	0.116	0.276	ND
Aug. 21, 02	4800	6.33	0.47	28.2	39.4	-606	Trace	ND	Trace	Trace	Trace	0.124	0.206	ND
Sep. 6, 02	6800	6.98	0.24	27.2	30.3	-600	0.036	0.013	0.143	ND	>0.192	0.148	0.174	ND
Sep. 25, 02	3750	7.80	0.22	25.1	29.1	-649	0.028	Trace	0.150	ND	>0.187	0.198	0.208	ND
Oct. 14, 02	5000	7.54	0.14	22.6	31.4	-635	Trace	0.011	Trace	Trace	>0.011	0.251	0.240	ND
Oct. 30, 02	5000	7.53	0.12	25.1	29.9	-656	Trace	0.022	0.194	ND	0.216	0.290	0.258	ND
Nov. 18, 02	6700	7.48	0.45	13.9	27.8	-651	Trace	ND	0.168	ND	>0.168	0.235	0.208	0.013
Dec. 2, 02	5800	7.33	0.54	13.7	23.4	-600	0.008	ND	0.108	ND	0.116	0.187	0.162	0.049
Dec. 20, 02	8050	7.43	0.32	20.6	21.3	-590	0.018	ND	0.129	ND	0.147	0.130	0.118	0.015
Jan. 7, 03	7950	7.36	1.62	10.4	16.4	-584	0.093	ND	0.227	ND	0.320	0.140	0.103	0.107
Jan. 27, 03	4775	7.27	1.19	12.3	15.32	-409	0.039	ND	0.095	ND	0.134	0.138	0.106	ND
Feb.10, 03	3800	7.37	0.55	19.0	16.6	-600	NS					0.135	0.102	ND
Mar.10, 03	13200	7.05	0.80	21.2	14.8	-532	0.01	-	0.073	ND	0.083	0.115	0.126	0.030
Mar.25, 03	7850	7.37	0.53	23.1	14.7	-630	0.01	Trace	0.180	ND	0.19	0.113	0.117	0.030
Apr.21, 03	5875	7.33	0.69	26.7	13.4	-642	Trace	-	0.120	ND	>0.120	0.104	0.093	0.018
May 9, 03	3450	7.27	0.35	33	11.19	-387	0.018	-	0.099	ND	0.117	0.114	0.089	0.014

^aND = Not Detected (Detection limit for ICP-AES: 0.011 mg/L for As; 0.004 mg/L for Cu; 0.003 mg/L for Cr)

^bTrace = <0.005 mg/L

^cNS = No Sample Available

Table C.5: Results for Lysimeter 5 (MSW Untreated Wood Added)

Date Collected	Volume Collected (mL)	pH	DO (mg/L)	Temp (°C)	Cond (uS/cm)	ORP (mV)	HPLC-ICP-MS					ICP-AES		
							As(III) (mg/L)	As(V) (mg/L)	DMAA (mg/L)	MMAA (mg/L)	Total As (mg/L)	Total As (mg/L)	Total Cr (mg/L)	Total Cu (mg/L)
Jul. 17, 02	2090	4.40	1.60	33.9	34.3	-508	3.780	0.405	ND	ND		3.75	4.09	0.356
Aug. 6, 02	11,185	5.29	0.53	27.1	38.2	-545	2.071	0.261	ND	ND	2.33	2.43	1.61	ND
Aug. 21, 02	4690	5.98	0.37	26.0	39.8	-591	0.474	0.173	Trace	ND	> 0.647	0.793	0.635	ND
Sep. 6, 02	4975	5.84	0.34	28.2	39.4	-584	0.296	0.105	0.137	ND	0.537	NS	NS	NS
Sep. 25, 02	2750	6.10	0.47	25.4	36.4	-605	0.300	0.111	0.052	ND	0.463	0.793	0.324	ND
Oct. 14, 02	3900	6.11	0.35	23.6	38.9	-625	0.211	-	0.172	ND	0.383	0.549	0.311	ND
Oct. 30, 02	4550	6.85	0.12	25.6	32.1	-666	0.090	0.010	0.570	0.077	0.747	0.801	0.276	ND
Nov. 18, 02	6000	7.38	0.28	12.0	27.1	-664	0.074	0.096	0.389	0.043	0.602	0.541	0.338	0.532
Dec. 2, 02	5500	7.35	0.34	13.6	23.3	-610	0.074	0.080	0.212	0.063	0.428	0.446	0.325	0.003
Dec. 20, 02	4350	7.41	0.24	20.0	21.6	-611	0.104	0.127	0.361	0.101	0.693	0.374	0.170	ND
Jan. 7, 03	6250	7.43	0.42	10.4	19.5	-584	0.188	0.312	0.438	0.206	1.144	0.232	0.118	ND
Jan. 27, 03	5000	7.27	0.42	11.7	16.52	-418	0.199	0.472	0.390	0.240	1.301	0.324	0.194	ND
Feb. 10, 03	2125	7.29	0.26	18.4	17.3	-642						0.249	0.123	ND
Mar. 10, 03	12,600	7.10	0.27	21.5	17.1	-665	0.096	0.168	0.187	0.071		0.407	0.144	0.0437
Mar. 25, 03	8250	7.37	0.16	22.0	15.7	-670	0.027	0.354	0.282	0.147	0.810	0.781	0.149	0.0458
Apr. 21, 03	6300	7.28	0.24	26.7	14.3	-649	0.024	0.379	0.106	0.226	0.734	0.787	0.144	0.0304
May 9, 03	3000	7.24	0.18	32.8	11.84	-429	0.162	0.637	0.104	0.134	1.04	0.655	0.117	0.0189

^aND = Not Detected (Detection limit for ICP-AES: 0.011 mg/L for As; 0.004 mg/L for Cu; 0.003 mg/L for Cr)

^bTrace = <0.005 mg/L

^cNS = No Sample Available

Table C.6: Results for Lysimeter 6 (C&D With CCA-Treated Wood Added)

**APPENDIX D,
SUPPLEMENTAL QA/QC INFORMATION**

This page left intentionally blank.

Purpose: This appendix is intended to supplement the Quality Assurance – Quality Control (QA/QC) information provided in the text. This information is provided in the context of a research study that permits for flexibility in method development and analysis for the purpose of expanding the knowledge base.

Supervisory Structure

Three key faculty members provided oversight. These faculty members include Dr. Timothy Townsend of the University of Florida, who is an expert in solid waste management, Dr. Yong Cai of Florida International University, who is an arsenic chemist, and Dr. Helena Solo-Gabriele of the University of Miami, who is an expert in CCA-treated wood issues. All three faculty members have considerable experience conducting research projects. Dr. Timothy Townsend supervised Jin-Kun Song, Dr. Jenna Jambeck, Brajesh Dubey, and Dr. Yong-Chul Jang of the University of Florida. Dr. Yong Cai and Dr. Helena Solo-Gabriele supervised Dr. Bernine Khan of the University of Miami. Drs. Townsend, Cai, and Solo-Gabriele and their students would meet several times during the year to design the experiments and to discuss the progress of the study. They would also correspond frequently by telephone and email. Furthermore, Dr. Helena Solo-Gabriele served on the thesis committees of Brajesh Dubey, Jin-Kun Song, and Dr. Jenna Jambeck who were part of Dr. Townsend's group. Dr. Yong Cai served on the thesis committee of Dr. Bernine Khan who was part of Dr. Solo-Gabriele's group. The work contained within this report was the subject of several theses. A considerable amount of additional documentation concerning the methods and results of this study are provided in these theses and in corresponding conference proceedings and journal publications.

Dr. Timothy Townsend's group took the lead on the following items.

- pH stat experiments (conducted by Brajesh Dubey, Jin-kun Song and Dr. Bernine Khan. Dr. Bernine Khan went to Dr. Townsend's lab to conduct the experiments collectively with Brajesh Dubey and Jin-Kun Song.)
- TCLP and SPLP analysis (performed by Brajesh Dubey, Jin-kun Song and Dr. Bernine Khan. Dr. Bernine Khan went to Dr. Townsend lab to conduct the experiments collectively with Brajesh Dubey and Jin-Kun Song)
- Lysimeter study and all corresponding measurements with the exception of arsenic species (conducted by Dr. Jenna Jambeck)
- Chromium speciation analysis and experimental design for experiments requiring chromium speciation analysis (conducted by Jin-Kun Song)
- Total metals analysis of liquids and solids (conducted by Dr. Jenna Jambeck for the lysimeter study and Brajesh Dubey for the pH stat and TCLP/SPLP experiments.)

Dr. Yong-Chul Jang provided additional supervision and input concerning the chromium speciation study and the lysimeter work.

Dr. Yong Cai took the lead on the following..

- Arsenic speciation analysis (conducted by Dr. Bernine Khan at Dr. Cai’s laboratory). Arsenic speciation analysis was conducted on the leachates from the pH stat experiments, TCLP, SPLP, lysimeter samples, and groundwater samples near C&D facilities.

Dr. Helena Solo-Gabriele took the lead on the following plus the overall lead on the project.

- Coordinating sample collection in the vicinity of C&D facilities. These samples were analyzed for arsenic species by Dr. Bernine Khan. Total arsenic was measured by commercial laboratories as contracted by the C&D operators.
- Experimental design for projects requiring arsenic speciation analysis.

All three faculty members (Townsend, Cai, and Solo-Gabriele) would provide oversight on all aspects of the work contained in this report. Dr. Helena Solo-Gabriele served as the lead on this oversight. Furthermore, throughout the course of this project, the interim results were presented during public meetings during which feedback was obtained concerning experimental design and results.

Laboratory Analyses

Laboratory analysis in this study followed: a) methods standardized by regulatory agencies and b) methods employed by the research community. Methods standardized by the regulatory agencies were used for processing samples (e.g. TCLP and SPLP). Modifications of these methods were utilized to evaluate the impact of pH on metals leaching (e.g. pH stat test). Methods standardized by regulatory agencies were used for the analysis of traditional analytes (e.g. total metals in liquid and solid samples) and for chromium species analyses. Arsenic speciation analysis followed protocols that were utilized by the research community. The method for arsenic speciation analysis was chosen after the completion of a literature review. This literature review is documented in Townsend et al. 2001.

The protocols utilized for pre-processing samples and for metals analysis are described in the text of this report and are summarized in the tables D.1 and D.2 below.

Regulatory/Standardizing Agency Developing Method	Method No.	Method Title
US EPA 1996 (SW-846)	1311	Toxicity Characteristic Leaching Procedure (TCLP)
US EPA 1996 (SW-846)	1312	Synthetic Precipitation Leaching Procedure (SPLP)
US EPA 1996 (SW-846)	3010	Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy
US EPA 1996 (SW-846)	3050	Acid Digestion of Sediments, Sludges, and Soils
US EPA 1996 (SW-846)	3060	Alkaline Digestion for Hexavalent Chromium
US EPA 1996 (SW-846)	6010	Inductively Coupled Plasma – Atomic Emission Spectrometry
US EPA 1996 (SW-846)	7199	Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography
AWPA, 1999	A9-99	Analysis of Treated Wood and Treating Solutions by X-ray Spectroscopy

Table D.1: Methods Employed for Analyses that have been Standardized by Regulatory/Standardization Agencies

Purpose	Instrumentation Used	Method Employed
Arsenic Species Analyses	HPLC-HG-AFS (Analyzes only As(III), As(V), MMAA, DMAA) Used for pH stat test, TCLP, SPLP	See section II.1.a
Arsenic Species Analyses	HPLC-ICP-MS (Analyzes for all arsenic species) Used for lysimeter leachate and groundwater near C&D facilities	See section II.1.b
Total Metals in Ash Samples	Neutron Activation using Nuclear Reactor	Standard methods employed by the Reactor Facilities at the University of Florida and Massachusetts Institute of Technology. More details in text of current report and in Solo-Gabriele et al. 1999.

Table D.2: Methods Employed for Analysis which were Utilized by the Research Community

Number of Replicates and Controls

Considerable replication was performed in this study. In addition to conducting replicates using the same analytical methods for the same samples, the same samples were also analyzed for the same parameter using a different method (e.g. the analysis of arsenic in wood for sample “X” using XRF, AA, and ICP). A summary is provided below concerning the replication of samples.

pH Stat Experiment

Sample collection and preparation are detailed in section III.1. Analysis of solid wood is detailed in table III.1 in the main text. Cr(VI) was analyzed in triplicate and total metals (As, Cr, and Cu) analyzed in quintuplicate by ICP-AES. The sawdust was also analyzed by XRF and AA. Results from the sawdust analysis were consistent across each of the methods. Leachates from pH stat experiments were analyzed in duplicates for both arsenic and chromium species and for total metals. The new wood sample served as the control for the weathered wood sample (and vice versa) since the objective this experiment was to determine if there were differences in the species leached from new and weathered wood.

TCLP and SPLP Tests

Sample collection and preparation are detailed in section IV.1. The unburned solid wood samples were analyzed by XRF in quintuplicate and by ICP-AES in duplicate, and for Cr(VI) by IC in triplicate. The ash samples were analyzed in duplicate by ICP-AES and by neutron activation by two different reactor facilities (U.Florida and MIT). Two separate extractions were performed for each sample run through TCLP and SPLP. Each extraction was analyzed for arsenic species by HPLC-HG-AFS and for total arsenic by ICP-AES. The sum of the arsenic species was compared to the total by ICP-AES. A subset of these samples (the SPLP extracts and the TCLP extracts for the ash) were analyzed for total chromium by ICP-AES and for Cr(VI) by IC. Untreated wood (unburned and burned) was included throughout as a negative control.

Lysimeter Study

Design of the lysimeters along with sample collection and preparation are detailed in section V.1 and V.2. Each sample was analyzed once for arsenic species using HPLC-ICP-MS and was analyzed once on a routine basis for total arsenic. Occasionally duplicates were run for total arsenic and the results of those duplicates are provided below (Table D.6). The reproducibility of duplicate analyses for the lysimeter digestates was always within 25% with the majority of the analyses within 5%. Each “CCA” lysimeter was paired with its corresponding control lysimeter that did not contain added CCA-treated wood.

Date	Reproducibility		
	As	Cu	Cr
Lys 2 6/12/2002	3.4%	12.5%	4.0%
Lys 2 6/25/2002	0.4%	3.1%	0.7%
Lys 2 7/17/2002	3.1%	5.9%	3.6%
Lys 2 8/21/2002	7.3%	21.6%	12.4%
Lys 2 9/6/2002	3.30%	0.40%	0.40%
Lys 2 1/07/2003	0.90%	3%	1%
Lys 2 7/30/2003	0.46%	0.24%	0.37%
Lys 3 8/6/2002	20.0%	<0.004	24.0%
Lys 4 9/06/2002	2.7%	<0.004	5.5%
Lys 5 6/25/2002	1.5%	<0.004	1.2%
Lys 5 8/6/2002	6.0%	<0.004	5.6%
Lys 5 8/21/2002	11.4%	<0.004	15.8%
Lys 6 7/17/2002	9.4%	<0.004	0.60%

Table D.6: Reproducibility of Lysimeter Leachate Results Based Upon Duplicate Acid Digestion and Analysis

Groundwater Near C&D Debris Disposal Facilities

Sample collection and processing is detailed in section VI.2. Samples were collected from downgradient wells and from background wells, where results from the corresponding background well served as the control. Each sample was analyzed once by HPLC-ICP-MS for arsenic species. Each corresponding sample was also analyzed for total arsenic by the corresponding commercial laboratory, as contracted by the C&D facility.

Results from Blank, Replicate, and Spike Analysis

Below are tables that summarize the results from blanks, replicates, and spike analyses (Tables D.4 to D.6). Spike recoveries were typically very good with values between 80 and 110%.

Sample	Arsenic (mg/L)	% Recovery	Copper (mg/L)	% Recovery	Chromium (mg/L)	% Recovery
Blank	0.015		<0.05		0.013	
Blank MS	89.13	89%	91.42	91%	94.3	94%
Blank MSD	87	87%	89.5	89%	92	92%
pH 6 sample	4.52		0.91		1.38	
pH 6 Sample MS	106.74	101.92	97.42	96.51	103.25	101.87
pH 6 Sample MSD	101.23	96.41	102.17	101.26	98.26	96.88

Table D.4: Results from Spike Analysis on Samples from the pH stat Experiments

Sample	Spike Conc. (mg/l)	Sample Conc. (mg/l)	100 % Recovery	% Recovery
Blank	-	BDL	-	-
Blank with Spike	1	1.169	1	116.9
Blank with Spike	10	10.65	10	106.5
Blank	-	BDL	-	-
Blank with Spike	10	10.6	10	106.0
Blank	-	BDL	-	-
Blank with Spike	1	0.9834	1	98.34
Blank with Spike	1	0.9953	1	99.53
Blank (SPLP)	-	BDL	-	-
Blank with Spike (SPLP)	1	0.9928	1	99.3
Blank	-	BDL	-	-
Blank with Spike	1	1.013	1	101.3
Blank with Spike	1	1.035	1	103.5
Blank (TCLP)	-	BDL	-	-
Blank with Spike (TCLP)	1	1.012	1	101.2
Blank with Spike (TCLP)	1	1.033	1	103.3
Untreated Ash	-	BDL	-	-
Untreated Ash with Spike	10	11.68	10	116.8
New CCA Wood #6	-	52.14	-	-
New CCA Wood #6 with Spike	10	61.08	62.14	98.3
New CCA Wood #6 with Spike, Duplicate	10	61.26	62.14	98.6
Untreated Wood Ash	-	BDL	-	-
Untreated Wood Ash with Spike	1	0.9833	1	98.3
Untreated Wood Ash with Spike, Duplicate	1	0.9697	1	97.0
Untreated Ash (SPLP)	-	BDL	-	-
Untreated Ash (SPLP) with Spike	1	1.014	1	101.4

Table D.5: Results from Spike Analysis for Total Chromium in CCA-treated Wood and CCA-treated Wood Ash

Sample Name	As	Cu	Cr
Blank MS 8/6/02	117%	115%	122%
Blank MSD 8/6/02	116%	117%	124%
Lys 1 MS 8/6/02	119%	112%	123%
Lys 1 MSD 8/6/02	120%	115%	123%
MS Blank 9/19/02	103%	100%	111%
MSD Blank 9/19	105%	99%	111%
Lys 5 9/6/02 MS	96%	86%	74%
Lys 5 9/6/02 MSD	90%	81%	75%
Lys 1 MS 12/20/02	95%	89%	106%
Lys 1 MSD 12/20	99%	97%	107%
Lys 3 MS 12/20/02	92%	88%	88%
Lys 3 MSD 12/20	93%	87%	90%
Lys 5 MS 12/20	91%	83%	77%
Lys 5 MSD 12/20	99%	86%	88%
MS Blank 12/26	101%	89%	110%
MSD Blank 12/26	96%	86%	103%
MS Blank 2/17/03	92%	105%	99%
MSD Blank 2/17	92%	100%	98%
Lys 1 MS 1/7/03	92%	100%	94%
Lys 1 MSD 1/7/03	79%	98%	98%
Lys 3 MS 1/7/03	92%	95%	86%
Lys 3 MSD 1/7/03	87%	98%	83%
Lys 5 MS 1/7/03	94%	97%	83%
Lys 5 MSD 1/7/03	94%	94%	83%

Table D.6: Matrix Spike Recoveries for the Lysimeter Samples

Reproducibility, Precision, and Detection Limits for Cr Speciation Analyses

Chromium species were measured for Cr(VI) using the IC method. Cr(III) was determined by difference from measurements of total chromium using ICP-AES. The detection limit for Cr(III) using ICP-AES was 0.17 mg/l. The detection limit for Cr(VI) using IC was 0.04 mg/l. Data from the instruments (peak areas) were converted to sample concentration units using a calibration curve. The coefficient of correlation for the calibration curve was than 0.999. All samples for the pH stat experiment (Chapter III) and solvent extractions (Chapter IV) were extracted in duplicates, so the standard deviations of the results represent both the analytical variability as well as the variability of the solvent extraction.

One blank, one blank spike, one matrix spike, and one duplicate were performed per digestion batch. The concentration of hexavalent chromium in the blanks were less than the method detection limit (0.04 mg/l). Either K_2CrO_4 (soluble hexavalent chromium) or $PbCrO_4$ (insoluble hexavalent chromium) were used for blank spike and matrix spike. Recoveries of blank spike and matrix spike were within recovery range of 80 % to 120 %, and 75 % to 125 %, respectively (Table D.7).

Sample	Spike Conc. (mg/l)	Sample Conc. (mg/l)	100 % Recovery	% Recovery
Blank	-	BDL	-	-
Blank S	1	1.1	1	110.0
Blank	-	BDL	-	-
Blank S	1	1.04	1	104.0
Blank	-	BDL	-	-
Blank S	1	1.01	1	101.0
Blank	-	BDL	-	-
Blank S	1	1.14	1	114.0
Blank	-	BDL	-	-
Blank S	0.1	0.103	0.1	103.0
Blank	-	BDL	-	-
Blank S	1	1.14	1	114.0
Blank	-	BDL	-	-
Blank S	14.96	14.17	14.96	94.7
Blank	-	BDL	-	-
Blank S	5	4.92	5	98.4
0.1 ppm check	0.1	0.11	0.1	110.0
0.1 ppm check	0.1	0.1	0.1	100.0
0.1 ppm check	0.1	0.101	0.1	101.0
CCA-treated Wood Ash #10	-	0.58	-	-
CCA-treated Wood Ash #10 MS	10	9.19	10.58	86.9
Untreated Wood Ash	-	BDL	-	-
Untreated Wood Ash MS	1	0.98	1	98.0
New CCA-treated Wood #1	-	1.43	-	-
New CCA-treated Wood #1 MS	5	6.79	6.43	105.6
New CCA-treated Wood #4	-	0.31	-	-
New CCA-treated Wood #4 MS	5	4.03	5.31	75.9

Table D.7: Results for CrVI Spike Analysis on CCA-treated Wood & Ash

Reproducibility, Precision, and Detection Limits for As Speciation Analyses

Arsenic species were analyzed using either HPLC-HG-AFS or HPLC-ICP-MS. For HPLC-HG-AFS, standards and blanks for the arsenic species were included within each set of samples analyzed. The blanks associated with each run were below detection limits. The detection limit for arsenic species was 2 $\mu\text{g/L}$ and was determined by spiking a deionized water sample with relatively small amounts of arsenic to obtain the lowest quantifiable concentration. All standards contained the four species (As(III), As(V), MMAA, and DMAA). Analytical reproducibility was within $\pm 10\%$ for each species as observed from replicate analyses. Deionized water contained no detectable arsenic. All samples for the pH stat experiment (Chapter III) and solvent extractions (Chapter IV) were extracted in duplicates. The standard deviations of the results represent both the analytical variability as well as the variability of the solvent extraction. Total arsenic was determined from speciation analysis by summing the concentrations of the individual arsenic species. An independent measure of total As was also measured for each sample based upon sample digestion and analysis by ICP-AES. The coefficient of variation for the As speciation analysis, computed by dividing the overall standard deviation by the overall mean and then multiplying by 100, for the total arsenic species in the pH experiment was 10%. For the SPLP and TCLP, the coefficient of variation for the unburned and ash samples was ± 8.3 and $\pm 4.2\%$, respectively.

For HPLC-ICP-MS standards and blanks for the arsenic species were included within each set of samples analyzed. The blanks associated with each run were below detection limits. The detection limit for the groundwater samples (Chapter VI) was 2 $\mu\text{g/L}$ and was determined by spiking a deionized water sample with relatively small amounts of arsenic to obtain the lowest quantifiable concentration. For the lysimeter samples (Chapter V), the detection limit was 5 $\mu\text{g/L}$ and it was obtained by determining the lowest quantifiable concentration when a lysimeter sample containing no detectable arsenic was spiked with arsenic. Reproducibility of the speciation analysis was between 5 and 10% when comparing replicates of the same sample. Total arsenic was determined from speciation analysis by summing the concentrations of the individual arsenic species. An independent measure of total As was also measured for each sample based upon sample digestion and analysis by ICP-AES for the lysimeter samples (Chapter V) or by analysis from an independent commercial laboratory for the groundwater samples (Chapter VI).