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**New Lines of CCA-Treated Wood Research:  
In-Service and Disposal Issues**

Submitted March 19, 2001

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Report #00-12

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## LIST OF ABBREVIATIONS AND ACRONYMS

AAS	Atomic Absorption Spectrometry
ACQ	Alkaline Copper Quat
AES	Atomic Emission Spectrometry
AFS	Atomic Fluorescence Spectrometry
APDC	Ammonium Pyrrolidine Dithiocarbamate
As	Arsenic
As(III)	Arsenite
As(V)	Arsenate
AsB	Arsenobetaine
AsC	Arsenocholine
AsH <sub>3</sub>	Arsine
Ave.	Average
AWPA	American Wood Preservers Association
AWPI	American Wood Preservers' Institute
BDL	Below Detection Limit
CBA	Copper Boron Azole
CC	Copper Citrate
CCA	Chromated Copper Arsenate
CDDC	Copper Dimethyldithiocarbamate
C&D	Construction and Demolition
CHG	Chemical Hydride Generation
Cr	Chromium
Cr(III)	Trivalent Chromium
Cr(VI)	Hexavalent Chromium
Cu	Copper
CZE	Capillary Zone Electrophoresis
DDAC	Didecyldimethyl Ammonium Chloride
DDC	Dimethyldithiocarbamate
DEP	Department of Environmental Protection

## **LIST OF ABBREVIATIONS AND ACRONYMS (Con'd)**

DI	De-ionized
DMAA	Dimethylarsinic Acid
EHG	Electrochemical Hydride Generation
EPA	Environmental Protection Agency
EP Tox	U.S. Environmental Agency Toxicity Test
FID	Flame Ionization Detector
GC	Gas Chromatography
GF	Graphite Furnace
GWCTL	Groundwater Cleanup Target Level
GWGC	Groundwater Guidance Concentrations
HCl	Hydrochloric Acid
HG	Hydride Generation
HPLC	High Performance Liquid Chromatography
IC	Ion Chromatography
ICP	Inductively Coupled Plasma
LD <sub>50</sub>	Lethal Dose Where 50% of the Population Dies
LMAC	Listed Metals Advisory Council
MEP	Multiple Extraction Procedure
MIBK	Methyl Isobutyl Ketone
MMAA	Monomethylarsonic Acid
MPCA	Minnesota Pollution Control Agency
MS	Mass Spectrometry
MSW	Municipal Solid Waste
MW	Molecular Weight
NaBH <sub>4</sub>	Sodium tetraborohydride
NM	Not Measured
pcf	Pounds per Cubic Foot
PTFE	Polytetrafluoroethylene
RCRA	Resource Conservation and Recovery Act
SCTL	Soil Cleanup Target Level
SDDC	Sodium Dimethyldithiocarbamate or Silver Diethyldithiocarbamate

## **LIST OF ABBREVIATIONS AND ACRONYMS (Con'd)**

SFPA	Southern Forest Products Association
SPLP	Synthetic Precipitation Leaching Procedure
SSL	Soil Screening Level
Std. dev.	Standard Deviation
TAG	Technical Advisory Group
TC	Toxicity Characteristic
TCLP	Toxicity Characteristic Leaching Procedure
THF	Tetrahydrofuran
TSD	Thermionic Specific Detector
TMAO	Trimethylarsine Oxide
UF	University of Florida
UM	University of Miami
USEPA	U.S. Environmental Protection Agency
UV	Ultra Violet
UV/Vis	Ultra Violet – Visible Light Region
WET	Waste Extraction Test

## UNITS OF MEASURE

%	parts per hundred
Fg	microgram
Fg/l	micrograms per liter
F1	microliter
Fm	micron (1 millionth of a meter)
atm	atmospheres
°C	degrees Celcius
Eh	measure of electron activity
ft <sup>3</sup>	cubic feet
g	grams
lb/ft <sup>3</sup>	pounds per cubic foot
lbs.	pounds
mg	milligrams
mg/kg	milligrams of chemical per kilogram of wood or soil
mg/kg/day	milligrams of chemical per kilogram of body weight per day
mg/l	milligrams per liter
ml	milliliter
mm	millimeter
ng	nanogram
nl	nanoliter
nm	nanometer
M	Molar concentration units
mM	Millimolar
N	normality (equivalents per liter)
pcf	pounds of chemical per cubic foot of wood
pH	measure of the hydrogen ion activity
ppb	parts per billion
ppm	parts per million
ppt	parts per trillion
V	Volts or Volume

## ABSTRACT

This research was initiated in response to a series of perceived data gaps that were identified during the deliberations for a potential ban on chromated copper arsenate (CCA) during the 1999 hearings held in Minnesota. This project was designed to answer some of these data gaps through a set of three short-term studies and by conducting a set of literature reviews in areas that should be evaluated over a longer term. The three short-term projects focused on a) evaluating the impacts of CCA-treated decks on the soils located below them, b) developing an inventory of CCA-treated products within Florida, and c) evaluating leaching characteristics of unburned CCA-treated wood and construction and demolition (C&D) debris wood mulch. The literature reviews focused on identifying laboratory methods for arsenic speciation analysis, chromium speciation analysis, and for analysis of leachates from alternative-chemical treated wood products.

The impacts of CCA-treated decks on soils were evaluated by collecting surface soil samples and cores from below nine decks located within three cities in Florida. Results showed that the average arsenic concentration in the “below deck” soils was 28 mg/kg whereas the average arsenic concentration of the control samples was 1.5 mg/kg. For chromium and copper, the average of the “below deck” soils was 34 and 40 mg/kg, respectively, whereas the average of the controls was less than 10 mg/kg for both metals. The depth of the impact was observed to a depth of 3 inches for chromium and copper and to a depth of 8 inches for arsenic. The arsenic concentration in “below deck” soils exceeded Florida’s residential Soil Clean-up Target Level of 0.8 mg/kg for all samples collected below confirmed CCA-treated decks. The volume of the impact for all CCA-treated decks located throughout Florida is estimated at 25,000 acres or 60 million tons of soil.

The amount of arsenic associated with CCA-treated wood currently in service in Florida is estimated at 26,800 tons. This quantity is enough to increase the arsenic concentration of a volume of water equal to 650 times the size of Lake Okeechobee by 10 ug/L, which is the proposed federal drinking water limit. Given the potential for significant environmental impacts, efforts should focus on recovering as much of this arsenic as possible. Approximately 1500 tons or 5% of the total amount of arsenic in products currently in service can be recovered from utility poles. Approximately 4,100 tons or 15% of the arsenic are associated with marine and fresh water applications. Recapturing the arsenic from these use sectors will require coordination with major Florida utilities and marine and fresh water contractors.

Results of standardized leaching tests show that new CCA-treated wood leaches enough arsenic to routinely fail the U.S. EPA’s TCLP. If a regulatory exemption were not in place, discarded CCA-treated wood would frequently require management as a hazardous waste. Leaching of arsenic occurs at similar levels in tests using synthetic rainwater indicating that leaching is a concern in environments besides landfills. If new CCA-treated wood were managed with the same restrictions as other types of wastes, the disposal in unlined landfills would not be allowed. This also corroborates the fact that metals leach from CCA-treated wood decks (and other similar structures) to the underlying soil. The leaching of all three metals increases as the size of the wood decreases. Previous experience showing that CCA-treated wood occurs in recycled wood from C&D debris was again demonstrated in leaching tests. Nearly all of the C&D debris wood mulch samples tested leached arsenic at concentrations greater than drinking water standards, indicating that these mulch samples should not be land

applied.

As a result of the literature review, analytical methods have been identified for the analysis of chromium species, arsenic species, and for the analysis of the organic co-biocides associated with alternative waterborne preservatives. These methods will be implemented in future studies focusing on characterizing the leachates from CCA-treated wood and alternative-chemical treated wood.

The overall results of this study indicate that CCA-treated wood does impact the environment during its service life by increasing the metal concentrations of soil. The potential impacts of these releases on human and ecological health, however, are open to interpretation. This study also emphasizes the need to better manage CCA-treated wood upon disposal. Due to the large quantity of metals and the leaching characteristics of CCA-treated wood, as much of the arsenic should be recovered prior to disposal as mulch or in unlined landfills. Future research should focus on identifying cost effective means of ultimate disposal for CCA-treated wood waste.



## **CHAPTER I**

# **MOTIVATION, OBJECTIVES, AND BACKGROUND**

## 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. The Council specifically evaluates whether or not products containing these metals should be banned from the State. Since the CCA chemical (and not necessarily CCA-treated wood<sup>1</sup>) contains hexavalent chromium, the focus of deliberations was on the use and sale of the CCA chemical. Although Minnesota's Listed Advisory Council did not vote for a ban on the CCA chemical, the Council did recognize the significant disposal issues associated with CCA-treated wood and therefore concluded that disposal of CCA-treated wood requires "prompt, thorough consideration, and possible action to protect the environment from the deposition of large volumes of arsenic..... We do not have the authority to recommend banning CCA-treated wood because the treated wood is not a specified product.... Therefore, we strongly urge that treated wood be disposed of by methods which safeguard the environment and our citizens." (Listed Metals Advisory Council, personal communication to the Commissioner of MPCA 2000)

During the deliberations, many issues were highlighted concerning CCA-treated wood that were not the focus of earlier research conducted by the Florida CCA-treated wood research team. Specific issues discussed during the meeting included: 1) the impacts of CCA-treated wood during its service life, 2) the amounts of CCA-treated wood used by major industries, 3) the availability of alternative chemicals and their potential impacts on the environment and, 4) chromium and arsenic speciation of the leachates from CCA-treated wood. Many deliberations were marred by lack of scientific data. The Florida research team, recognizing the gap in information, thereby embarked to address these issues through a request for supplemental funds to the "year 3" study. The request was approved in September 1999 by the Florida Center for Solid and Hazardous Waste. This report focuses solely on the research funded through the supplemental funds.

## I.2 OBJECTIVES

The overall goal of this study was to address some of the issues that were debated during the Minnesota hearings through a set of three short-term studies and by conducting a set of literature reviews in areas that will be evaluated over a longer term. Specifically, the objectives of the short-term studies were to: a) document metals concentrations in soils located in the

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<sup>1</sup> The chromium in CCA-treated wood is added in its hexavalent form. After a waiting period (which is temperature dependent) the chromium is converted to its trivalent form and thereby becomes "fixed" into the wood.

vicinity of decks made of CCA-treated wood, b) identify the quantity of CCA-treated wood used by major industries, and c) conduct TCLP and SPLP tests on unburned CCA-treated wood and construction and demolition (C&D) debris mulch.

Currently there is huge reservoir of CCA-treated wood in use within Florida today (540 million cubic feet, estimated) and a large fraction of this wood, roughly 36%, is associated with outdoor decks (SFPA, personal communication). Given this large reservoir, it was of interest to determine the impacts of CCA treated decks on the surrounding environment. The purpose of the first short-term study was to evaluate whether or not enough metals leach from CCA-treated decks to increase the concentrations of the soil above background levels. In this particular study soils below decks were sampled and analyzed for arsenic, chromium, and copper concentrations. These results were then compared to background concentrations for the site and to Florida regulatory guidelines.

One of the goals of disposal-end management is to recapture as much of the CCA chemical before it is mixed with other components of the solid waste stream. Knowledge concerning where the current CCA reservoirs reside will help to prioritize which products to recapture so that the treated wood is not commingled with other solid wastes. The purpose of the second short-term project was to determine the distribution of the arsenic associated with CCA-treated wood within different use sectors. In particular statistics are provided for U.S. production (by product type) and two use sectors in Florida (utility poles and fresh/marine water applications). Statistics were used to estimate the total amount of arsenic associated with CCA-treated wood currently in service.

The last short-term project was intended to complete the analysis of CCA-treated wood and C&D debris mulch using standardized leaching tests. All of the earlier leaching tests conducted through the UM/UF research program utilized CCA-treated wood ash. Given that the wood waste market is now shifting towards the production of mulch it is likely that CCA-treated wood is inadvertently mixed with this disposal stream. Therefore in order to assess this disposal route, it is important to evaluate the leaching characteristics of the unburned CCA-treated wood and C&D debris mulch. In this study, CCA-treated wood samples were subjected to a set of 5 different leaching tests. Twenty samples of C&D debris mulch were evaluated using the standard SPLP. Results were then compared to regulatory guidelines.

It was envisioned at the outset of the “year 3 supplemental” study that a long-term research plan could be established for evaluating chromium and arsenic speciation in leachates from CCA-treated wood and that non-arsenical treated wood products should also be included within a leaching study. A literature review to evaluate the most suitable analytical methods for arsenic and chromium speciation as well as alternative wood treatment preservatives was therefore incorporated as part of the “year 3 supplemental” study.

The organization of this report is consistent with the “year 3 supplemental” objectives and is

- Metals Concentrations in Soils Below Decks Made of CCA-Treated Wood (Chapter II)
- Inventory of CCA-Treated Wood in Florida (Chapter III)
- Leaching of Chromium, Copper, and Arsenic from New CCA-Treated Wood and

- C&D Debris Mulch (Chapter IV)
- Literature Reviews for Future Research (Chapter V)
  - Analytical Methods for Chromium Speciation (Section V.1)
  - Analytical Methods for Arsenic Speciation (Section V.2)
  - Laboratory Methods for the Analysis of Alternative Chemicals (Section V.3)

Given the diverse nature of the research tasks, conclusions corresponding to each task are provided within the each chapter rather than having one concluding chapter for all the work presented. The report ends with a chapter which provides a summary of the primary conclusions and recommendations for future work (Chapter VI) .

### **I.3 BACKGROUND**

Wood is treated with chemical preservatives so it can resist biological degradation. Chromated copper arsenate (CCA) treated wood 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. CCA-treated wood is the most widely used type of treated wood (AWPI 1999) representing about 80% of the wood preservation market today. Although the production of CCA-treated wood was commercialized in the 1960s, it was not until the 1980s that CCA-treated wood dominated the market due to large increases in the demand for the product. Given that CCA-treated wood generally maintains its structural integrity for 20 to 40 years, disposal quantities of CCA-treated wood will increase significantly in the near future (Solo-Gabriele and Townsend 1999).

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.

## **CHAPTER II**

# **METALS CONCENTRATIONS IN SOILS BELOW DECKS MADE OF CCA-TREATED WOOD**

## **CHAPTER II, METALS CONCENTRATIONS IN SOILS BELOW DECKS MADE OF CCA-TREATED WOOD**

This chapter begins by describing the motivation and objectives of the study (section II.1) and the methods used for soil sampling (section II.2) and soil analysis (section II.3). Results are separated into three sections. The first of these sections (section II.4) focuses on the metals concentrations of the surface soil samples collected through this study. Section II.5 focuses on the results of physical measurements performed on the soil samples and section II.6 focuses on the results from the soil core analysis. The chapter closes with a summary and conclusion (section II.7).

### **II.1 MOTIVATION AND OBJECTIVES**

Earlier studies have found elevated levels of metals in the vicinity of CCA-treated wood structures. Arsenic concentrations observed in soils below decks in Connecticut, for example, averaged 76 mg/kg (3 to 350 mg/kg range) whereas the background soil values averaged 3.7 mg/kg (1.3 to 8.3 mg/kg range) (Stilwell and Gorney 1997). For chromium, the average concentration below the decks was 43 mg/kg whereas background samples averaged 20 mg/kg; and copper concentrations of 75 mg/kg were reported on average below the decks, whereas background concentrations were 17 mg/kg. In Canada, elevated metals concentrations were observed in the immediate vicinity of CCA-treated utility poles. Arsenic concentrations as high as 550 mg/kg were observed in the soil in the immediate vicinity of the poles; chromium concentrations were as high as 200 mg/kg whereas copper was as high as 1000 mg/kg. In general metal concentrations were higher for older poles and concentrations generally dropped-off considerably within 4 inches from the pole (Cooper 1997). Among the three metals evaluated in these studies, arsenic appears to exceed risk-based regulatory guidelines by the largest margin. For example, the U.S. EPA soil screening level (SSL) is 0.4 mg/kg for arsenic (direct exposure) whereas Florida's soil clean-up target levels for arsenic is 0.8 mg/kg for residential areas and 3.7 mg/kg for industrial areas. The U.S. soil screening guidance concentration for chromium is 390 mg/kg and there is no SSL for copper. Florida's clean-up target levels for chromium (as chromium VI) and copper are 210 and 110 mg/kg respectively for residential areas and 420 and 76,000 mg/kg for industrial areas. The objective of the work summarized in this chapter was to evaluate the impacts of CCA-treated wood decks on surrounding soils located within the State of Florida. Soils below decks were sampled and compared to background concentrations to determine the additional load of metals due to the presence of CCA-treated decks. To provide a point of reference, the concentration of metals in the soils below the decks were also compared to Florida's clean-up target levels. All three metals (chromium, copper, and arsenic) were evaluated through this study. However, a particular focus was provided on the arsenic results.

### **II.2 METHODS OF SOIL SAMPLING**

Nine structures were sampled throughout Florida to evaluate the impacts of CCA-treated decks on the underlying soil. Three decks were sampled in Gainesville on November 18, 1999, three in Miami on November 27, 1999 and three in Tallahassee on December 6, 1999. The sites were revisited during June and July 2000 in order to collect additional soil control samples and to confirm that the decks were indeed CCA treated.

Immediately prior to sample collection, a grid was set up below the decks using rope. This provided a uniform distribution of sampling points below each deck. At each site, eight surface samples were taken with the exception of the first site (site BR, the 34<sup>th</sup> Street footbridge in Gainesville) where nine surface samples were collected. A diagram of the grid along with the location where each sample was collected is provided in appendix A. The surface samples were collected within the top one inch of the ground. After thorough mixing, each sample was split; one for the University of Florida for metals analysis and the other for archiving at the University of Miami. Extra surface soil was collected in a plastic bag at each site in order to analyze the soil for moisture content, volatile solids, and grain size distribution. During the first visit to each deck two control samples (a.k.a. background samples) were also collected at each site, again with the exception of the first site where five controls were collected. Additional controls were collected during the second visit to each deck so that the total number of controls equaled the number of samples collected below the corresponding deck. In other words, after the second sampling effort the total number of controls collected for all the decks was 8 (2 from the first trip and 6 from the second) except for site BR where a total of 9 controls (5 from the first trip and 4 from the second) were collected. The sites for the controls were determined by their location with respect to the grid. Locations upstream of the grid were preferred, ranging from 50-100 feet away. In addition, at each site, a soil core sample of approximately seven inches in depth was collected in order to determine the vertical distribution of Cr, Cu, and As. Each core was taken approximately in the center of the grid that was set up below each structure. The samples were collected using a 1 and 1/8" diameter unslotted stainless steel probe fitted with a plastic liner (Forestry Suppliers, Inc., Jackson, MS). A different plastic liner was utilized for each site. After collection, all sample containers were placed in plastic bags and put in a cooler with ice for transportation to the laboratory.

## **II.2.a Site Description**

The Gainesville sites were at the 34th Street footbridge, the main walkway at Paynes Prairie, and the deck at Bivens Arm Park. The three in Miami were a deck at Oleta River Park, a playground at A.D. Barnes Park, and a lifeguard tower at Tropical Park. The three sites at Tallahassee were a deck at Lake Talquin, a deck at Maclay Gardens, and a footbridge at Tom Brown City Park. Each site was given a two letter abbreviation for sample tracking. A listing of these abbreviations is provided in table II.1.

Decks identified for soil sampling varied in age between 2 years (Tom Brown City Park) to 19 years (Lake Talquin) (table II.1). All decks used in this study were confirmed as CCA treated except for the deck at Lake Talquin. CCA treatment was confirmed by applying a chemical stain and by using x-ray fluorescence to quantify the retention level of CCA within either wood bores or sawdust samples collected from each deck. Sawdust and wood bores utilized for analysis corresponded to the outer 6/10 inch of wood as specified by AWPA standards. The stain utilized was PAN indicator which when applied to the surface of the deck resulted in a distinctive color change when metals were present (See Blassino et al. 2000 for more details concerning this stain). X-ray fluorescence was conducted by Javaro Johnson of Robbins Manufacturing, Tampa, FL, using an ASOMA Model #1503. As shown from the data, all decks stained positive for CCA except for the Lake Talquin deck in Tallahassee. The deck at the 34<sup>th</sup> Street Bridge in Gainesville was characterized by a generally high CCA retention level (0.755 pcf) whereas extremely low retention values were obtained for the Lake Talquin deck in Tallahassee. The

XRF results for the deck at Oleta River Park were variable. The hand rail portion of the deck was characterized by a retention level of 0.005 pcf. The joists below the deck tested at 0.54 and 0.50 pcf and the support columns tested at 0.15 pcf. The general descriptions of each site are provided below.

City	Description of deck	Site Abbreviation	Year deck constructed	Age of deck when sampled	Results from Stain	CCA Ret. Level (pcf)
Gainesville	34th Street Footbridge	BR	1994	5 years	Positive	0.755
	Deck at Paynes Prairie	PP	1983-1984	~15 years	Positive	0.206
	Walkway at Bivens Arm Park	BP	1985	14 years	Positive	0.477
Miami	Deck at Oleta River Park	OP	1985	14 years	Positive	Variable (0.005-0.54)
	Playground at A.D. Barnes Park	AD	1990	9 years	Positive	0.261
	Lifeguard station at Tropical Park	TP	1993	6 years	Positive	0.206
Tallahassee	Footbridge at Lake Talquin	LT	1980	19 years	Negative	0.008
	Deck at Maclay Gardens	MG	1995	4 years	Positive	0.412
	Footbridge at Tom Brown City Park	TB	1998	2 years	Positive	0.247

Table II.1: Site Abbreviations and Ages of Decks Sampled

### Gainesville

*34<sup>th</sup> Street Bridge:* The 34th Street deck is a footbridge that runs parallel to NW 34th Street, between NW 30th Blvd and NW 33 Lane. It was built by the Florida Department of Transportation within the past decade. The plans for the original construction of the bridge indicate that the pilings were treated at 2.5 pcf and the handrails, decking, and stringers were treated at 1.2 pcf. These retention levels are exceptionally high and support the high retention level measurement (0.755 pcf) obtained for this particular deck. The surface soil samples were collected from below the bridge, where the soil was somewhat rocky. The land was sloped beneath the bridge, from a high at NW 34<sup>th</sup> Street toward a low at control sample location C01 (figure A.2 in appendix A). Six of the nine control samples (C02, C03, C04, C06, C07, and C08) were collected upstream of the grid and three downstream (C01, C05, and C09). One of the core samples was taken in the center of the “below deck” sampling grid, while the other was taken at a downstream location near C01, the farthest downstream control.



*Paynes Prairie:* The deck at Paynes Prairie leads out to an expanse of wetland. The soil sample corresponded to the portion of the deck that is used as a walkway for pedestrians who wish to view the prairies. During the first sampling trip the area was dry. To the west of the walkway stood a CCA-treated wood fence. A few months after the first sampling trip, construction began at the site. A concrete barrier was put in place of the fence and the area below the deck became waterlogged. This proved to make further sample collection somewhat difficult.

*Bivens Arm Park:* Bivens Arm Park is maintained by the City of Gainesville and contains a treated wood pedestrian walkway through the park. The walkway at Bivens Arm Park is covered with trees limiting the amount of direct sunlight to the area. This particular deck was pressure washed shortly before sample collection.

### *Miami*

*Oleta River Park:* The deck at Oleta River Park serves as a walkway for a bathroom facility. Dense vegetation surrounded the deck at the location sampled. From the original plans obtained for this particular site, it was noted that only some of the structure was pressure treated, while the rest of the structure was made of Cedar. Construction drawings indicate that the floor and roof decking of the bathroom facility, for example, were to be built with Alaskan Yellow Cedar, while the interior of the structure was to be built with Western Red Cedar. Originally, it was not clear whether or not the deck that led to the bathroom facility was CCA treated. Stains and analysis of the decks using XRF confirmed that the handrail portion of the deck was not CCA treated. CCA treatment was confirmed within the support columns (0.15 pcf) and joists (0.54 pcf and 0.50 pcf) below the decks. The original plans for the deck indicated that the deck boards were to be constructed of Alaskan Yellow Cedar; however, inspection of the deck indicates that some of the deck boards (especially those closer to the bathroom facility) may have been replaced with CCA-treated wood. Several of the deck boards closest to the bathroom facility tested positive using the chemical stains.

*A.D. Barnes Park:* The playground at A.D. Barnes Park is a combined playground and walkway characterized by various levels. Samples were collected at a portion of the deck that was a few feet off of the ground. Martha MacDonald from Miami-Dade Parks and Recreation indicated that this deck was constructed of 0.4 pcf CCA-treated wood. XRF analysis confirmed CCA treatment. Upon inspection of the structure it was noted that part of the structure included small vertical bars between the deck and handrails. These bars consisted of painted metal.

*Tropical Park:* The lifeguard station at Tropical Park is located adjacent to a lake. This tower consists of a shaded enclosure for the lifeguard and a ramp that leads up to the enclosure. The station was rebuilt shortly after Hurricane Andrew in 1993, possibly on the same site as a previous tower. The area below the tower was characterized by two levels that were separated by a concrete wall. The portion below the lifeguard enclosure was grassy and flat; the portion below the ramp was sandy and beach-like in appearance and sloped away from the lifeguard enclosure toward the lake. Samples were collected below each portion of the lifeguard station.

## *Tallahassee*

*Maclay Gardens:* The deck at Maclay Gardens leads into a portable office building. The siding of the office building appeared to be composed of vinyl. The soil was very loose and easy to collect.

*Tom Brown City Park:* The footbridge at Tom Brown City Park sits around the perimeter of a lake. Sometimes, the area sampled below the deck can get flooded at times of heavy rain. The structure was originally built in 1978. The original pilings were left in place when the deck and handrails were replaced in January of 1998. Ashley Edwards from Tom Brown Park indicated that most of the wood for this deck was treated with either 0.4 or 0.25 pcf. Furthermore an end tag was found below the deck during sampling. The end tag came from wood rated at 0.25 pcf. This deck was confirmed positive for CCA treatment through XRF analysis.

*Lake Talquin:* Soils were collected from below a footbridge located at River Bluff State Park, which is immediately adjacent to the lake. The area is covered with trees that limit the amount of direct sunlight to the area. Moss was observed growing on the surface of this particular deck. This deck tested negative for CCA-treated wood and pentachlorophenol using chemical stains. The presence of pentachlorophenol was tested using Penta-Check provided by Wood Protection Products, Inc. from Charlotte, North Carolina. Sawdust samples collected from the handrails confirmed that this portion of the deck was not CCA treated. Construction drawings obtained for the deck, however, indicated that the support columns for the deck may be pressure treated. Whether or not these support columns were in fact treated with CCA-treated wood has not been confirmed. The minimum distance between the closest surface sample and support column was 1 foot.

## **II.3 METHODS OF SOIL ANALYSIS**

Soils were analyzed for their physical characteristics and for their metals content. Physical characteristics measured included volatile solids content and grain size distribution. Measurement of metals concentrations required sample pre-processing, digestion, and analysis.

### **II.3.a Physical Characteristics**

#### *Volatile Solids Analysis*

Volatile solids are an indirect measure of the bulk organic content of a soil. The method used to measure the volatile solids concentration of the soil samples was a modification of method 2540E *Standard Methods* (APHA 1995). The analysis began by weighing between 5 and 10 grams of moist soil and placing this soil in a drying oven at 100 °C for 24 hours. The soil samples were removed from the oven, cooled, and weighed. After weighing they were immediately placed in a furnace at 450 °C for 5 hours. During this step it is presumed that all of the volatile solids present in the soil sample were lost. The samples were then reweighed and the volatile solids content was computed on a % weight basis

## *Grain Size Analysis*

Sieve analysis was run to determine the grain size distribution of the soil samples. Prior to sieve analysis, a sub-sample from each of the surface soil sampling sites collected below each deck was combined to form one large representative sample for each deck. The samples were oven-dried, weighed, and placed through a series of sieves. The sieves used were #4 (4.75 mm), #10 (2.0 mm), #20 (0.85 mm), #40 (0.425 mm), #60 (0.25 mm), #140 (0.106 mm), #200 (0.075mm). The sieve with the largest opening was placed on the top with the collection pan on the bottom. The entire stack was run through a shaker for approximately 10 minutes. Each sieve was then re-weighed and the grain size distribution was computed.

### **II.3.b Metals Concentrations**

#### *Sample Preparation*

All soil samples were stored at 4 °C prior to digestion and analysis. The soil core samples were separated into either 0.5 or 1.0 inch long sections. The first two inches were separated into 0.5 inch increments. The remainder of the core was separated into 1 inch increments. Immediately prior to digestion, soil samples (both surface soils and cores) were dried at 105 °C for 24 hours and the moisture content was computed.

It is important to note that all scoops, glassware, plastic containers etc. that came in contact with a sample were first acid rinsed to remove metal contamination as per standard quality control procedures.

#### *Sample Digestion*

Each dried soil sample was digested following EPA Method 3050B (USEPA 1996). Method 3050B is an open vessel method requiring the use of acid and oxidizing agents to reflux a sample on a hot plate for a period of 2 to 8 hours. This method provides a slightly different procedure depending on whether the digestate is being analyzed by flame aspiration or graphite furnace. The digestion procedure calls for weighing 2.0 g of sample into an Erlenmeyer flask, then adding 10 ml of 1:1 nitric acid and heating on a hotplate. After 15 minutes, the Erlenmeyer flask was removed from the hotplate and an additional 5 ml of concentrated nitric acid was added. The Erlenmeyer flask was then placed back onto the hotplate for an additional 30 minutes. If brown fumes were generated, 5 ml of concentrated nitric acid was added sequentially, until no more fumes were formed. When brown fumes ceased, the Erlenmeyer flask was heated for an additional 2 hours or until the final volume of the mixture was 5 ml. The Erlenmeyer flask was then removed from the hotplate and 3 ml of 30% hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>) was added and the solution was placed back onto the hotplate for 2 hours. Samples being digested for analysis using GF-AAS were then filtered through a Whatman 41 filter into a 100 ml volumetric flask. The sample in the volumetric flask was then diluted to volume with deionized water, at which point the sample was ready for analysis. Samples digested for analysis using Flame-AAS were subjected to an additional step. Ten ml of concentrated HCl was added and the samples were allowed to reflux for 15 minutes. The digestate was filtered through a Whatman 41 filter into a 100 ml volumetric flask. The sample was then diluted to volume with deionized water, at which point, the sample was ready for analysis.

### *Metals Analysis*

Metals analysis of the digestates was performed using a Perkin Elmer model 5100 atomic absorption spectrophotometer. This instrument was equipped with both a flame aspiration system and a graphite furnace with Zeeman background correction. Arsenic concentrations were measured using the graphite furnace technique. The graphite furnace was also used to measure the concentration of copper and chromium in the control samples. The Flame-AAS technique was employed for all other measurements of Cu and Cr. The graphite furnace was used to measure copper and chromium for the control samples due to the lower concentrations contained in the samples. The detection limit for the flame technique was 1 mg/L for both copper and chromium, whereas the detection limit for the graphite furnace was 5 µg/L for chromium and 10 µg/L for copper. Appropriate quality control and quality assurance procedures were followed in accordance with Florida Department of Environmental Protection Comprehensive Quality Assurance Plan # 960216.

## II.4 RESULTS OF METALS ANALYSES ON SURFACE SOILS

A total of 73 surface soil samples were collected under the nine decks and board walks in Gainesville, Miami, and Tallahassee. Among the 73 surface soils samples, 65 were collected from below decks that were confirmed to be treated with CCA. The remaining 8 samples were collected from below the Lake Talquin deck which is the only deck that did not show a positive measurement for CCA using either the stains or XRF. Stains and XRF samples were collected from the upper portions of the Lake Talquin deck. However, it is important to note that construction drawings for the Lake Talquin deck specify the use of pressure treated support columns. Whether or not these support columns were in fact CCA treated was not confirmed.

In addition to the surface samples collected below the decks, a total of 73 control soil samples were collected. Control samples were located at a distance removed from the deck and results from these samples are expected to represent background metals concentrations.

A summary of the results of arsenic, chromium, and copper analyses are provided in the following sub-sections. Due to the fact that the metals concentrations in some samples were found below the detection limit (BDL), two sets of statistics are reported. One set only includes the results that were above the detection limit. For the second set of statistics, the samples that were below the detection limit were set to zero and averaged with the data that were above the detection limit. The first set of statistics will be biased toward the high side and the second set will be biased toward the low side. The range of values from each set of statistics will include the true average of the samples. As observed from the subsequent data, the results from each computation method are very close to one another. Please refer to appendix A for details concerning the results for each individual deck.

### II.4.a Arsenic Results for Surface Soils

Arsenic was detected in all the surface soil samples collected from below decks. The arsenic concentrations for surface soils collected from underneath the decks ranged from 1.2 mg/kg (Miami site TP) to 217 mg/kg (Miami site OP) with an average of 28.5 mg/kg (table II.2). This average includes the results from all decks except for those from Lake Talquin. The average arsenic concentration of the control samples (without Lake Talquin) varied between 1.3 and 1.5 mg/kg depending upon how the non-detects were handled. Figure II.1 provides a plot of the average deck soil sample arsenic concentrations in relation to the average control sample arsenic concentration for each site. The average arsenic concentrations for surface soils collected below the decks are higher than the control samples at 95% confidence for 8 of the 9 decks. The only deck soils that were not elevated in concentration were those collected from below the Lake Talquin deck.

Of interest is the large variability of arsenic concentrations observed in the Oleta River Park deck samples (figure II.2). For this particular deck, surface soil samples ranged from 32 to 217 mg/kg of arsenic. The highest concentrations were measured at site S02 (112 mg/kg) and S07 (217 mg/kg). These sites line up along one particular horizontal line (See figure A.9 in appendix A for sample locations). To evaluate the possible reasons for this particular pattern in arsenic concentrations, the grid was re-created during a subsequent field trip to the site (after the metals data were available). It was found during this subsequent field trip that the joists

supporting the deck intersect immediately above S02 and S07 forming a “T” pattern. The deck was visited shortly after a storm event and dampness along the “T” portion of the joists was noticeable whereas at other portions of the joists it was not. It is likely that runoff from upper portions of the deck drip along the joists resulting in a concentrated input of rainwater at the point where the two joists intersect and thus causing the elevated arsenic concentrations at S02 and S07.

Location	Surface Soil Samples Collected Below Decks (all analyses above detection limit)					Controls (above detection limit)		Controls (BDL <sup>1</sup> = 0)		
	N	Average (mg/kg)	Std. Dev. (mg/kg)	Max. (mg/kg)	Min. (mg/kg)	N	Average (mg/kg)	N	Average (mg/kg)	
<b>Gainesville</b>	BP	8	41.6	22.8	87.9	15.6	8	2.61	8	2.61
	BR	9	10.7	9.15	33.2	4.05	5	0.46	9	0.26
	PP	8	9.56	4.50	18.1	3.54	4	1.03	8	0.52
total samples	25	20.2	20.2	87.9	3.54	17	1.61	25	1.09	
<b>Tallahassee</b>	TB	8	17.2	7.72	31.0	8.59	8	2.31	8	2.31
	MG	8	34.0	13.7	48.8	5.09	8	1.42	8	1.42
	LT	8	0.48	0.14	0.62	0.25	8	0.47	8	0.47
total samples <sup>2</sup>	16	25.6	13.8	48.8	5.09	16	1.86	16	1.86	
<b>Miami</b>	AD	8	33.9	20.7	81.2	15.5	8	1.98	8	1.98
	TP	8	4.30	2.32	7.47	1.18	8	1.13	8	1.13
	OP	8	79.1	60.7	217	31.7	8	0.66	8	0.66
total samples	24	39.1	47.3	217	1.18	24	1.26	24	1.26	
All Sites <sup>2</sup>	65	28.5	32.8	217	1.18	57	1.53	65	1.34	

<sup>1</sup>BDL=Below Detection Limit. Detection limit is 0.25 mg/kg based on sample dry mass of 2.0 g

<sup>2</sup>Does not include results from Lake Talquin, LT, deck

Table II.2: Arsenic Results for Surface Soils

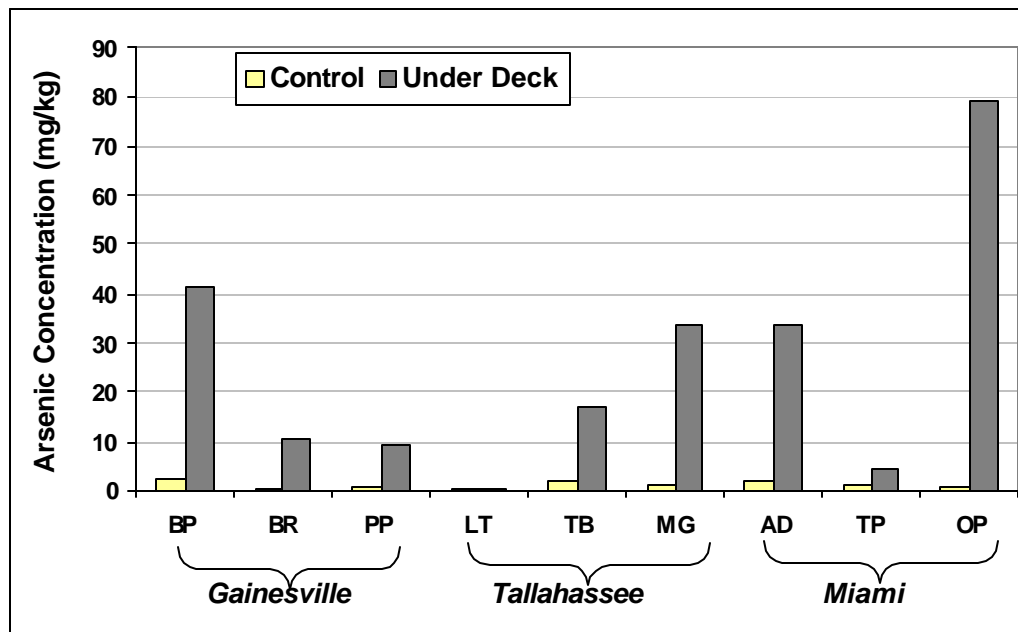


Figure II.1: Comparison of Mean Deck Arsenic Soil Concentration Versus Control Soil Concentrations

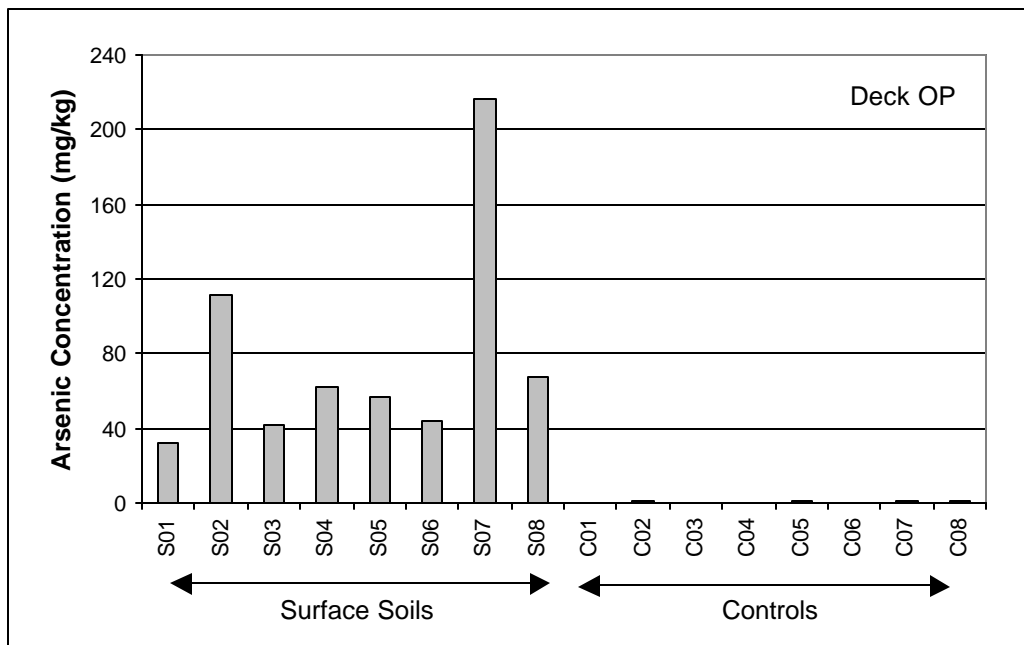


Figure II.2: Arsenic Concentration in Surface Soil Samples from the Oleta River Park Deck, Miami

#### II.4.b Chromium Results for Surface Soils

Of the 65 soil samples collected from below confirmed CCA-treated decks, 59 were above the detection limit for chromium. For the samples above the detection limit, the surface soil chromium concentrations ranged from a maximum of 198 mg/kg (site OP in Miami) to a minimum of 5.4 mg/kg (site TP in Miami) with an average of 34 mg/kg (table II.3). It is noted that the average, maximum, and minimum do not include site LT. The average of the corresponding controls varied from 8.6 to 9.8 mg/kg depending upon how the below detection limit samples were evaluated.

The average below deck soil chromium concentration is plotted in relation to the average control chromium concentration for each site in figure II.3. It is readily observed from this figure that the average of the deck soils were higher than the average of the controls for 6 of the 9 decks. Three decks (PP, LT, and TP) had higher chromium concentrations in the controls than in the deck soils. Statistically at 95% confidence limits, the soils below 3 of the 9 decks were elevated in chromium concentrations above that for the controls (BP, MG, and OP). At 80% confidence, 6 of the 9 deck soils (BP, MG, OP, BR, TB, AD) were elevated above background concentrations. As mentioned earlier, the average chromium concentration of the controls for three of the sites (PP, LT, and TP) was higher than that for the deck soils. Statistical significance was tested for this observation for 2 of the 3 decks. One deck (LT) could not be evaluated given that the results for all the deck soils were below detection limit. For PP, the higher average concentration of the control over the deck soil was not statistically significant at either 95% or 80% confidence limits. For the TP deck, the average of the control samples was elevated above the average of the deck soils at 80% confidence limits but not at 95% confidence limits.

Of interest is that within a site characterized by elevated chromium concentrations in the deck soils, the deck soil chromium concentrations are generally correlated with arsenic concentrations. This correlation generally corresponds to the stoichiometric ratio of CCA type C, thereby supporting the hypothesis that the cause of the elevated chromium and arsenic concentrations below the decks is due to the deck treatment with CCA. A representative plot illustrating the correlation is provided in figure II.4.

<i>Location</i>	Surface Soil Samples Collected Below Decks (all analyses above detection limit except for PP, LT & TP)					Controls (above detection limit)		Controls (BDL <sup>1</sup> = 0)		
		N <sup>3</sup>	Average <sup>4</sup> (mg/kg)	Std. Dev. <sup>4</sup> (mg/kg)	Max. (mg/kg)	Min. <sup>5</sup> (mg/kg)	N	Average (mg/kg)	N	Average (mg/kg)
<b>Gainesville</b>	BP	8	59.7	25.6	113.5	30.8	7	3.53	8	3.09
	BR	9	23.4	13.8	48.6	10.6	7	10.1	9	7.87
	PP	6(8)	15.3(11.5)	9.05(10.4)	28.6	7.80	8	19.2	8	19.2
total samples		23(25)	33.9(31.2)	26.0(26.6)	113.5	7.80	22	11.3	25	9.96
<b>Tallahassee</b>	TB	8	16.4	9.4	32.4	6.90	8	8.80	8	8.80
	MG	8	22.9	10.1	44.3	14.3	7	7.95	8	6.96
	LT	8	BDL <sup>1</sup>	---	BDL	BDL	6	4.58	8	3.43
total samples <sup>2</sup>		16	19.7	10.0	44.3	6.90	15	8.40	16	7.88
<b>Miami</b>	AD	8	39.5	31.5	113.6	13.8	8	12.7	8	12.7
	TP	4 (8)	6.19(3.09)	0.71(3.34)	6.85	5.35	6	9.01	8	6.76
	OP	8	71.1	56.6	198.5	32.0	6	4.82	8	3.61
total samples		20 (24)	45.5(37.9)	46.5(45.7)	198.5	5.35	20	9.22	24	7.68
All Sites		59 (65)	34.0 (30.8)	33.1 (33.0)	198.5	5.35	57	9.82	65	8.61

<sup>1</sup>BDL=Below Detection Limit. The detection limit for samples collected below the decks was 5 mg/kg based on a sample dry mass of 2.0 g. The detection limit for the control samples was 0.25 mg/kg based on sample dry mass of 2.0 g. The difference in the detection limits is due to the use of a flame AAS for the analysis of deck soils and graphite furnace AAS for the analysis of control soils.

<sup>2</sup>Does not include results from Lake Talquin, LT, deck

<sup>3</sup>Numbers in parentheses correspond to the total number of samples, including those below detection.

<sup>4</sup>Numbers in parentheses assumes a value of zero for samples that were BDL.

<sup>5</sup>Minimum excluding samples that were BDL.

Table II.3: Chromium Results for Surface Soils



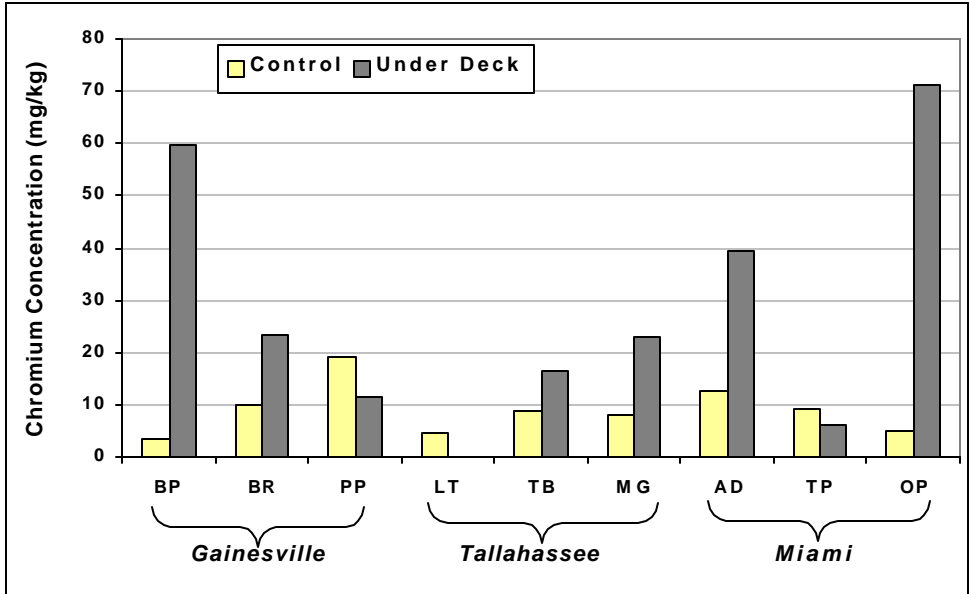


Figure II.3: Comparison of Mean Deck Soil Chromium Concentration Versus Control Soil Concentrations

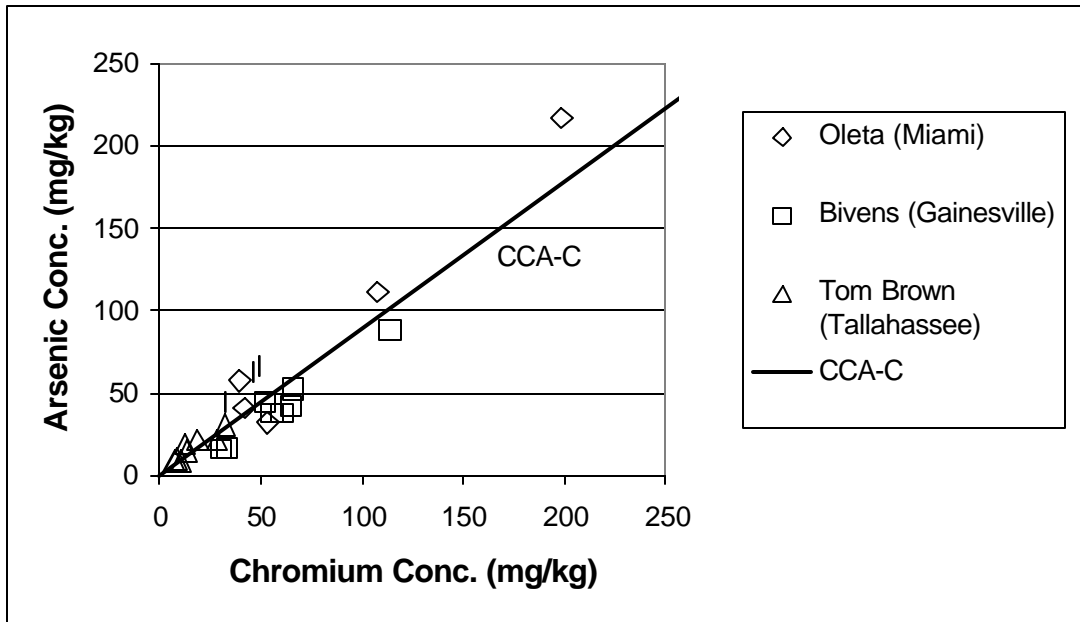


Figure II.4: Chromium Versus Arsenic Concentration for Surface Soils Collected From Three Decks

#### **II.4.c Copper Results for Surface Soils**

Of the 65 soil samples collected from below confirmed CCA-treated decks, 60 were above the detection limit for copper. For the samples above the detection limit, the surface soil copper concentrations ranged from a maximum of 216 mg/kg (site OP in Miami) to a minimum of 7.5 mg/kg (site BR in Gainesville) with an average of 40 mg/kg (table II.4). It is noted that the average, maximum, and minimum do not include site LT. The average of the corresponding controls varied from 6.1 to 6.7 mg/kg depending upon how the below detection limit samples were evaluated.

The average below deck soil copper concentration is plotted in relation to the average control sample copper concentration for each site in figure II.5. It is readily observed from this figure that the average of the deck soils were higher than the average of the controls for all of the sites sampled except for Lake Talquin. Statistically at 95% confidence limits, the soils below 6 of the 9 decks were elevated in copper concentrations above that for the controls (BP, BR, PP, MG, AD, OP). The three decks that did not show the elevated concentrations at 95% confidence were TB, LT, and TP. However it is important to note that TB deck soils were statistically elevated at 80% confidence. The TP soils were not significantly elevated at either 95% nor 80%. LT could not be tested statistically since all of the deck samples were below detection.

Of interest is that the copper concentrations appear to be correlated with arsenic concentrations within a particular site (figure II.6). However this correlation does not correspond to the stoichiometric relationship between arsenic and copper within CCA type C. Rather it appears as though there is more copper in the soil relative to arsenic. There are two potential explanations for this trend. The first is that the copper is preferentially leached from the CCA-treated decks. The second is that the copper leached from the CCA-treated decks is more tightly bound to the soil so that with subsequent washing it is not leached as readily from the soil as arsenic. This second hypothesis implies that there is some arsenic (and potentially chromium) that has been lost from the soils below the deck area and not accounted for.

Location	Surface Soil Samples Collected Below Decks (all analyses above detection limit except for LT & TP)					Controls (above detection limit)		Controls (BDL <sup>1</sup> = 0)		
	N <sup>3</sup>	Average (mg/kg)	Std. Dev. (mg/kg)	Max. (mg/kg)	Min. (mg/kg)	N	Average (mg/kg)	N	Average (mg/kg)	
Gainesville	BP	8	106.3	32.4	155.5	53.0	5	9.46	8	5.91
	BR	9	20.1	10.1	37.0	7.50	7	8.58	9	6.67
	PP	7 (8)	15.2(13.3)	6.14 (7.83)	26.00	9.0	8	4.60	8	4.60
total samples	24(25)	47.4(45.5)	46.7 (46.7)	155.50	7.50	20	7.21	25	5.77	
Tallahassee	TB	8	18.9	10.0	34.0	10.0	8	7.30	8	7.30
	MG	8	21.8	8.91	36.0	12.0	8	3.95	8	3.95
	LT	8	BDL <sup>1</sup>	---	BDL	BDL	5	3.31	8	2.48
total samples <sup>2</sup>	16	20.3	9.29	36.0	10.0	16	5.63	16	4.92	
Miami	AD	8	44.5	36.2	128.5	16.5	8	7.92	8	7.92
	TP	4 (8)	9.75(4.88)	1.19(5.27)	11.00	8.50	7	8.38	8	7.33
	OP	8	68.1	64.5	216.0	18.5	8	4.63	8	4.63
total samples	20 (24)	47.0(39.2)	50.0 (48.8)	216.0	8.50	23	6.91	24	6.63	
All Sites <sup>2</sup>	60 (65)	40.0 (37.0)	42.6(42.3)	216.0	7.50	59	6.66	65	6.05	

<sup>1</sup>BDL=Below Detection Limit. The detection limit for samples collected below the decks was 5 mg/kg based on a sample dry mass of 2.0 g. The detection limit for the control samples was 0.5 mg/kg based on sample dry mass of 2.0 g. The difference in the detection limits is due to the use of a flame AAS for the analysis of deck soils and graphite furnace AAS for the analysis of control soils.

<sup>2</sup>Does not include results from Lake Talquin, LT, deck

<sup>3</sup>Numbers in parentheses correspond to the total number of samples, including those below detection.

<sup>4</sup>Numbers in parentheses assumes a value of zero for samples that were BDL.

<sup>5</sup>Minimum excluding samples that were BDL.

Table II.4: Copper Results for Surface Soils

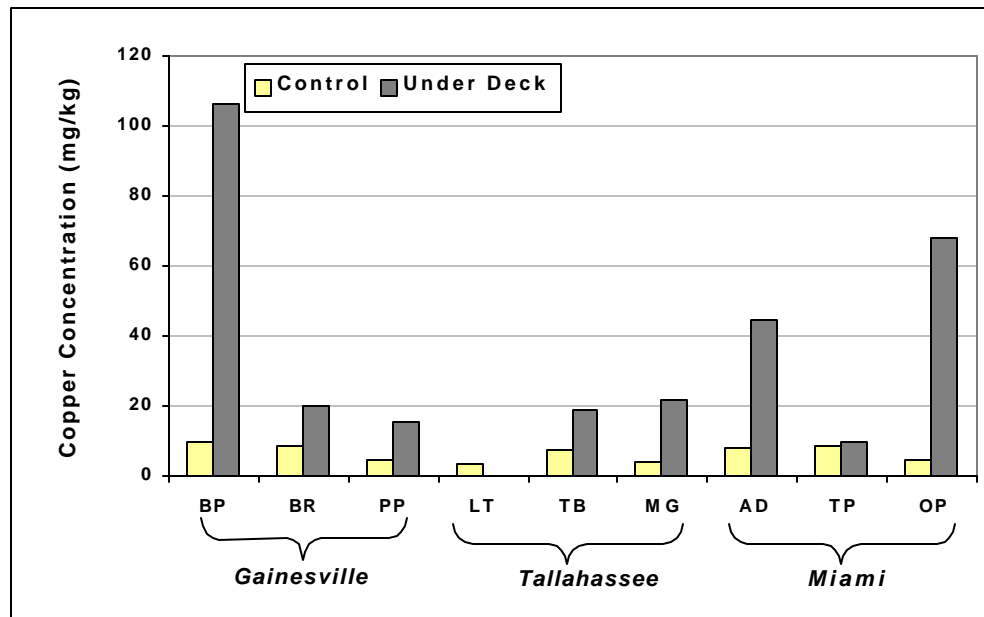


Figure II.5: Comparison of Mean Deck Soil Copper Concentration Versus Control Soil Concentrations

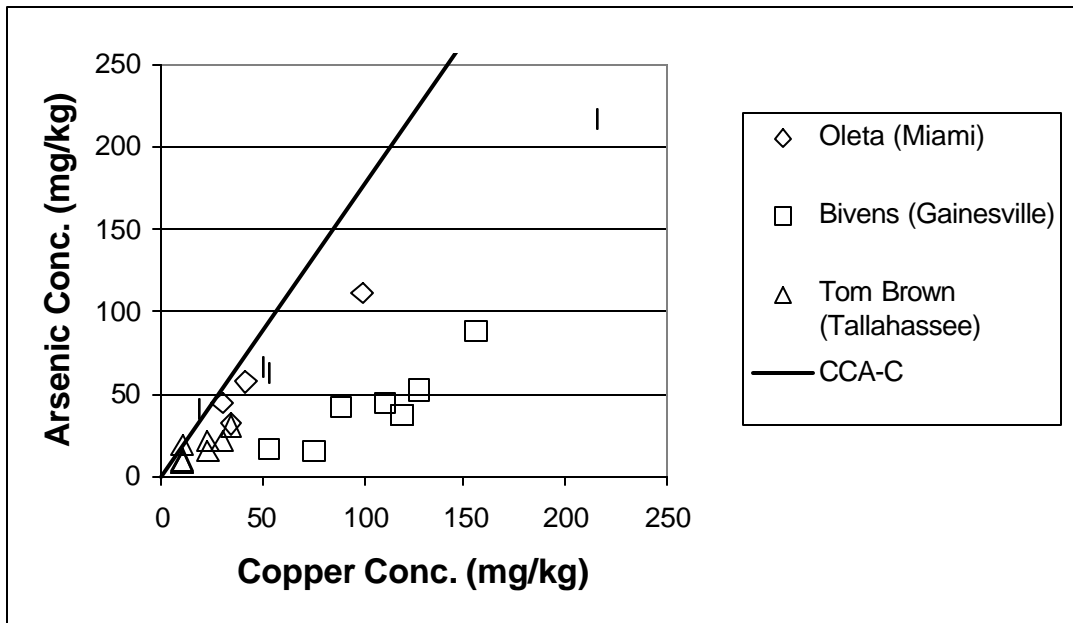


Figure II.6: Chromium Versus Arsenic Concentration for Surface Soils Collected From Three Decks

## II.5 RESULTS OF PHYSICAL MEASUREMENTS

Two sets of physical measurements were performed on the surface soil samples: volatile solids content and grain size analyses.

### II.5.a Volatile Solids Content

Results indicate that the volatile solids content of the surface soil samples varied from 2% to 26% (table II.5). The site characterized by the lowest volatile solids content was Tropical Park which had the consistency and appearance of a beach sand. The site characterized by the highest volatile solids content was Bivens Arm Park. Soils collected from Bivens Arm Park were dark brown in color and were characterized by a “sponge-like” consistency.

There appears to be a correlation between volatile solids content and soil metal concentrations. This correlation appears weak between sites but is very noticeable within a particular site. Between sites (figure II.7) it is noted that soils collected at Tropical Park had very low arsenic concentrations (4.3 mg/kg average) and also had a low volatile solids content (1.9%). Soils at Bivens Arm Park were characterized by the highest volatile solids content (26%) and the second highest average arsenic concentration (42 mg/kg). Exceptions to the general trend include the very low arsenic concentrations observed at Lake Talquin (0.48 mg/kg) even though the volatile content of the soils was at 12%. The low arsenic concentrations at Lake Talquin is likely due to the fact that this deck was not confirmed to be CCA-treated and was therefore not likely impacted by CCA. The second exception to the trend is noted at Oleta River Park which was characterized by the highest arsenic concentrations (79 mg/kg average) and relatively low volatile solids (4.4 %).

Correlations between volatile solids content and metals concentrations *within* a particular site were observed for 5 of the 9 decks. These decks included Bivens Arm Park, A.D. Barnes Park, Oleta River Park, Tropical Park, and Tom Brown Park. A representative plot of this relationship is provided in figure II.8, where it is observed that the highest arsenic concentration was observed for the deck soil site characterized by the highest volatile solids content. Similarly, the lowest arsenic concentrations were measured for sites characterized by low volatile solids. Due to the low arsenic concentrations observed for the control samples, no correlations were generally observed between arsenic concentrations and volatile solids content of the controls. The primary exception, however, was observed for control sample #2 (CO2) collected at Bivens Arm Park (figure II.8). This particular sample was characterized by a very high volatile solids concentration (75%) and for a control sample also had a relatively high arsenic concentration (13 mg/kg). The remaining control samples for this site were characterized by an average arsenic concentration of 1.1 mg/kg and average volatile solids concentration of 8%. The high arsenic concentration observed for sample C02 may be due to the extremely high volatile solids content.

City	Name/Description of deck	Site Abbreviation	Volatile Solids (%)	Grain Size, 50% finer (mm)
<b>Gainesville</b>	34th Street Footbridge	BR	3.5	0.343
	Deck at Paynes Prairie	PP	5.0	0.370
	Walkway at Bivens Arm Park	BP	26.4	0.387
<b>Miami</b>	Deck at Oleta River Park	OP	4.4	0.293
	Playground at A.D. Barnes Park	AD	9.7	0.339
	Lifeguard station at Tropical Park	TP	1.9	0.284
<b>Tallahassee</b>	Footbridge at Lake Talquin	LT	11.7	0.393
	Deck at Maclay Gardens	MG	4.4	0.387
	Footbridge at Tom Brown City Park	TB	4.6	0.390

Table II.5: Volatile Solids and Grain Size Data for Soils Collected Below Decks

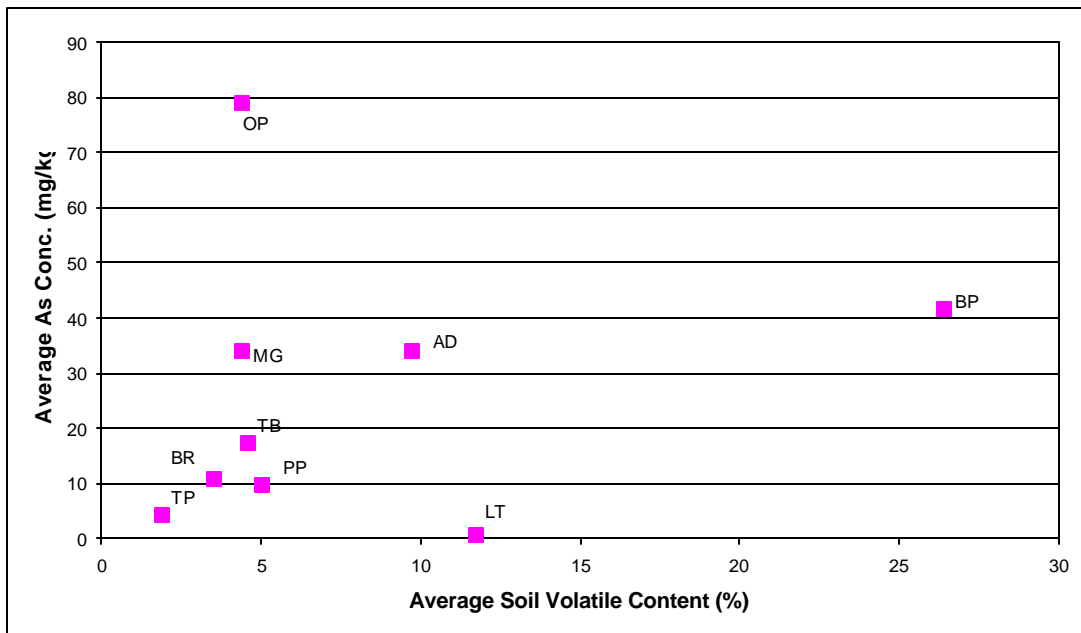


Figure II.7: Average Arsenic Concentration Versus Average Soil Volatile Content

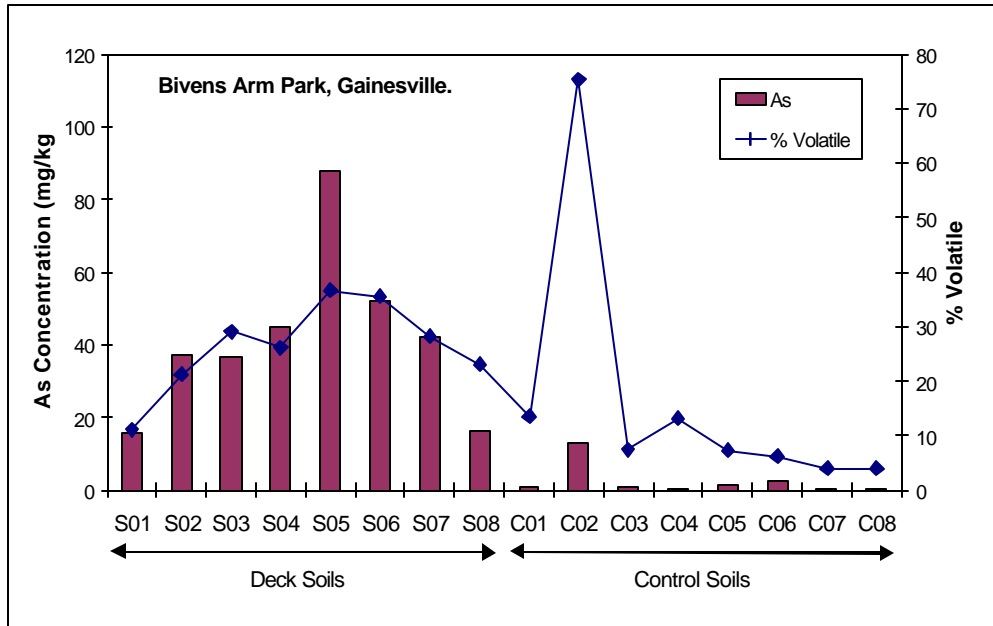


Figure II.8: Arsenic and % Volatile Concentration Per Sampling Station at Bivens Arm Park, Gainesville

### II.5.b Grain Size Distribution

Results from grain size analysis indicate that the soils below each deck were characterized by a similar grain size distribution (figure II.9). All soils were generally uniformly graded with an average size (50% finer) between 0.28 to 0.39 mm. This range of grain sizes corresponds to a medium sandy soil (Das 1985).

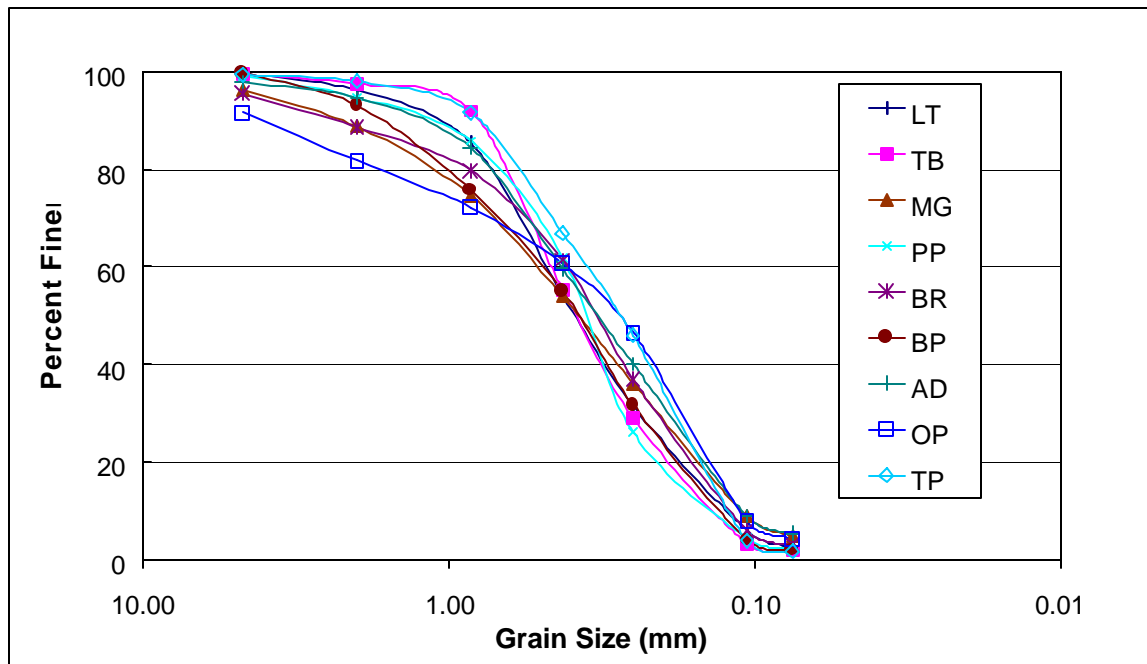


Figure II.9: Soil Grain Size Distribution

## II.6 RESULTS FROM SOIL CORE SAMPLES

In addition to the surface soil samples a set of eight soil cores were collected under the nine decks and boardwalks in Gainesville, Miami, and Tallahassee. (See figures A.28 to A.36 in appendix A for details.) One control soil core sample was collected at the Gainesville 34<sup>th</sup> Street boardwalk. The results from the cores collected below the decks (except for the Lake Talquin core) were averaged and compared to the value obtained for the control core collected at the 34<sup>th</sup> St. boardwalk in Gainesville. Results (figure II.10 and tables II.6 and II.7) suggest that the CCA-treated decks impact at least the upper 3 inches of soil below the decks. The depth of the impact appears deeper for arsenic than for chromium or copper.

Statistics from the soil cores for each individual site are provided in table II.8. Data indicate that the maximum concentrations of arsenic were found within the first two inches of the soil within all cores. The majority of the minimum arsenic concentrations are shown to be confined mainly to depths greater than five inches, with the exception of the MG deck in Tallahassee which had a minimum arsenic concentration at a depth of 3.5 in. The trends in the chromium concentrations from the soil core samples were not as consistent as those observed for arsenic. Five of the 8 cores did show an overall trend (BP, TB, MG, TP, and OP) with the highest chromium concentrations near the soil surface and lower concentrations at deeper depths. Overall, the maximum chromium concentrations occurred from 0.75 to 11.5 inches from the ground surface and the minimum chromium concentrations were measured at depths ranging from 1.75 to 9.9 inches. As for the copper results, five of the 8 cores showed an overall trend (BP, BR, PP, TB, and TP) with the highest copper concentrations near the soil surface and lower concentrations at deeper depths. For all nine cores evaluated, the maximum copper concentrations occurred from 0.25 to 9.5 inches below the surface and the minimum copper concentrations were measured at depths ranging from 2.5 to 10.5 inches below the surface.



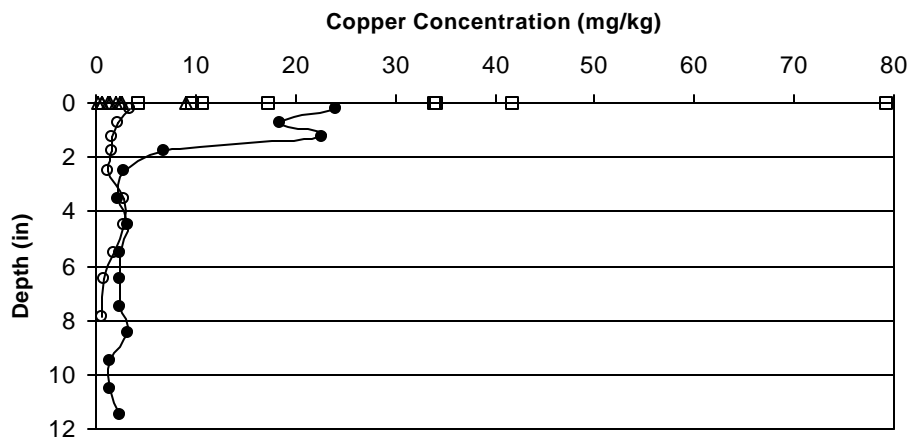
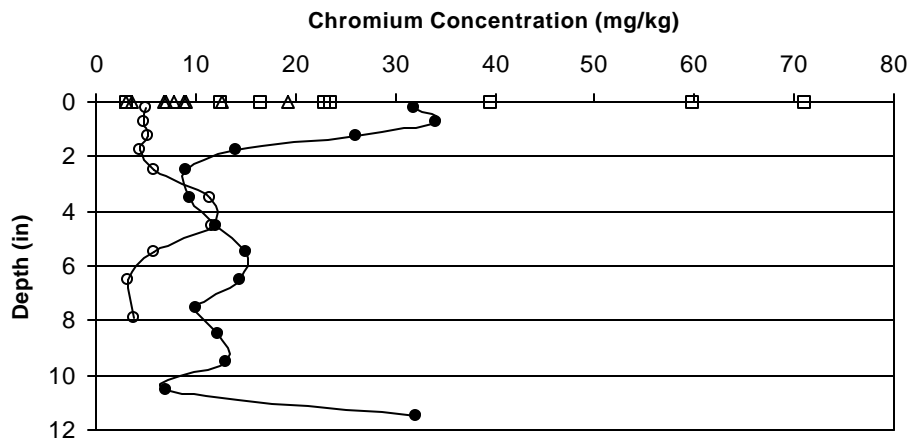
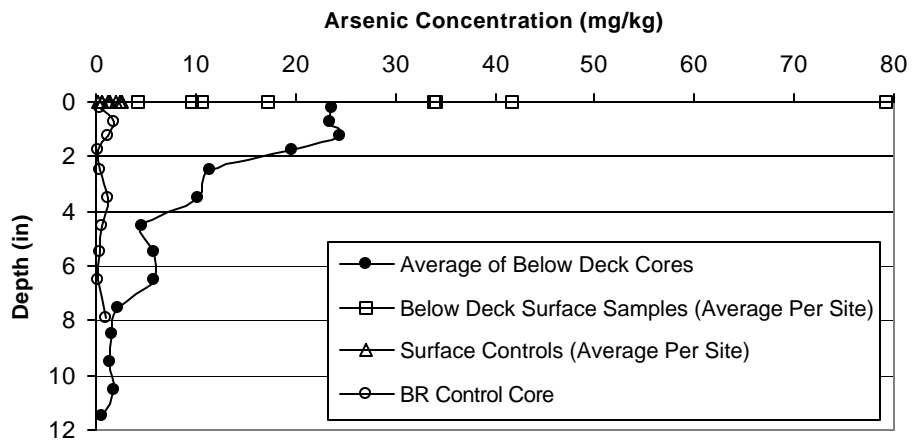


Figure II.10: Average of Soil Cores

Depth (in)	N (At Given Depth)	Average Metal Concentration (mg/kg)		
		As	Cu	Cr
0.25	8	23.66	24.01	31.89
0.75	8	23.40	18.48	34.01
1.25	8	24.45	22.64	26.13
1.75	8	19.70	6.79	14.12
2.5	8	11.33	2.75	9.06
3.5	8	10.27	2.29	9.34
4.5	8	4.70	3.26	11.99
5.5	8	5.87	2.37	15.11
6.5	7	5.84	2.50	14.47
7.5	7	2.16	2.43	9.95
8.5	6	1.54	3.23	12.16
9.5	6	1.46	1.47	13.03
10.5	3	1.79	1.49	6.92
11.5	1	0.58	2.32	32.08

Table II.6: Average Metal Concentration in Core Samples

Depth (in)	Average Metal Concentration (mg/kg)		
	As	Cu	Cr
0.25	0.32	3.32	4.97
0.75	1.76	2.20	4.84
1.25	1.10	1.63	5.29
1.75	0.12	1.57	4.43
2.5	0.30	1.28	5.80
3.5	1.28	2.85	11.46
4.5	0.60	2.84	11.70
5.5	0.33	1.71	5.90
6.5	0.16	0.76	3.25
7.9	0.96	0.62	3.80

Table II.7: Metal Concentration in BR Control Core Sample

Location	N	Average (mg/kg)	Standard Deviation (mg/kg)	Maximum		Minimum		
				Concentration (mg/kg)	Depth <sup>1</sup> (in)	Concentration (mg/kg)	Depth <sup>1</sup> (in)	
<b>Arsenic</b>								
Gainesville	BP	13	10.2	14.8	35.29	1.25	0.25	9.5
	BR	14	5.85	6.66	25.34	0.25	0.38	10.5
	PP	12	4.58	4.75	16.02	0.25	0.98	7.5
Tallahassee	TB	11	8.09	5.27	19.55	0.25	1.35	8.5
	MG	13	3.94	2.55	11.19	0.25	1.34	3.5
Miami	AD	12	1.84	1.36	4.97	0.25	0.73	9.8
	TP	10	30.88	24.16	67.58	1.75	3.64	4.5
	OP	8	39.76	24.10	64.61	0.75	2.55	5.6
All Sites		93	11.35	16.84	67.58	1.75	0.25	9.5
<b>Chromium</b>								
Gainesville	BP	13	17.5	25.0	64.0	0.75	0.56	4.5
	BR	14	17.1	8.64	32.1	11.50	4.25	10.5
	PP	12	29.0	14.8	51.8	0.25	4.10	1.75
Tallahassee	TB	11	7.87	5.88	23.0	0.25	3.18	9.9
	MG	13	15.7	9.92	47.0	6.50	8.18	7.5
Miami	AD	12	6.67	4.49	16.9	0.75	0.93	2.5
	TP	10	25.0	19.5	65.1	0.75	8.35	2.5
	OP	8	18.1	14.6	41.5	0.75	6.02	5.6
All Sites		93	16.9	15.5	65.1	0.75	0.56	4.5
<b>Copper</b>								
Gainesville	BP	13	22.8	37.5	108.0	1.25	0.10	7.5
	BR	14	5.84	4.25	18.3	0.25	0.69	10.5
	PP	12	5.36	9.63	30.5	0.25	0.29	2.5
Tallahassee	TB	11	5.12	6.56	23.8	0.25	0.61	9.9
	MG	13	3.47	0.62	4.71	9.50	2.39	3.5
Miami	AD	12	2.57	2.36	6.41	0.25	0.55	8.5
	TP	10	9.17	10.9	30.6	1.25	0.76	7.9
	OP	8	7.41	6.80	21.5	1.25	1.70	5.6
All Sites		93	7.77	16.0	108.0	1.25	0.10	7.5

<sup>1</sup>Depths correspond to the mid-point of the core portion analyzed. The upper 2 inches were analyzed in ½ increments and 1 inch increments thereafter. The top of the core corresponds to 0.25 inches.

Table II.8: Summary of Arsenic, Chromium, and Copper Soil Core Results

## II.7 SUMMARY AND CONCLUSIONS

This section focuses on summarizing the data from the preceding sections (II.7.a), computing theoretical arsenic concentrations below CCA-treated decks (II.7.b), computing the areal extent of the potential impacts of CCA-treated decks (II.7.c), and comparing the results of the arsenic analysis to clean soils standards (II.7.d).

### II.7.a Summary

Results indicate that CCA-treated decks do in fact impact the soils below them. The average arsenic concentration of surface soils below the decks was 28.5 mg/kg whereas the average of the surface soil controls was between 1.3 and 1.5 mg/kg. The differences between the below deck soils and controls was statistically significant at 95% confidence for 8 of the 9 decks evaluated. The only “below deck” surface soil found not to be elevated was the Lake Talquin deck. The Lake Talquin deck was the only deck that was not confirmed for CCA treatment. The data suggest that CCA-treated decks impact the soil arsenic concentrations up to a depth of 4 to 8 inches, thus confirming that the impacts are not limited to CCA-treated sawdust that may have been deposited on the soil during the deck’s construction. Within a particular site volatile solids content appears to be correlated with arsenic concentrations. This correlation is weak between sites.

The decks were also observed to impact soil chromium and copper concentrations. The average chromium and copper concentrations in the below deck soils were 34 and 40 mg/kg, respectively, for samples above detection limits. In comparison, the chromium and copper concentrations for the controls were 9.8 and 6.7 mg/kg, respectively, on average. The differences between below deck soils and controls was statistically significant at 95% confidence for 3 of the decks for chromium and for 6 of the decks for copper. The lack of statistical significance for the remaining decks may be due to the relatively higher background chromium and copper concentrations found at each site (versus that for arsenic). Chen et al., 1999, report that the geometric mean Florida soil concentration for arsenic, chromium and copper as 0.42 mg/kg, 8.45 mg/kg and 2.21 mg/kg respectively.

The ratio of the arsenic and chromium in the below deck surface soils was consistent with the stoichiometry of CCA type C, whereas the ratio of arsenic to copper in the below deck surface soils suggests preferential leaching of copper from the deck or preferential sorption of copper onto the below deck soils.

### II.7.b Theoretical Concentrations of Arsenic Below CCA-Treated Decks

A set of computations were performed to estimate the resultant increase in soil arsenic concentrations assuming that a particular fraction of the CCA chemical were to leach from CCA-treated decks. These computations were performed in order to determine whether the amount of arsenic measured in the soil was reasonable. The computations assume that 12 ft<sup>3</sup> of treated wood covers a soil area of 64 ft<sup>2</sup>. The concentration of arsenic in the deck wood is assumed to be 2000 mg/kg which is equivalent to a 0.3 pcf retention level. The density of the soil is assumed to be 2.65 g/cm<sup>3</sup> and the porosity is assumed at 0.33. The results from such a computation (figure II.11) indicate that in order to increase the soil concentrations by 25 mg/kg

in the upper 8 inches, only 15% of the CCA chemical needs to leach. If the impact is assumed to be limited to the upper 2 inches, then less than 5% of the CCA chemical needs to leach in order to increase the soil concentration by 25 mg/kg. This analysis indicates that the results from the soil sampling study are consistent with a reasonable fraction of CCA chemical leached from the decks. The analysis also suggests that only a relatively small fraction of the CCA chemical needs to leach from CCA-treated decks in order to observe measurable impacts on the soil.

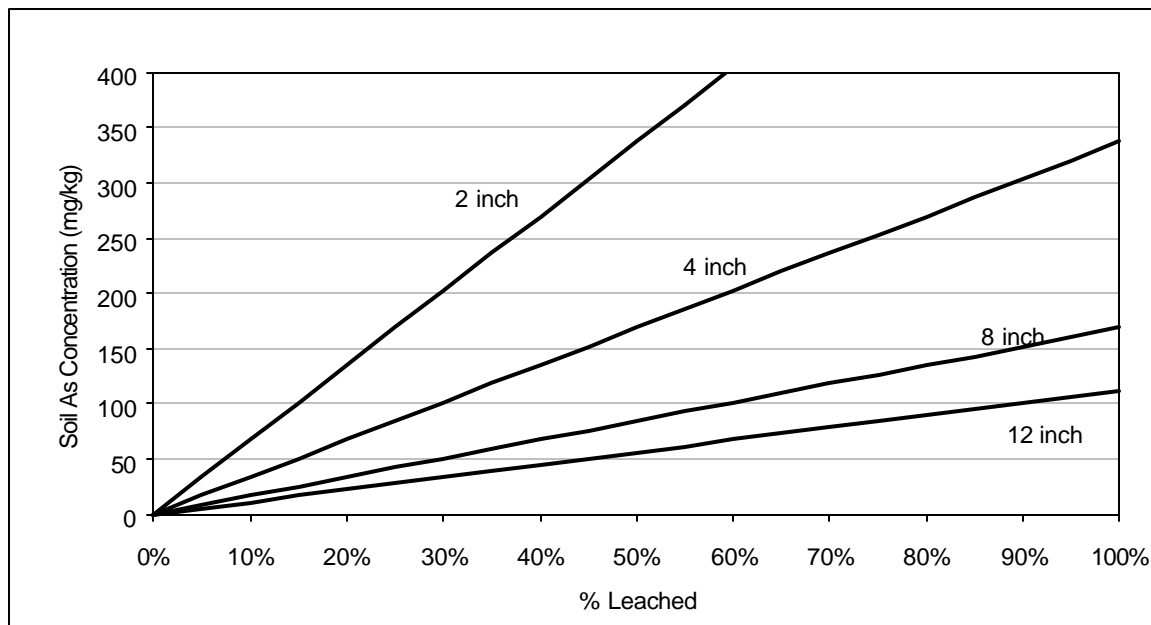


Figure II.11: Theoretical Soil Arsenic Concentration Versus % CCA Leached and Depth of Soil Impacted

### II.7.c Areal Extent of Potential Impacts of CCA-Treated Decks

Approximately 565 million cubic feet of CCA-treated wood have been sold within Florida and of this quantity approximately 36% is used for decks (See chapter III for more information concerning these statistics). In order to convert from cubic feet of wood product to square feet of area, assumptions must be made about the typical construction of a deck. For this computation, it is assumed that an 8 foot by 8 foot deck is covered with 1.5 inch thick deck boards and that the deck is supported by 3 x 6 inch joists around the perimeter. Thus the amount of wood needed for a 64 square foot deck is 12 cubic feet  $[8 \times 8 \times (1.5/12) + 4 \times 8 \times (3/12) \times (6/12)]$ . The equivalent surface area of soil in Florida covered by decks is therefore 25,000 acres  $[565 \times 10^6 \times 0.36 \times (64/12) / 43,560]$  or 39 square miles. If it is assumed that the effects are observed in the upper 8 inches, then it is estimated that 60 million tons of soil have been impacted by CCA-treated decks in Florida.

## II.7.d Comparison of Arsenic Data to Clean Soil Standards

The deck soil sample arsenic concentrations were compared to Florida's Soil Cleanup Target Levels (SCTLs). The Florida SCTLs are risk-based soil concentrations that have been developed for a number of different pollutants, including arsenic. The SCTLs have been developed using a set of assumptions regarding the properties of the soil; the characteristics of the exposure; and specific chemical toxicity. A number of different SCTLs have been developed for application in various land use scenarios and for both direct exposure (ingestion, dermal contact, and inhalation) and leaching to groundwater. Although the SCTL may be modified for site-specific conditions, properties of a generic Florida soil were used in the SCTL development (e.g organic carbon content).

The residential SCTL for direct exposure is 0.8 mg/kg. The mean arsenic concentration exceeded 0.8 mg/kg at eight out of the nine sites studied. The one site that was below the 0.8 mg/kg SCTL was the Lake Talquin site in Tallahassee which was the only deck sampled that was not constructed of CCA-treated wood. Every sample collected under the Lake Talquin foot bridge was less than 0.8 mg/kg. All 65 of the remaining samples exceeded the residential SCTL for arsenic. The industrial SCTL for direct exposure is 3.7 mg/kg. As with the residential SCTL, the mean arsenic concentration for each site exceeded the industrial SCTL with the exception of Lake Talquin. Sixty two of the remaining 65 samples exceeded the industrial SCTL. Figure II.12 shows all soil samples compared to the SCTLs.

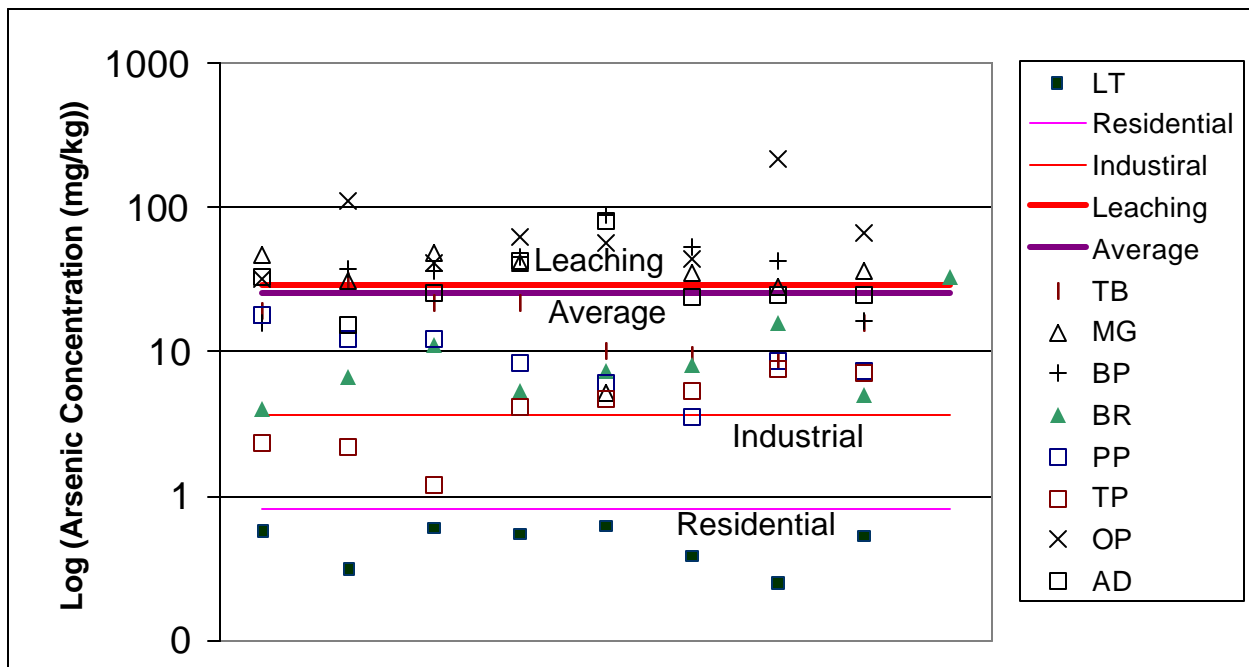


Figure II.12: Log of Arsenic Concentrations

The SCTL for leaching to groundwater (based on the groundwater standard of 50µg/l) is 29 mg/kg. The mean arsenic concentration was greater than 29 mg/kg at 4 of the 9 sites. Twenty-four of the 73 deck soil samples collected were above the leaching-to-groundwater SCTL. It is worth noting that since the leaching SCTL is based on the current primary drinking

water standard of 50 µg/l, if this standard is lowered, the SCTL will be lowered accordingly. The U.S. EPA, 2001, has proposed lowering the standard for arsenic from 50 µg/l to 10 µg/l. If the proposed standard is finalized at 10 µg/l, the arsenic leaching SCTL would be lowered to 5.8 mg/kg, in which 7 of the 8 sites CCA-treated deck sites would exceed the level and 54 of the 65 surface soil samples (excluding site LT) would exceed.

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**CHAPTER III**  
**INVENTORY OF CCA-TREATED WOOD IN FLORIDA**

## **CHAPTER III, INVENTORY OF CCA-TREATED WOOD IN FLORIDA**

This chapter begins by describing the need to compile statistics for CCA-treated wood usage in Florida (section III.1) and is followed by 5 sections (sections III.2 through III.6) which describe the different statistics compiled through this study. The chapter ends with a summary and conclusion (section III.7).

### **III.1 INTRODUCTION**

This chapter is a compilation of statistics relevant to estimating the quantity of CCA-treated wood in different use sectors. The first set of statistics (section III.2) corresponds to the quantity of CCA-treated wood relative to that of untreated wood. These statistics can be used to estimate the fraction of all wood disposed that is composed of CCA-treated wood. This statistic is of significance for recycling operations given that the economics and environmentally appropriate methods for recycling wood waste are dependent upon the presence and quantity of CCA-treated wood in this waste stream.

The remaining statistics described in this chapter focus primarily on estimating the distribution of CCA-treated wood within different use sectors. An inventory for CCA-treated wood and ultimately arsenic within use sectors is a necessary component of a disposal management plan that focuses on recovering the arsenic in CCA-treated wood. Once the major use reservoirs of the chemical are identified, strategies can then be developed to recover this material from these reservoirs. Section III.3 provides statistics for production and disposal of CCA-treated wood by product type, specifically lumber, timbers, and fence posts versus utility poles and crossties. The approach utilized in this study was similar to our earlier study (Solo-Gabriele et al. 1998) in that readily available industry statistics were compiled concerning the production of different CCA-treated wood products. These statistics were coupled with a mass balance equation to forecast disposal quantities into the future. Statistics from our earlier study were updated with more recent data, and used to estimate the total amount of arsenic associated with CCA-treated wood currently in service (section III.4).

An additional goal of the current study was to further break-down the use of CCA into specific use categories, given that there are many different sectors that utilize lumber, timbers, and poles. Use distributions compiled by the Southern Forest Products Association (SFPA) for the U.S. are presented in section III.5. In section III.6, an in depth study was conducted to estimate the quantity of CCA-treated wood used in Florida for salt/fresh water docks and utility poles. These two use categories were chosen for three reasons. First these uses represent a concentrated source of the CCA chemical. Typically, utility poles are treated at 0.60 pcf whereas poles used for fresh water docks are treated at 0.80 pcf and poles used for salt water docks are treated at 2.5 pcf, the highest retention level typically manufactured. This differs from wood used in above ground applications which is typically treated at 0.25 pcf. If arsenic were to be recovered, considerably more chemical would be thus recovered per cubic foot of wood from utility, marine, and freshwater poles than from other use sectors. The second reason that these use reservoirs were chosen for further study was because they are associated with a particular industry which may make it easier to recover the treated wood. For example, the number of utilities within Florida is relatively small and their disposal operations are generally centralized.

Marine and freshwater installations (and removals) of treated wood products are generally performed by a contractor rather than by individual homeowners, with one contractor serving many different homeowners. So, if treated wood were to be recovered from these use sectors, regulators need only to focus on the utility companies and/or marine contractors to recover the bulk of the treated wood product, rather than focus on the entire population within the State. The third reason these use categories were chosen was because no waterborne alternative-chemical treated wood products are generally available for these “heavy duty” applications, whereas for “light applications,” such as for above ground and ground contact uses, several waterborne alternative chemicals have been standardized through the AWPA and marketed for use. A particular emphasis is placed on waterborne alternatives due to their paintability, non-oily and non-odorous nature, which makes them ideal for residential use. However, it is important to emphasize that there are oilborne alternative chemicals available for “heavy duty” applications (e.g. poles), where the oily nature of the treated wood product is not of aesthetic significance. The demand for CCA will likely continue, nevertheless, for marine/freshwater docks as a result of the demand for a non-oily products and no waterborne alternative for this application. As a consequence, the disposal of at least the docks will likely continue in the long term as long as a demand for waterborne treatment wood products for this application continues into the future. It is therefore important to develop a strategy by which the wood used for these “heavy duty” applications, in particular the docks, are recovered prior to disposal within the rest of the waste stream.

### **III.2 PROPORTION OF CCA-TREATED WOOD AMONG TREATED AND UNTREATED WOOD**

The Southern Forest Products Association (SFPA) located in Kennar, LA, compiles U.S. statistics for southern pine usage including data concerning the quantity of southern pine that is treated versus that which is untreated. Statistics compiled by the SFPA for treated wood correspond to the reported volumes from treaters who subscribe to quality assurance/quality control inspection services that are accredited. It is estimated that roughly 85 to 90% of all treated wood is handled by these types of inspection services (Dave Mason, SFPA, personal communication). Southern Pine also likely represents the bulk of the wood that enters the construction and demolition disposal stream in Florida (Dave Mason, SFPA, personal communication). Other wood species, such as Cedar and Spruce Pine Fir, likely represent small fractions of the wood used for construction purposes. Cedar is significantly more expensive than Southern Pine and Spruce Pine Fir is grown primarily in Canada. Given the large distance between Canada and Florida, the use of Spruce Pine Fir in Florida would be less economical due to transportation costs. The statistics, however, do not account for wood species that may be imported from the Caribbean and Central and South America. There are a few treatment plants that import wood from Central and South America, treat it in Florida, and then re-export to other countries located in the Caribbean and/or Central and South America.

Statistics (table III.1 and figure III.1) show that the quantity of Southern Pine used in the last eight years (between 1992 and 1999) has a slight increasing trend between 1.2 and 1.4 billion cubic feet of wood product. Of this quantity, between 36% to 43% was treated. Between 1987 and 1991, the total amount of Southern Pine sold in the U.S. was roughly 1 billion cubic feet with up to 48% of the wood treated. Prior to 1987, a smaller quantity of Southern Pine was produced and the proportion of treated wood within this quantity was also smaller. During 1980,

0.7 billion cubic feet of Southern Pine were produced. Of this quantity, only 23% was treated.

These statistics indicate an increase in not only the quantity of treated wood ultimately disposed, but also the proportion of wood that is treated. The fraction within the disposal stream can potentially be as high as 40 to 50%.

Year	Production (billion ft <sup>3</sup> )			Percent Treated
	Treated	Untreated	Total	
1980	0.158	0.525	0.683	23.2
1981	0.200	0.500	0.700	28.6
1982	0.217	0.517	0.733	29.5
1983	0.267	0.583	0.850	31.4
1984	0.325	0.567	0.892	36.4
1985	0.358	0.517	0.875	41.0
1986	0.400	0.592	0.992	40.3
1987	0.500	0.542	1.042	48.0
1988	0.508	0.550	1.058	48.0
1989	0.492	0.550	1.042	47.2
1990	0.500	0.575	1.075	46.5
1991	0.500	0.542	1.042	48.0
1992	0.508	0.667	1.175	43.3
1993	0.508	0.692	1.200	42.4
1994	0.508	0.742	1.251	40.6
1995	0.508	0.717	1.226	41.5
1996	0.475	0.800	1.272	37.4
1997	0.500	0.842	1.343	37.2
1998	0.492	0.858	1.347	36.5
1999	0.500	0.875	1.375	36.4

Table III.1: Historical Southern Pine Production Statistics (from SFPA)

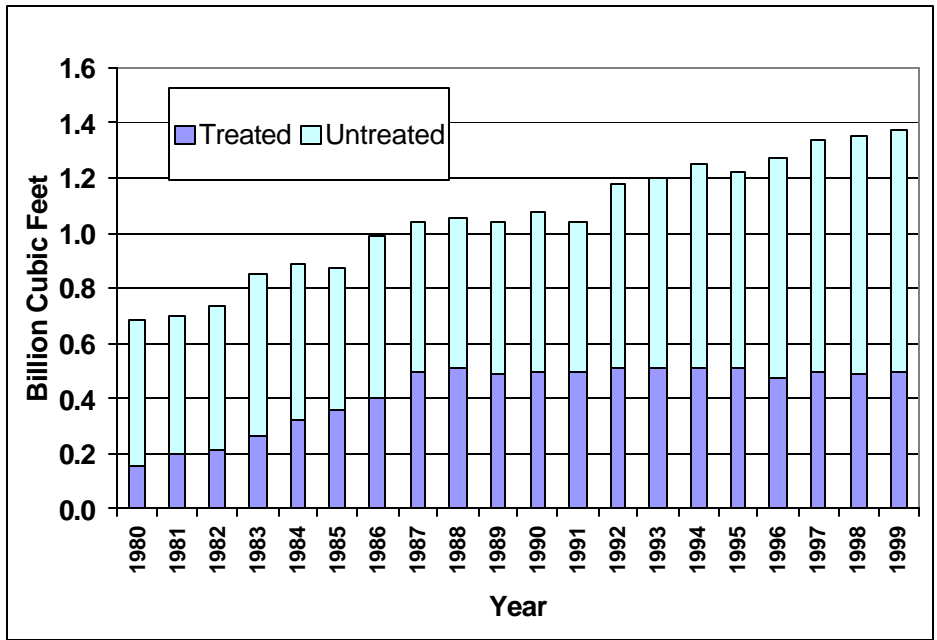


Figure III.1: Historical Southern Pine Production Statistics

### **III.3 PRODUCTION AND DISPOSAL OF CCA-TREATED WOOD BY PRODUCT TYPE**

The disposal forecast (Solo-Gabriele and Townsend 1999) originally developed by the research team covered the years from 1964 to 1996. Although production statistics were compiled in terms of different products (e.g. lumber and timbers versus poles), the disposal forecast did not separate disposal into these different products. The purpose of this section of the study was to update the forecast with additional years of statistics and to expand the disposal forecast to include disposal projections of different products. These data were used in the following section (section III.4) to estimate the quantity of treated wood (in terms of tons of arsenic) currently in service.

#### **III.3.a Brief Description of the Disposal Forecast Model**

The original disposal forecast model developed for Florida (Solo-Gabriele et al. 1998) is based upon a mass balance approach where production statistics are coupled with assumptions concerning typical service lives of treated wood. Production statistics were compiled from yearly industry reports published by the American Wood Preservers' Association (AWPA) and the American Wood Preservers' Institute (AWPI). The AWPA and AWPI compile statistics for the entire U.S. and/or regions of the U.S and separate production into different use categories such as lumber/timbers versus poles. The reports also provide details concerning individual treatment plant cylindrical volumes. The cylindrical volume capacity for plants in the U.S., southern region, and Florida were computed and used to extrapolate production statistics for Florida. The extrapolation procedure utilized to estimate Florida's production statistics was verified through an independent questionnaire sent to Florida's wood treatment plants.

Once production statistics were computed for Florida, the disposal forecast model then assumed that 2.5% of the production is immediately disposed due to cutoffs and accidents. The service life of the remaining 97.5% was then prorated over a ten year period. Prior to computing the disposal of the remaining 97.5%, the production quantities of these treated wood products were separated into two groups. Group 1 products consisted of lumber, timbers, fence posts, and "other." The "other" category included plywood, switch ties, and crossarms. The quantity of wood in the "other" category was generally less than 20% of the quantities of lumber, timbers, and fence posts. Group 1 products were assumed to be characterized by an average service life of 25 years. Disposal of these products was prorated as follows: 25% last 20 to 22 years, 50% last 23 to 27 years, and the remaining 25% last 28 to 30 years. Group 2 products included poles and crossties and were assumed to be characterized by an average service life of 40 years. Disposal of group 2 products was prorated by assuming that 25% of the products are disposed after 35 to 37 years, 50% of the products are disposed after 38 to 42 years, and the last 25% are disposed after 43 to 45 years. Please see Solo-Gabriele et al. 1998 for more details about this model.

#### **III.3.b Updates to the Disposal Forecast Model**

The disposal forecast model developed for Florida was updated to include U.S. and regional statistics compiled by the AWPA for 1961, 1962, 1963, and 1997. No production statistics were available from AWPA or AWPI for 1998. Furthermore, projections for U.S. treated wood production were added for the years 1999 to 2004. These projections were obtained through the

Southern Forest Products Association (SFPA) which has developed its own model to predict treated wood usage within various markets. The SFPA model is based upon information provided the Forest Products Laboratory, Wood Products Council, and from several government sponsored projects. The SFPA model uses various economic indicators including housing starts, repair/remodel index, etc. The model forecasts several construction markets including residential construction, non-residential construction, industrial construction, and remodeling (Steven Bean, SFPA, personal communication). Specifics concerning the results of this forecast are provided in table B.1 in appendix B. According to the SFPA, the U.S. treated southern pine market is expected to stabilize at roughly 0.49 billion cubic feet per year during 2000 to 2002. A drop to 0.47 billion cubic feet per year is anticipated during 2003 and 2004.

### **III.3.c Results**

Results show that production of CCA-treated wood products increased significantly between 1980 and 1990 (figure III.2 and III.3). Since 1990, production statistics were more varied but in general show a net increase in CCA-treated wood production over that observed during the 1980s. Results also show that group 1 (lumber, timber, fence posts, and other) represent the bulk of the CCA-treated wood products (between 92 and 97% by a cubic foot basis) with group 2 (poles and crossties) representing a much smaller fraction. Also of interest is the finding that the disposal of group 1 products will occur at an earlier time period. Measurable quantities of group 1 products are being disposed today and (assuming that current production statistics continue) disposal quantities will likely peak for group 1 products during the year 2020. Disposal of significant quantities of group 2 products will not be observed until after the year 2004. The peak in the disposal of group 2 products will not be observed until after the year 2040.

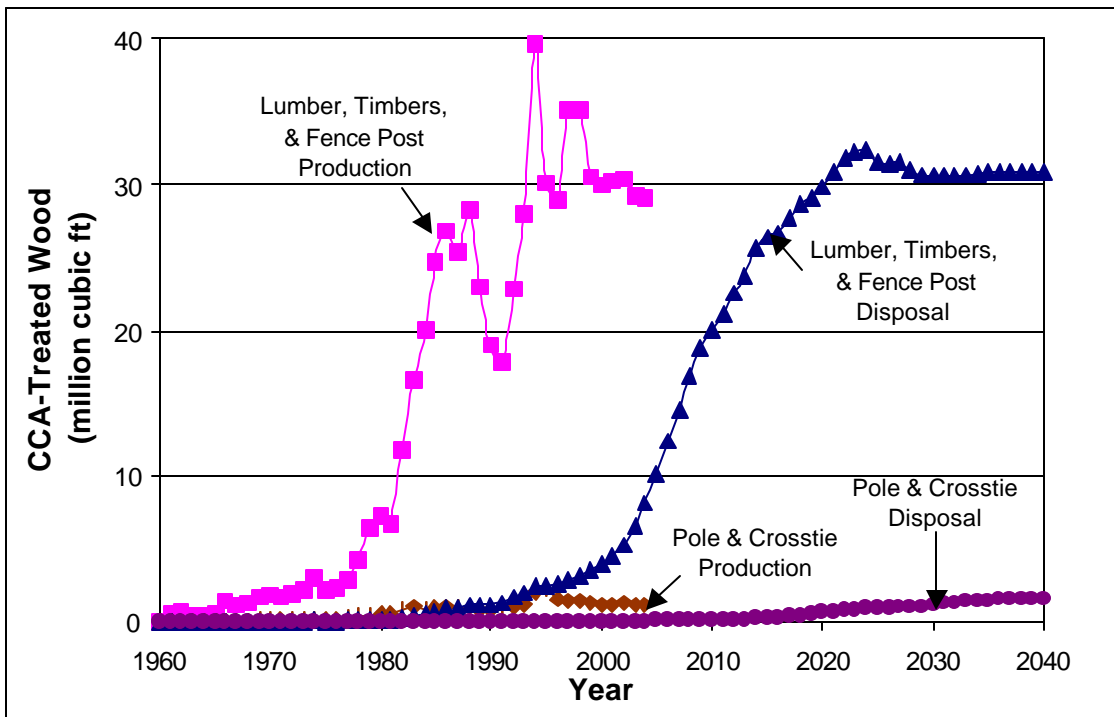


Figure III.2: Estimated Production and Disposal Quantities for Lumber, Timbers, and Fence Posts

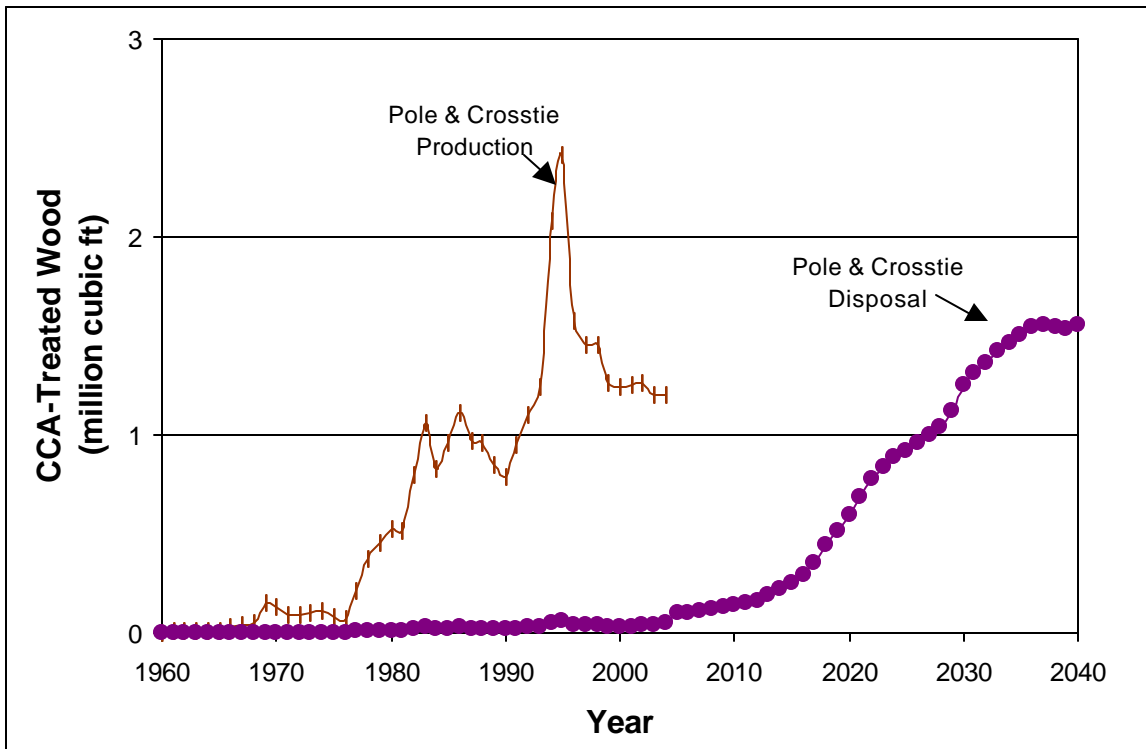


Figure III.3: Estimated Production and Disposal Quantities for Poles and Crossties



### III.4 QUANTITY OF ARSENIC ASSOCIATED WITH CCA-TREATED WOOD CURRENTLY IN SERVICE

The purpose of this section is to describe the methods (section III.4.a) and results (III.4.b) of computations designed to estimate quantity of arsenic associated with CCA-treated wood. This estimate is then used in subsequent sections to determine the fraction of the arsenic (from CCA-treated wood that is currently in service) that can be attributed to utility poles and fresh/marine water applications.

#### III.4.a Methods

In order to compute the quantity of arsenic associated with CCA-treated wood currently in service, the quantities of CCA-treated wood computed in section III.3 were summed where the sum of the production quantities for any given year ( $\sum P$ ) minus the sum of the disposal quantities ( $\sum D$ ) was then equal to the quantity in service ( $S_n$ ) in any given year,  $n$ . In equation format this quantity is given by the following.

$$S_n = \sum_{i=1960}^n P_i - \sum_{i=1960}^n D_i \quad \text{equation III.1}$$

Quantities of CCA-treated wood in units of cubic feet were then converted to pounds of CCA chemical and pounds of arsenic by assuming that the average retention level of CCA-treated wood products in Florida was 0.45 pcf and that 22% of the CCA chemical is composed of arsenic. The conversion factor between cubic feet and pounds of arsenic was therefore 0.099 ( $0.099 = 0.45 * 0.22$ ).

The 22% arsenic composition of the CCA chemical is consistent with the composition of CCA-type C (AWPA 1999). The 0.45 pcf value was obtained by considering two different sources of information. The first source of information was from our extrapolation of industry statistics for the southeast region. Our extrapolation included both treated wood volume (cubic feet) and amount of chemical (pounds). These values are included in Solo-Gabriele et al. 1998. The ratio of the two was taken to determine the average retention value for Florida in pounds per cubic feet (pcf). The value varied from 0.09 pcf to 0.93 pcf. The more recent industry-based data (from the mid-80's to the present) indicates that yearly values are between 0.2 to 0.34 pcf. The second source of information came from the questionnaires that were sent to wood treaters throughout Florida, as part of the "year 1" study (Solo-Gabriele et al. 1998). Among those facilities that responded to the questionnaires (>60% response rate which is about 2 times the response rate that is obtained by the industry), it was found that 48% of the wood volume was treated at 0.25 pcf, 9% was treated at 0.4 pcf, 17% was treated at 0.6 pcf, 9% was treated at 0.8 pcf, and 17% was treated at 2.5 pcf. The overall average from the questionnaires was 0.76 pcf. The 0.76 pcf value appeared high in comparison to the first estimate method so an average was taken towards the low end. The result was an estimate of 0.45 pcf for CCA-treated products sold within Florida. The 0.45 pcf value is likely a conservative estimate given the large amount of CCA-treated wood used for marine applications in Florida and the fact that some retail establishments are moving towards stocking CCA-treated wood with a 0.4 or 0.6 pcf retention level rather than the minimum of 0.25 pcf.

It is important to note that the computations do not take into account the fact that some CCA will leach during the service life of treated wood products. Available data concerning % leached during service are highly variable but indicate that losses can vary from 10% to 50% of the total amount of CCA originally present in the treated wood product (Cooper 1993; Solo-Gabriele et al. 2000). **Again it is emphasized that the statistics presented herein do not account for the fact that some CCA will leach during the service life of treated wood.**

### III.4.b Results

By the year 2000, the cumulative amount of CCA-treated wood sold in Florida is 580 million cubic feet of which approximately 40 million cubic feet would have been disposed leaving 540 million cubic feet currently in-service (table III.2 and figure III.4). These quantities of CCA-treated wood correspond to 28,600 tons of arsenic sold in Florida and 1,800 tons disposed. **The amount of arsenic currently in service in Florida due to CCA-treated wood is estimated at 26,800 tons.** This quantity does not account for the fact that some CCA will be leached during the service life of treated wood.

Given the assumptions in the disposal forecast model, the cumulative quantity disposed will increase exponentially between the year 2000 and 2020. The quantity of CCA-treated wood in service will likely reach a steady state value of 800 million cubic feet of wood product (or 39,700 tons of arsenic) by the year 2015. The steady state value is due to the assumption in the model that the yearly production of CCA-treated wood after the year 2004 is equal to the estimate for the year 2004.

Year	Cumulative Quantities (Estimated)					
	Million Cubic Feet			Tons of Arsenic		
	Sold In Florida	Disposed In Florida	In-Service In Florida	Sold In Florida	Disposed In Florida	In-Service In Florida
1970	10.7	0.3	10.5	531	13	518
1980	47.4	1.2	46.2	2,350	59	2,290
1990	259	8.9	250	12,800	440	12,400
2000	578	36	542	28,600	1,800	26,800
2010	903	154	749	44,700	7,600	37,100
2020	1230	420	809	60,800	20,800	40,000
2030	1550	753	801	76,900	37,300	39,700
2040	1880	1080	803	93,100	53,300	39,700

Table III.2: Cumulative Amount of CCA-Treated Wood Sold, Disposed, and In-Service In Florida

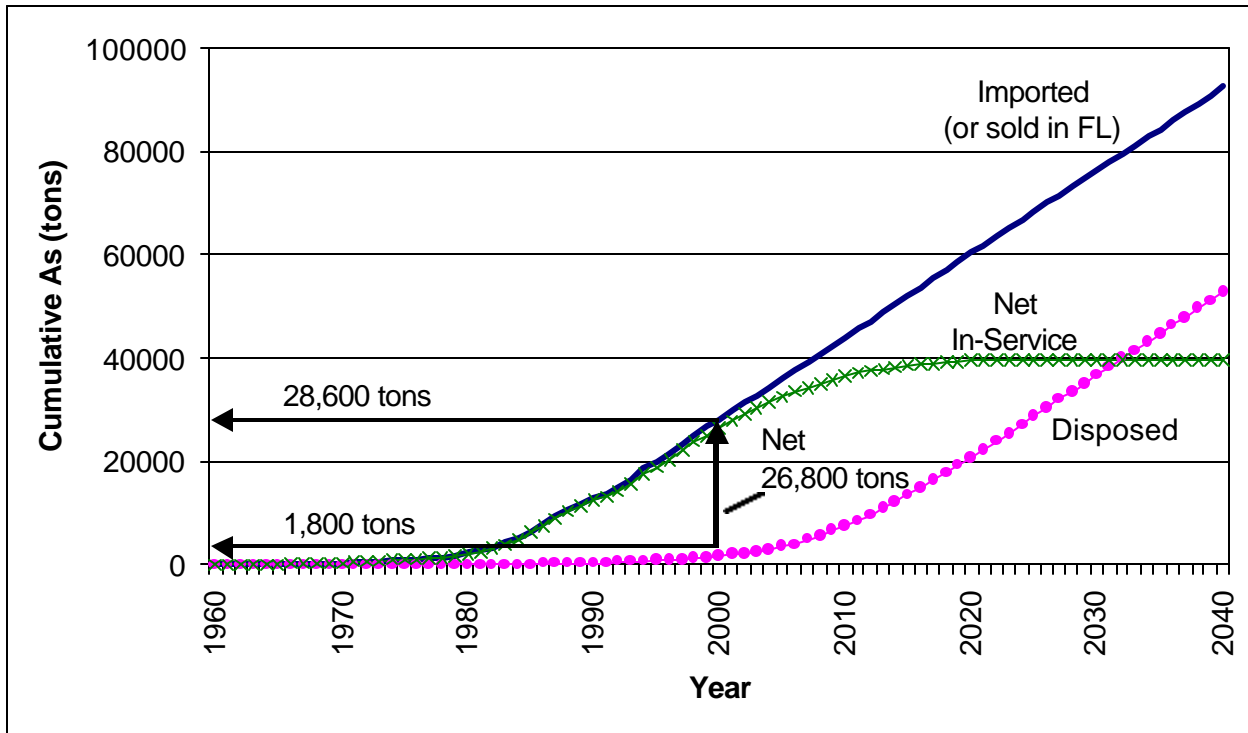


Figure III.4: Cumulative Amount of CCA-Treated Wood Sold, Disposed, and In-Service in Florida

### III.5 U.S. STATISTICS FOR THE DISTRIBUTION OF CCA-TREATED WOOD AMONG DIFFERENT USE SECTORS

U.S. statistics for the distribution of CCA-treated wood among different use sectors have been compiled by the Southern Forest Products Association (SFPA). These statistics were obtained from the SFPA model described in section III.3.b. For the year 2000 (figure III.5), the SFPA model estimates that 36% of treated Southern Pine will be used for outdoor decks, 18% for marine applications, 15% for landscaping, 10% for highway construction, and 8% for fences. Products in the "other" category include wood used for framing, foundations, and for export purposes.

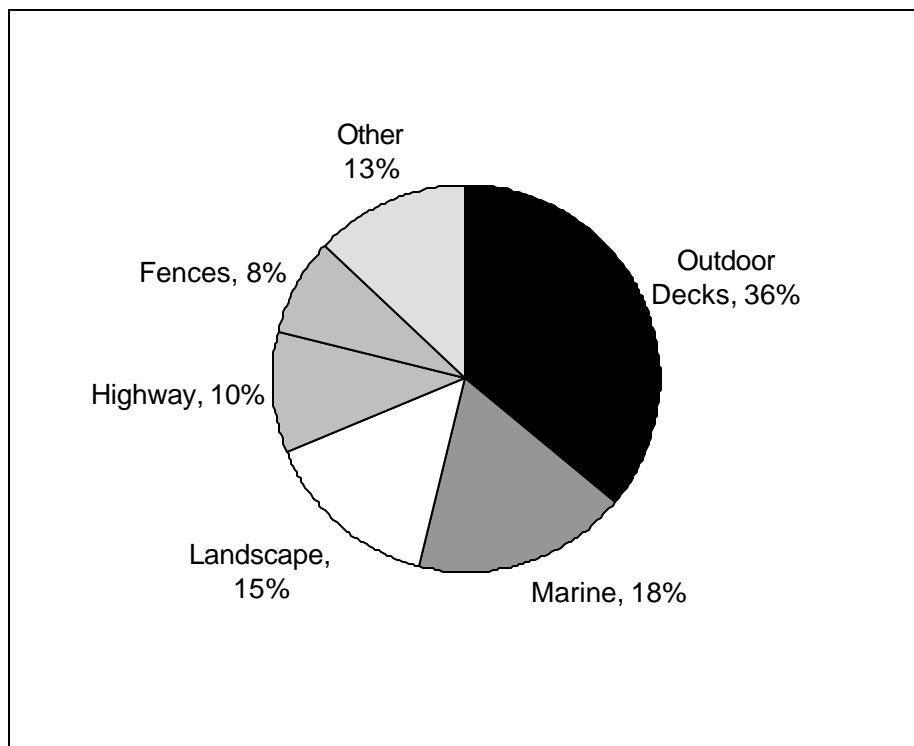


Figure III.5: Forecasted Treated Southern Pine Markets for the U.S. in the year 2000 (from SFPA)

The SFPA has also published information gathered by the Southern Pine Council and the APA - The Engineered Wood Association concerning marine construction ([http://www.sfpa.org/memberspg/Marine%20Construction%20Study/1999\\_Marine\\_Rpt.htm](http://www.sfpa.org/memberspg/Marine%20Construction%20Study/1999_Marine_Rpt.htm)). This data is based upon a survey sent to U.S. marine contractors. Results of the survey indicate that Southern Pine was used in roughly 90% of marine construction. Of the southern pine used for marine applications, 91% was used in the south. The distribution of wood between various marine products (table III.3) indicates that docks represent 32% of the marine market; bulkheads and piers represent 51% collectively. Other smaller contributors include wharfs (6.6%), marinas (4.4%), boardwalks (3.1%), and non-highway bridges (3.1%).

Type of Structure	Treated Southern Pine Lumber Volume Consumed in the U.S. in 1998 (million cubic feet)	Percent of Total
Docks	25.2	32.0%
Piers	20.2	25.6%
Wharfs	4.8	6.1%
Marinas	3.4	4.3%
Bulkheads	20.2	25.6%
Boadwalks	2.5	3.2%
Non-highway Bridges	2.5	3.1%
Total	78.9	

Table III.3: Amount of Treated Southern Pine Wood Used for Marine Applications in the U.S. during 1998

### **III.6 TREATED WOOD USE IN FLORIDA, UTILITY POLE AND MARINE/FRESH WATER APPLICATIONS**

The statistics given in section III.5 corresponded to the entire U.S. A considerable effort went into verifying the amount of CCA-treated wood used in Florida for utility poles (section III.6.a) and fresh/marine water uses (section III.6.b).

#### **III.6.a Utility Poles**

The amount of CCA-treated wood associated with utility poles was estimated using two methods. The first method utilized Florida's production and disposal statistics for poles/crossties for the years 1961 through 2000 as obtained through the disposal forecast model (section III.3). The reason that crossties were included in this computation is due to the manner in which the disposal statistics were originally compiled. Poles and crossties have similar service lives and were therefore lumped together in order to forecast disposal. Although crossties are lumped with poles it is important to note that the amount of CCA-treated crossties is small (< 3%) relative to the amount of CCA-treated poles.

Florida's production and disposal quantities for the 1961-2000 period were summed (see table B.2 in appendix B) in order to estimate the quantity of poles currently in service. Results from this computation indicate that approximately 26 million cubic feet of poles have been sold within Florida since 1961. Of this quantity 0.7 million cubic feet have been disposed, leaving 25 million cubic feet currently in service. Assuming that this quantity is treated at 0.6 pcf, this quantity of CCA-treated wood contains roughly 1700 tons of arsenic or roughly 6% of the arsenic associated with all the CCA-treated wood currently in service (table III.4).

The second method was based upon a questionnaire that was sent to Bell South, the major telephone utility in Florida, and to electric utilities which serve a population of more than 300,000. A total of 5 electric companies met these criteria, including Florida Power Corporation,

Florida Power and Light Inc., Jacksonville Electric, Seminole Electric, and Tampa Electric. The questionnaire inquired about the total cubic feet and retention level of CCA-treated products used by the utilities during 1998. Not all companies responded to this particular question on the questionnaires. For those companies that did, the quantity of treated wood used by that particular company was scaled against the population served to obtain the amount of CCA-treated wood per person. This value was then multiplied by the entire population of Florida (15.1 million) to estimate the quantity of CCA-treated utility poles purchased for use in Florida during 1998,  $CCA_{\text{Florida},1998}$ . This computation is illustrated by the following equation:

$$CCA_{\text{Florida},1998} = \frac{P_{\text{Florida},1998}}{P_{\text{utilities},1998}} * CCA_{\text{utilities},1998} \quad \text{equation III.2}$$

where  $P_{\text{Florida},1998}$  is the population of Florida during 1998,  $CCA_{\text{utilities},1998}$  is the quantity of CCA-treated utility poles purchased in 1998 by the responding utilities, and  $P_{\text{utilities},1998}$  is the population served during 1998 by the responding utilities. Using this equation, approximately 1.2 million cubic feet of CCA-treated wood was purchased by the Florida utility industry during 1998. Roughly 1.17 million were used for utility poles and 0.03 million were used for cross-arms. This quantity of treated wood corresponds to roughly 360 tons of the CCA chemical or 80 tons as arsenic, assuming that utility poles are treated at 0.6 pcf and cross-arms are treated at 0.4 pcf.

In order to estimate the total amount of CCA-treated wood currently in service associated with utility poles, the quantities computed for 1998 were then scaled against the production statistics from 1961 to 2000 using the following equation.

$$CCA_{\text{Florida},\text{year}^{\text{x}}} = \frac{CCA_{\text{Florida},1998}}{CCA_{\text{US},1998}} CCA_{\text{US},\text{year}^{\text{x}}} \quad \text{equation III.3}$$

where  $CCA_{\text{Florida},1998}$  is the quantity of CCA-treated wood purchased by the utility industry in 1998 (computed from equation III.2 above),  $CCA_{\text{US},\text{year}^{\text{x}}}$  is the quantity of poles produced in the U.S. during year “x”, and  $CCA_{\text{US},1998}$  is the quantity of poles produced in the U.S. during 1998. Yearly estimates for  $CCA_{\text{Florida},\text{year}^{\text{x}}}$  are provided in table B.2 in appendix B.

Given an estimate of the historical production statistics for CCA-treated utility poles in Florida, this data was then input into the disposal forecast model (section III.3) to estimate disposal quantities. A year by year estimate for utility pole disposal is given in table B.2 in appendix B. The sum of the CCA-treated utility poles purchased between the years 1961 and 1998 ( $SUM,CCA_{\text{purchased}}$ ) minus the sum of the CCA-treated utility poles disposed between 1961 and 1998 ( $SUM,CCA_{\text{disposed}}$ ) is then used to estimate the amount of CCA-treated utility poles currently in service ( $SUM,CCA_{\text{in-service}}$ ). In equation format this is expressed as follows.

$$SUM,CCA_{\text{in-service}} = SUM,CCA_{\text{produced}} - SUM,CCA_{\text{disposed}} \quad \text{equation III.4}$$

Computations indicate that  $SUM,CCA_{\text{produced}}$  is 21.6 million cubic feet of treated wood which is roughly equivalent to 6,480 tons of CCA chemical or 1,430 tons of arsenic. The value of  $SUM,CCA_{\text{disposed}}$  is estimated at 0.5 million cubic feet of treated wood which is roughly equivalent to 160 tons of CCA chemical or 36 tons of arsenic. Taking the difference of these two quantities, the estimated quantity of CCA-treated utility poles currently in service within Florida is 21.1 million cubic feet which is equivalent to 6,320 tons of CCA chemical or 1,390

tons of arsenic. Using this computation method, the tons of arsenic in utility poles and crossarms represents roughly 5% of the arsenic found within all treated wood products within the State of Florida (table III.4).

Units	Sum of CCA-Treated Utility Poles In Florida (1961-2000)					
	Purchased		Disposed		In-Service	
	Method 1	Method 2	Method 1	Method 2	Method 1	Method 2
Million Cubic Feet	26.1	21.6	0.7	0.5	25.4	21.1
Tons of CCA	7830	6480	200	160	7620	6320
Tons of Arsenic	1720	1430	43	36	1680	1390
% Arsenic within Utility Poles Versus Arsenic in All Treated Wood Products					Method 1	Method 2
					6.3	5.2

Table III.4: Summary of Computations for CCA-treated Utility Poles  
Currently In-Service

### **III.6.b Marine and Fresh Water Applications**

A considerable effort during this portion of the study focused on estimating the amount of CCA-treated wood associated with boat docks in Florida. It was then assumed that this number represented 32% of all wood used in marine applications. This percentage is consistent with statistics compiled by the Southern Pine Council (see section III.5).

Estimates for the amount of CCA-treated wood used for boat docks in Florida were computed on a county by county basis. Efforts focused on enumerating the number and characteristics of boat docks for three counties: Alachua, Leon, and Miami-Dade. Miami-Dade was chosen as county type #1 which is representative of counties with a relatively large coastline. Leon County was chosen as county type #2 which was representative of a county with no marine coastline but a considerable number of freshwater lakes. Alachua (county type #3) is representative of an interior county with no coastline and a limited number of interior freshwater lakes. The quantity of CCA-treated wood associated with boat docks within each of these three counties was then scaled against the population within the county to obtain a value of CCA-treated wood per person for each county type. All the counties within Florida were then categorized as a type #1, #2, or #3 county and the amount of CCA-treated wood associated with docks within one particular county was computed by multiplying the county's population by the amount of CCA-treated wood per person for a particular county type.

The number and characteristics of docks within each of the three focus counties was compiled from copies of building permits, review of aerial photographs, contact with the County Property Appraisers Office, and contact with local dock manufacturers.

#### *Number of Docks Within Each County*

For Alachua County, information concerning the number of docks was obtained from two sources: from aerial photographs and from the County Appraiser's Office (Jim Ousley, Computer Operations Manager for Alachua County). The number of docks from the County Appraiser's Office was 486 and the number counted from aerial photographs was 415. The Property Appraiser's Office and aerial photographs were also used for estimating the number of boat docks in Leon County. The estimate from the Property Appraiser's Office was 450 and from the aerial photographs was 450. In viewing the aerial photographs for Leon County it was noted that many docks also had a boat shed associated with them. The number of boat sheds estimated from the aerial photographs was 149 which indicates that roughly 33% of the docks in Leon County also have a boat shed. For Miami-Dade County, 6,000 docks have been permitted since 1980. This figure was provided by Cynthia Guerra of Miami-Dade County's Department of Environmental Resources Protection's Coastal Division.

#### *Characteristics of Docks Within Each County*

The materials of construction and the size of docks from each county (table III.5) were obtained from building permits and by contacting local dock manufacturers. For Alachua County, 41 permits were available for the 1994 to 2000 time period. The average surface area of the docks was 700 ft<sup>2</sup>. Roughly 56% of the docks were specified as CCA-treated, 10% were constructed with CCA-treated wood and some other material, 29% consisted of unknown wood, and 5% were constructed of unknown wood plus other building materials (figure III.6). Given



these statistics it was assumed that 87% of all docks in Alachua County were treated with CCA. The 87% included the 56% that were specified as CCA-treated, one half of the docks that were constructed of CCA-treated wood and some other material, plus 90% of decks made of unknown wood. All the docks within Alachua County were freshwater docks. Typical construction consisted of 0.8 pcf, 2" x 8" CCA-treated pilings spaced 8 feet on center. The wood not in direct contact with the water, such as the deck boards and joists, were generally treated at 0.25 pcf. The average volume of wood used to construct a dock was estimated at 194 ft<sup>3</sup>. The amount of CCA chemical associated with a typical Alachua County dock is 99 pounds. The computations made to estimate these quantities are provided in appendix B.

Seventy-eight dock permits were reviewed for Leon County. These permits were obtained from the Leon County Department of Growth and Environmental Management and corresponded to the 1993 to 2000 time period. The permits from Leon County consistently listed the surface area of the docks (average of 630 ft<sup>2</sup> for CCA-treated docks) but were not very specific as to the materials used in the construction of the docks. Thirty-one percent of the permits specifically stated that CCA-treated wood was used for construction. Fifty-five percent of the dock permits indicated that the material of construction was wood, but no specifications were given concerning the type of wood. The remaining 14% of the permits did not specify the type of building material used (figure III.6). The large fraction of "unknown wood" and "unspecified material" was of concern. All individuals contacted, including those from the Property Appraisers Office, local dock manufacturers, and from the Department of Growth and Environmental Management, indicated that essentially all the wood used for constructing docks was pressure treated. For computation purposes it was therefore assumed that 95% of all docks in Leon County were CCA treated. This value includes the 31% that were specified as CCA and 92% of the docks where either the material or wood treatment type was not specified. Other specifications of the docks including retention levels, size of pilings, and spacing between pilings were the same as that provided for Alachua County. The amount of CCA chemical and wood associated with a typical Leon County dock (without a boatshed) was estimated at 88 pounds of chemical or 173 cubic feet of wood, respectively. Those with a boat sheds were estimated to contain 138 pounds of CCA chemical and 248 cubic feet of wood.

One hundred dock permits were reviewed for Miami-Dade County. Records were available back to 1980. Permits reviewed within Miami-Dade County provided detail concerning the size (average 320 ft<sup>2</sup> surface area) and materials of construction for each dock. Approximately 49% of the docks were constructed of CCA-treated wood only. Fifteen percent were constructed of CCA-treated wood plus another building material and 11% were constructed of an unspecified type of wood. Of interest within Miami-Dade County is the relatively large fraction of docks constructed with concrete (9%) and concrete plus another material other than CCA-treated wood (9%). There was also a significant fraction of docks constructed with building materials within the "other" category (7%). Building materials within the "other" category included docks built partially of plastic lumber, fiberglass, greenheart wood, and aluminum. For computation purposes it was assumed that 65% of the docks in Miami-Dade County were CCA treated. This percentage includes the 49% that were specified as CCA treated, and 62% of the docks constructed of CCA-treated wood plus another building material and docks constructed of unknown wood. The retention levels of the boat docks in Miami-Dade County tend to be high due to the saltwater environment where the docks are found. Pilings are generally 1 foot in diameter and treated to 2.5 pcf. Wood used for decking and joists were generally treated at 0.6 pcf. The amount of CCA chemical and wood per dock was estimated at 540 pounds of CCA

and 252 cubic feet of wood.

	County		
	Alachua	Leon	Miami-Dade
No. of Docks (Estimated)	486	450 (149 of these have a boat shed)	6,000
No. of Permits Reviewed	41	78	100
Fraction of Docks Treated with CCA	0.87	0.95	0.65
Estimated No. of CCA-treated Docks	423	428	3,900
Ave. Surface Area of CCA-Treated Docks (ft <sup>2</sup> )	700	630	320
Ave. Volume of Wood per CCA-Treated Dock (ft <sup>3</sup> )	194	173 (without boat shed) 248 (with boat shed)	252
Pounds of CCA Chemical Per Dock	99	88 (without boat shed) 138 (with boat shed)	540
Pounds of CCA Chemical within all Docks in County	41,900	44,800	2,106,000
Pounds of Arsenic Per Dock	22	23	119
Pounds of Arsenic within all Docks in County	9,200	9,850	463,300
Volume of CCA-Treated Wood within all Docks in County (ft <sup>3</sup> )	81,800	84,700	982,800

Table III.5: General Dock Characteristics

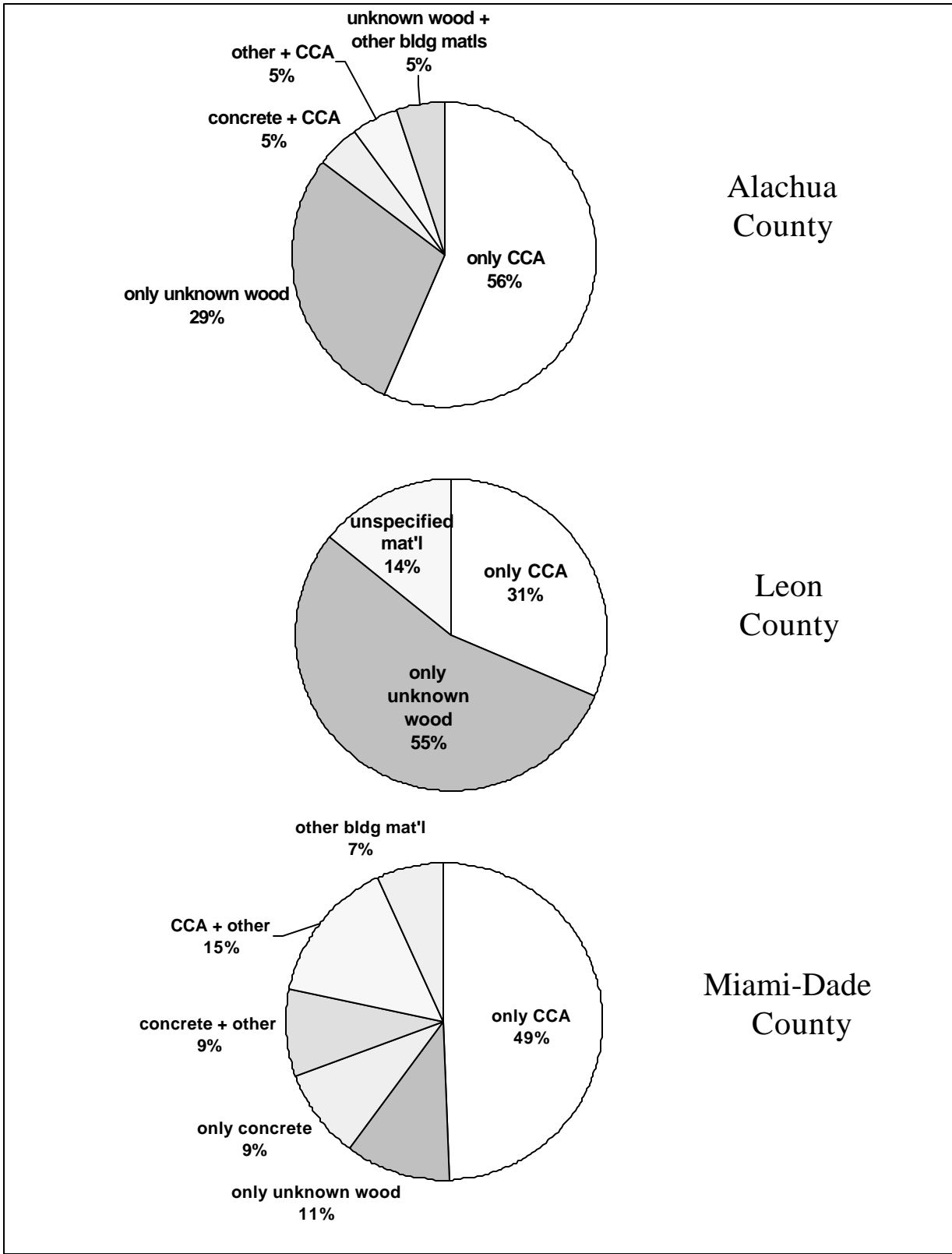


Figure III.6: Materials of Construction for Fresh and Marine Water Docks in Alachua, Leon, and Miami-Dade Counties

*Estimates for CCA-Treated Docks In Florida*

The amount of CCA chemical associated with boat docks within Alachua, Leon, and Miami-Dade County was divided by the population of each county (table B.3, appendix B). A value of "CCA per person" was then assigned to each county throughout the State. The value assigned was based upon the characteristics of that county. Type #1 consisted of all counties similar to Miami-Dade County i.e. coastal counties. Type #2 consisted of counties similar to Leon County, characterized by large lakes or rivers, while type #3 were those counties similar to Alachua County which do not border the coast and do not have large lakes or rivers (See figure III.7). The populations of each of the Florida counties were gathered and the cubic feet of CCA-treated wood and pounds of CCA chemical per county were calculated by multiplying the population by the corresponding "CCA per person." The cubic feet and pounds of CCA chemical per county were then added together to provide the amount for the entire state of Florida. Using the fact that 22% of CCA is made up of arsenic, the amount of arsenic associated with docks within Florida was then computed as 1322 tons (table III.6).

County	Type	Vol. of Wood in all County CCA-Treated Docks (ft <sup>3</sup> )	CCA within all Boat Docks in County (pounds)	Population	CCA Chemical per person (pounds/person)
Alachua	3	81,800	41,900	198,000	0.211
Leon	2	84,700	44,800	216,000	0.207
Miami-Dade	1	982,800	2,106,000	2,180,000	0.970
Sum for Entire State		6,627,000	12,025,000	15,100,000	0.796
Pounds of Arsenic Associated with Boat Docks in State					2,646,000

Table III.6: CCA Per Person for Each County Evaluated

*Estimate for CCA-Treated Wood In All Marine Applications*

According to SFPA published data (see table III.3), docks represent roughly 32% the wood used for marine applications. A rough estimate for Florida for the amount of wood utilized in marine applications is therefore given by the following equation.

$$CCA_{\text{marine\_applications}} = \frac{CCA_{\text{docks}}}{0.32} \quad \text{equation III.5}$$

where  $CCA_{\text{docks}}$  is the amount of CCA chemical associated with marine and freshwater docks in Florida and  $CCA_{\text{All\_marine\_applications}}$  is the amount of CCA chemical associated with all marine and freshwater applications in Florida. Using this equation, approximately 18,800 tons of CCA chemical is associated with marine and freshwater applications in Florida. This quantity of CCA corresponds to 4,130 tons of arsenic. The tons of arsenic in marine/fresh water applications

represents roughly 15% of the arsenic found within all treated wood products within the State of Florida (table III.7).

Units	CCA-Treated Wood Used for Salt and Fresh Water Applications
Cubic Feet	21 million
Tons of CCA	18,800
Tons of Arsenic	4,130
% Arsenic Uses for Marine and Salt Water Applications Versus Arsenic in All Treated Wood Products	15.4%

Table III.7: Summary of Computations for CCA-treated Wood Used for Salt and Fresh Water Applications In Florida

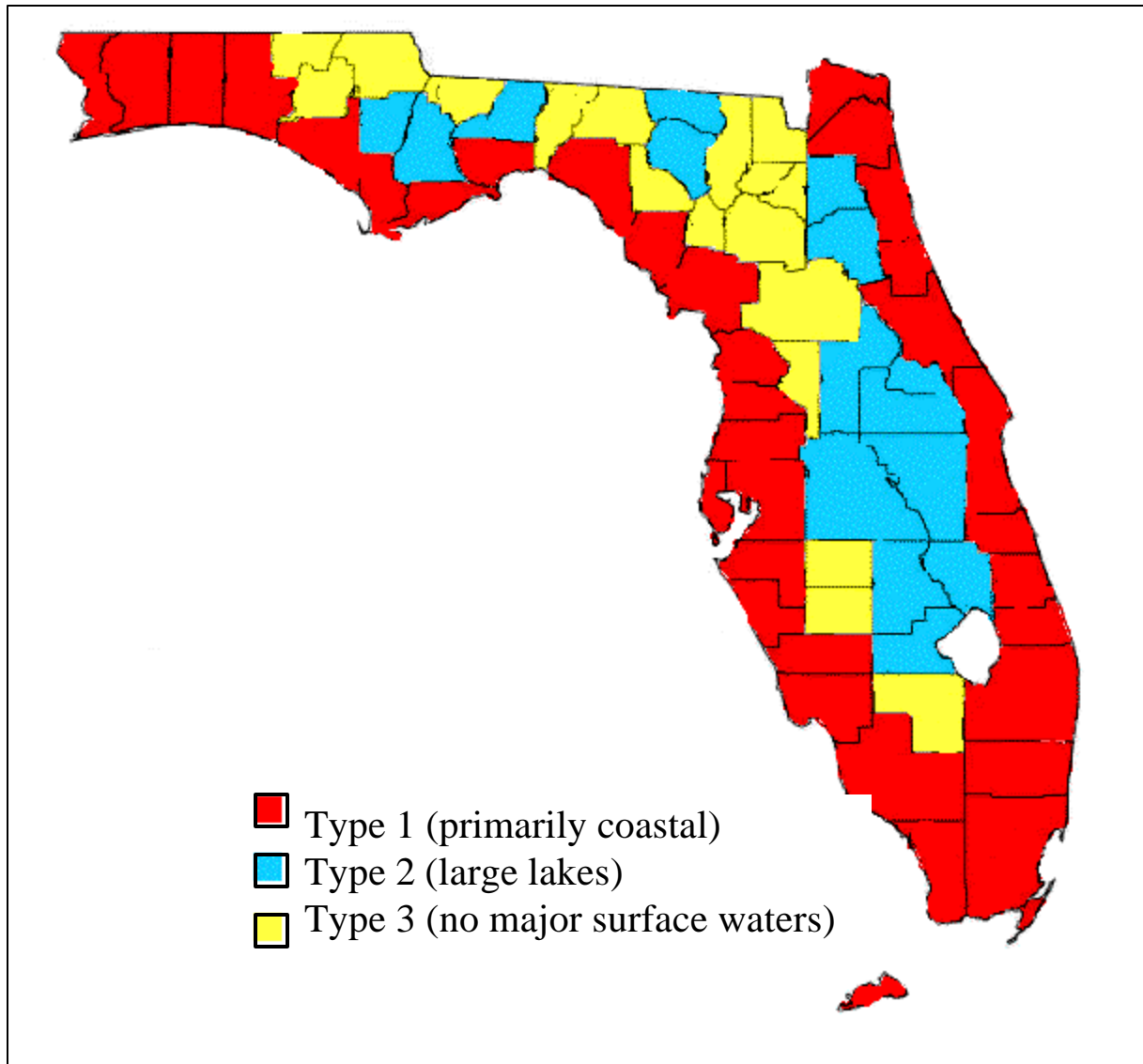


Figure III.7: Florida Counties Classified by Type

### III.7 SUMMARY AND CONCLUSIONS

#### *Proportion of CCA-Treated Wood Among Treated and Untreated Wood*

Data compiled by the SFPA indicates that the proportion of CCA-treated wood among treated and untreated wood sold in the U.S. can be as high as 40 to 50%. These numbers are high relative to the current proportion of CCA-treated wood observed in the disposal stream. During 1996 the proportion was measured at 6% (Tolaymat et al. 2000). During 1999 the proportion was found to vary between 9 and 10% for two wood recycling facilities that sort CCA-treated wood from other wood types and 30% for a facility that did not practice active sorting. The data provided by the SFPA is consistent with the measured values and indicates that the proportion of CCA-treated wood within the disposal sector will increase in the future. The current proportions and the future increases in CCA-treated wood greatly restrict the current uses of the recovered material for mulch and wood fuel. At a 50% proportion the wood mixture would fail SPLP (see chapter 5 of this report), thereby not permitting it to be disposed of as mulch if regulations used for other solid wastes were applied. If the wood were to be burned, the ash would fail TCLP given that only a 5% proportion of CCA-treated wood is needed to cause an exceedance of TCLP criteria (Solo-Gabriele et al. 1999).

#### *Disposal Forecast Model*

The disposal forecast model indicates that the majority (roughly 95% on a cubic foot basis) of treated wood sold and disposed in the State of Florida is in the form of lumber, timbers, and fence posts (group 1 products). Roughly 5% on a cubic foot basis is in the form of poles and crossties (group 2 products). The disposal forecast model indicates that disposal of group 1 products is currently being observed and should reach a peak in disposal quantities by the year 2020. The disposal of group 2 products has not yet been observed in significant quantities. This finding may be part of the reason that recycling operations by utility companies have been successful to date. Essentially, the wood that has been reused through utility company operations is relatively small in quantity and has not yet reached the end of its service life making it structurally sound and aesthetically pleasing. It is likely that once major transmission and distribution lines are decommissioned (once the treated wood reaches a 40 year service life) that the quality of the CCA-treated wood from these lines will not be as conducive for reuse and recycling purposes. Furthermore, much larger quantities of treated wood will be disposed potentially saturating available reuse markets. A plan is needed for handling the forecasted increases in the quantities of CCA-treated wood ultimately disposed. It is likely that existing reuse and recycling options will not be suitable for handling the large quantities of CCA-treated wood disposed in the near future.

#### *The Amount of Arsenic Associated with Different CCA-Treated Wood Use Sectors*

The amount of arsenic currently in service due to CCA-treated wood use in Florida is estimated at 26,800 tons. This quantity of arsenic has the capacity to increase the concentration of  $6.5 \times 10^9$  tons of soil (which is equivalent to the soil within the upper 1 inch of the entire state) by 4 mg of arsenic per kilogram of soil. It has the capacity to increase  $6.5 \times 10^{14}$  gallons of water (equivalent to 650 times the size of Lake Okeechobee) by 10 ug/L which is the proposed federal drinking water limit (USEPA 2001). Without a proper disposal management plan this

quantity of arsenic will be dispersed within the Florida environment and can potentially contaminate our water and soil resources.

In order to recover this arsenic, a disposal management plan should be in place which will recover as much of the arsenic associated with CCA-treated wood as is feasible. A management plan aimed at recovering CCA-treated utility poles will be capable of recovering approximately 1500 tons or 5 to 6 % of the arsenic currently in service (figure III.8). A significant fraction (4,130 tons or 15 %) of the arsenic associated with treated wood can be recovered from wood used for marine and fresh water applications. The remaining quantities of CCA-treated wood (according to SFPA) are associated with outdoor decks, landscaping, fences, and highway construction. Programs should be put in place to recover wood from these sectors as well. Recovery of treated wood used in highway construction will require cooperation from the State Highway Department. Recovery of treated wood used for outdoor decks, landscaping, and fences will require either educating the general public (including demolition contractors) about the proper disposal of treated wood or implementing an efficient sorting system at construction and demolition recycling facilities that will remove CCA-treated wood from other wood types. One positive aspect about these use sectors (other than utility poles and products used for marine/freshwater applications) is that non-arsenical alternative wood treatment chemicals have been standardized for these other applications. The use of these non-arsenical wood treatment preservatives should be encouraged to minimize the quantity of CCA-treated wood that is ultimately found within Florida's disposal stream.

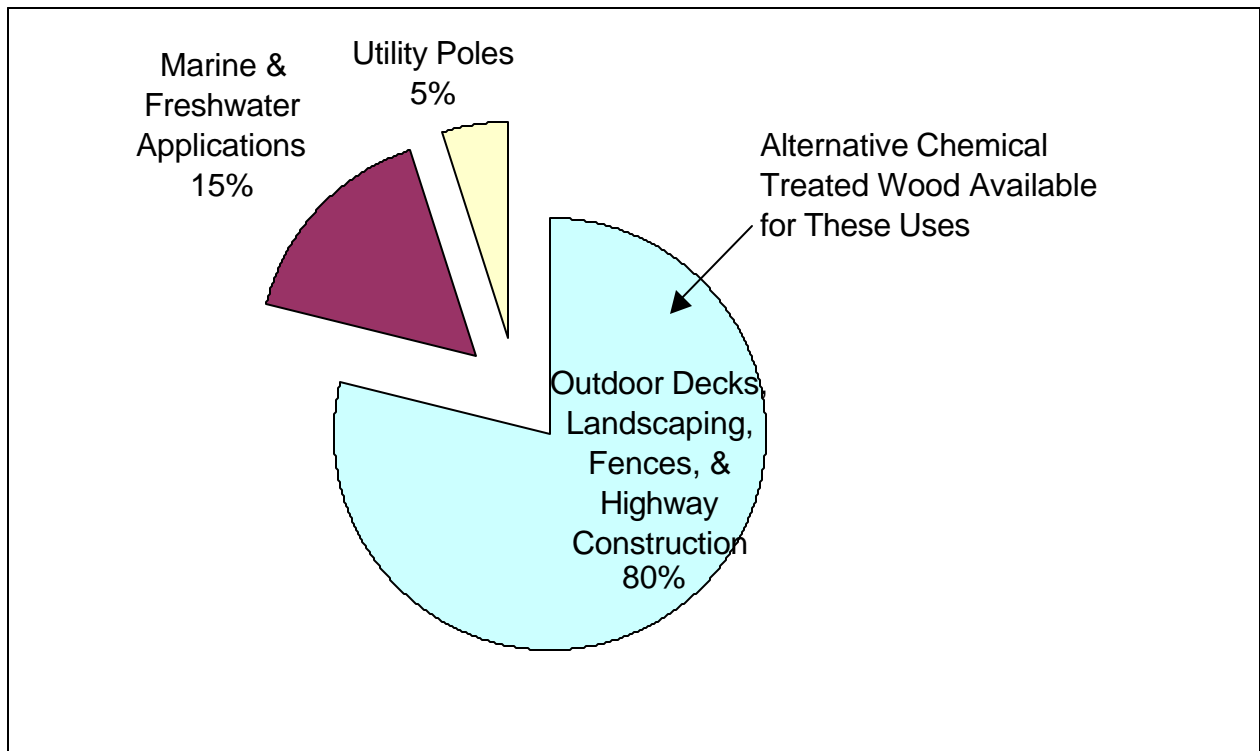


Figure III.8: Summary of Use Sectors for CCA-Treated Wood (Distribution based upon pounds of arsenic associated with each sector)

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**CHAPTER IV**

**LEACHING OF CHROMIUM, COPPER, AND  
ARSENIC FROM NEW CCA-TREATED WOOD AND  
C&D DEBRIS WOOD MULCH**

## **CHAPTER IV. LEACHING OF CHROMIUM, COPPER, AND ARSENIC FROM NEW CCA-TREATED WOOD AND C&D DEBRIS WOOD MULCH**

This chapter summarizes the results from leaching tests conducted on new CCA-treated wood and on wood mulch from C&D debris recycling facilities. This chapter begins by describing the motivation for this study (section IV.1) and by providing background information on the issue of metal leaching from CCA-treated wood in a variety of disposal scenarios (section IV.2). The specific objectives of the study are provided in section IV.3 followed by a description of the methods used (section IV.4). The results are presented in two sections. Section IV.5 focuses on results obtained for new CCA-treated wood and section IV.6 focuses on results for C&D debris wood mulch. The chapter ends with a discussion of major findings and a conclusion (section IV.7).

### **IV.1 MOTIVATION**

The primary disposal sectors for discarded CCA-treated wood in Florida are construction and demolition (C&D) debris landfills and C&D debris recycling facilities (Solo-Gabriele et al. 1998). At C&D debris landfills, CCA-treated wood is disposed along with other components of C&D debris (e.g. untreated wood, concrete, drywall, etc) by burial in excavated pits or compaction in large above ground piles. Unlike landfills for municipal solid waste, Florida does not require liners for C&D debris landfills and the leachate produced by rainwater passing through the waste migrates to the underlying soil and groundwater. At C&D debris recycling facilities, some CCA-treated wood is separated out and recovered for reuse or sent to a landfill for disposal, but much of the treated wood is indistinguishable from the untreated wood and is thus managed as part of the facility's overall recovered wood stream. This mixed wood stream is recycled in one of two primary markets: boiler fuel or wood mulch. The three major disposal sectors for CCA-treated wood in Florida are thus 1) combustion, 2) land application as mulch, and 3) disposal in a landfill.

Previous research demonstrated that the presence of CCA-treated wood in processed C&D debris wood fuel had a major impact on how the residual ash from the wood combustion process could be managed (Solo-Gabriele et al. 1998). Leaching tests conducted on the ash showed that As, Cr, and Cu did leach in sufficient concentrations to trigger regulatory disposal restrictions. Disposal of the ash by application to soil or burial in a landfill, without restrictions, would in many circumstances increase risk to human health and the environment. The examination of metal leachability using standardized regulatory leaching tests thus provided a useful means for assessing the impact of CCA-treated wood on the first of the three management scenarios listed above.

The results of the ash leaching tests cannot be applied to assess the other two primary disposal sectors for CCA-treated wood in C&D debris: landfill disposal and reuse as mulch. In these scenarios, it is the leaching of As, Cr, and Cu directly from the unburned wood that must be evaluated. While the metals in CCA are considered "fixed" to the wood from a wood preservative perspective, there is scientific evidence (Cooper 1991; Cooper and Ung 1992; Gifford et al. 1997; Henningson et al. 1984), suggesting that metals do leach from treated wood

in sufficient amounts to increase soil concentrations above naturally occurring levels. Even a small release of a metal from the wood, one that would be considered negligible from a treatment efficacy standpoint, may cause an increase in surrounding environmental concentrations to above regulatory risk-based levels. This is most notably true for arsenic, the heavy metal in CCA with the most stringent risk-based concentration limits. The evaluation of CCA-treated wood impact on disposal in landfills and land applied mulch requires a similar evaluation as conducted for the ash, but instead of conducting leaching tests on the ash, leaching tests on the wood must be conducted. Leaching tests on unburned CCA-treated wood would also shed light on the issue of leaching during service, something that was observed to occur in Chapter II.

## **IV.2 BACKGROUND ON LEACHING**

### **IV.2.a Leaching from Landfills**

Disposal in landfills remains the predominant method of managing solid waste in Florida, including construction and demolition debris. A concern traditionally associated with the disposal of waste in landfills is potential contamination of groundwater beneath the landfill. As rainfall contacts the surface of the landfill, some runs off as stormwater, some evaporates, and some percolates through the landfill surface and into the underlying waste. As water travels through the waste, chemicals leach (or migrate) from the waste materials into the percolating water to form a fluid referred to as landfill leachate. Modern sanitary landfills for hazardous waste or municipal solid waste address the problem of leachate formation by constructing liner systems composed of low permeability barrier layers (geomembranes, compacted soil). The leachate is collected and subsequently, removed from the landfill and treated appropriately. Some states require liners for landfills that receive C&D debris, while others do not. Florida is an example of a state where C&D debris landfills do not require liner systems. Requirements for groundwater monitoring were recently enacted for Florida C&D debris landfills. At this time, however, very little data is available on the impact of C&D debris landfills on groundwater quality. Because of the slow travel time associated with many groundwater systems, it may take a number of years after waste has been disposed in an unlined landfill before it is detected in the surrounding groundwater.

Florida's population relies heavily on groundwater for drinking water and assessing the potential impacts of wastes disposed in unlined landfills is a very important issue. One component of C&D debris entering unlined C&D debris landfills in Florida is CCA-treated wood. Recent laboratory work indicates that the presence of CCA-treated wood in C&D debris does result in elevated concentrations of As, Cr, and Cu in the leachate (Townsend et al. 2000). A clear understanding as to how much of the treatment chemical leaches from a treated wood product, the rate at which it is released, and the factors that control leachate are not well understood. One method to assess the potential of CCA-treated wood to leach As, Cr, and Cu in the landfill environment is to conduct batch leaching tests on the wood. While no single laboratory test can adequately simulate the complexities in an environment such as a landfill, standardized batch tests can provide insight as to the amount of chemicals that might be leached, the impact of different waste disposal conditions, and what type of landfill a waste should be disposed in accordance to current waste management regulations and policies.

## **IV.2.b Leaching from Wood Mulch**

Viable markets for materials recovered from solid waste are crucial for the successful implementation of any recycling program. This is true for wood recovered from C&D debris recycling operations. Information gathered during the first year of research on this project indicated that the primary market for wood recovered from C&D debris was as boiler fuel (Solo-Gabriele and Townsend 1999). C&D debris facility operators processed (mechanically size-reduced) recovered wood and transported the material to one of several co-generation facilities in South Florida. Since this time, market conditions have shifted and a new market for C&D debris wood has become landscaping mulch. Because of its grayish color, discarded wood is often less desirable than cypress or pine bark as a source of mulch, but the advent of coloring agents designed to dye wood to more aesthetically pleasing colors has helped introduce C&D recycled wood to the horticultural mulch market.

The use of C&D debris wood containing CCA-treated wood as landscaping mulch may present some environmental risk because of the presence of arsenic, chromium, and copper. While Florida C&D recycling facilities are required to separate treated wood from untreated wood prior to using as mulch, the complete removal of treated wood is an extremely difficult task using current technology and management practices. In some cases C&D facility operators do not understand that treated wood should not be included in mulch. Even with complete education, it is difficult for facility operators to distinguish CCA-treated wood from untreated wood by sight. When wood is painted, weathered, or dirty, identification of CCA treated wood from other wood is very difficult. In 1997, CCA-treated wood was documented to be in the recovered wood stream at C&D recycling facilities in Florida at approximately 6% (Tolaymat et al. 2000). Research conducted in 1999 at three Florida C&D debris recycling facilities found CCA-treated wood to make up between 9% and 30% of the recovered wood (Solo-Gabriele et al. 2000). This is complicated by the anticipated increase in CCA-treated wood entering the waste stream over the coming decades.

It may be argued that if CCA-treated wood does not pose an unreasonable risk to human health and the environment when used for its intended purpose (e.g. a fence post in the environment, a deck), then its presence in landscaping mulch should represent no more of a risk. A few notable differences between the presence of CCA-treated wood as mulch and its presence in its intended use should be discussed. First, since the wood is size reduced to produce mulch, the surface area available for leaching is much greater. This increased surface area results in greater leaching potential. The smaller particle size also makes the direct human exposure pathway a realistic scenario. The wood treating industry recommends that small particles of CCA-treated wood such as sawdust be cleaned up and disposed of properly. Second, the placement of mulch represents the final disposition of the wood. The wood contained in the mulch will, under most circumstances, remain on the ground and ultimately become integrated into the underlying soil. Finally, the assumption that CCA-treated wood used as intended does not pose an unreasonable risk is challenged by the results presented in chapter II. Because of these issues and the potential impact on the reuse of recycled wood from C&D debris facilities, it is important to gain a better understanding as to how much chemical leaching might occur from mixed C&D wood containing CCA-treated wood.

## IV.2.c Laboratory Methods for Testing Leaching

A series of standardized leaching tests are available for evaluating disposal options for wastes. The simplest of these tests are batch tests that involve subjecting a waste sample to a solvent and then comparing the concentration of the contaminant within the solvent (or leachate) to a particular regulatory level. If the level is exceeded then the waste fails the test and should therefore not be disposed in the manner for which the test was developed. The more common tests include the Toxicity Characteristic Leaching Procedure (TCLP) and the Synthetic Characteristic Leaching Procedure (SPLP). The TCLP method is used to determine whether or not a waste is hazardous due to its toxicity characteristic as outlined within the Resource Conservation and Recovery Act (RCRA). The solvent used in this test simulates the acidic conditions found inside a municipal solid waste landfill. If a waste fails the TCLP, then it should be disposed in a hazardous waste landfill (versus a municipal solid waste landfill), unless an exemption is provided for a particular waste. Two of the three metals used to preserve CCA-treated wood are regulated under RCRA. These metals include arsenic and chromium. TCLP regulatory limit exist for both these metals is 5 mg/l. There are no TCLP regulatory limits for copper. It is important to note, however, that CCA-treated wood has been exempted at the federal level from being classified as a hazardous waste even if it exceeds TCLP limits for arsenic or chromium.

The leaching fluid used in the Synthetic Precipitation Leaching Procedure (SPLP) simulates rainfall. The condition where this test is generally applied is to an environment outside of a landfill where leaching may occur, such land application of a recycled waste material as ash or compost. In Florida, the leachate concentrations from the SPLP are compared to Florida Groundwater Guidance Concentrations (GWGC). The GWGC for chromium, copper, and arsenic are 0.1, 1, and 0.05 mg/L, respectively.

Other less common leaching tests include EP Tox, WET, and MEP tests. EP Tox is an older technique that was originally recommended through RCRA but was subsequently replaced with TCLP in 1984. Depending upon pH conditions of the leaching fluid in contact with the waste, EP Tox requires that acid be periodically added during the extraction step until a specified pH is reached. The periodic addition of acid resulted in losses of some organic compounds, in particular those that could volatilize. For this reason, the EP Tox method was replaced with the TCLP, which does not require that the vessel be opened on a periodic basis during extraction. The Waste Extraction Test (WET) is the leaching procedure used by the State of California. This test is similar to the TCLP test except in the organic acid used. TCLP uses an acetic acid leaching solution whereas WET uses citric acid (CCR 1998). Unlike the TCLP, which regulates the RCRA 8 metals, California's WET levels are compared to 17 different regulated metals in that state. The WET limits for arsenic and chromium is 5.0 mg/L for metals. No limit is placed upon copper. The Multiple Extraction Procedure (MEP) is a sequential batch leaching test which simulates long-term leaching characteristics in a landfill. This test, as with the TCLP test, is used to simulate worst case leaching conditions in which the waste is exposed to multiple acid rainfalls while being disposed of in an improperly managed/designed sanitary landfill. The MEP is a combination of the EP Tox test and repetitive exposure to a low pH SPLP solution. It is noted that the MEP results are not used for regulatory purposes per say. Instead they are used to estimate long term leaching within the landfills.

In addition to differences in the characteristics of the extraction fluid used in various leaching tests, particle size may also play a part in the amount of metals leached into the extraction fluid. In most cases, the smaller the particle size, the greater the amount of chemical released due to a larger surface area of waste in contact with the leaching fluid. Most leaching tests, however, require that the waste samples be small enough to pass a given sieve size (Musson et al. 2000, Van der Sloot 1997). The impact of different particle sizes on leaching characteristics of new CCA-treated wood will be evaluated in subsequent sections.

### **IV.3 OBJECTIVES**

The following objectives were established to investigate the issue of As, Cr, and Cu leaching from CCA-treated wood.

1. Determine the leachability of new CCA-treated wood using the U.S. EPA's Toxicity Characteristic Leaching Procedure (TCLP) to determine how discarded CCA-treated wood would have to be managed if the current RCRA exemption from the definition of a hazardous waste was not in place.
2. Determine the leachability of new CCA-treated wood using the U.S. EPA's Synthetic Precipitation Leaching Procedure (SPLP) to determine how discarded CCA-treated wood should be managed according to current waste management policy in Florida for wastes disposed in environments where rainfall could result in chemical leaching.
3. Conduct other standardized leaching tests (including TCLP and SPLP) on new CCA-treated wood at a series of different particle sizes to evaluate the factors that influence the leaching of heavy metals from the material (size, leaching chemical, leaching time).
4. Conduct SPLP on samples of wood mulch collected from C&D debris recycling facilities and purchased as landscaping materials to assess the leachability of As, Cr, and Cu that results from the presence of CCA-treated wood. This information is needed to assess the impact of treated wood on the recyclability of the material according to current State guidelines for beneficial reuse of waste materials.

### **IV.4 METHODS**

Leaching tests were performed on two different sets of samples: new CCA-treated wood and mulch collected from C&D debris recycling facilities. The tests performed on CCA-treated wood included TCLP, SPLP, EP Tox, WET, and MEP. A total of 10 new CCA-treated wood samples were utilized for testing. These samples were purchased from home and garden supply stores located in Gainesville, FL.

Leaching characteristics of the mulch samples were analyzed *using the SPLP only*. The mulch samples were composed of actual C&D debris wood. The amount of treated wood present, the retention value of any treated wood present (if any) and the degree of previous leaching were unknown. The purpose of the SPLP was to evaluate the reuse of this material in a

land application setting, the scenario that the SPLP simulates. A total of 20 different samples were evaluated. These samples included: 13 samples of recycled C&D wood, 2 samples of recycled vegetative waste wood, 2 samples of commercial colored mulch, and 3 commercial mulches believed to not contain C&D debris wood to serve as controls (table IV.3). Details concerning sample collection, and analysis are provided below.

#### **IV.4.a Sample Collection**

Two different sets of samples were collected. These included samples of new CCA-treated wood and samples of mulch.

##### *New CCA-Treated Wood*

A total of 10 samples of new CCA-treated wood were purchased from local retail establishments located in Gainesville, Florida (table IV.1). These samples included CCA-treated wood characterized by different dimensions (2"x 4", 2"x 6", 2"x 8", and 4" x 4"), different brands (identified as brands 1 through 5), and different standard retention levels. Two of the 10 samples contained water repellent agents (brand 4). These repellents were included within the CCA formulation and were therefore introduced into the wood pores through pressure treatment. The particular wood samples were selected in an effort to provide a representation of the types of treated wood currently sold to the home consumer. Each sample was size reduced into 4 sample size categories, so that the impact of surface area could be evaluated. In each case, the total sample weight used in each test was 100 g, the amount prescribed by the TCLP and SPLP. The sizes included one- 100 g block, five- 20 g blocks, chipped wood (typical size 1 ½ inch by ½ inch), and sawdust. These forty samples were subjected to TCLP and SPLP tests. All four size categories for sample J (brand 5, 2 x 4, 0.4 pcf retention rating) were also subjected to the full suite of regulatory tests, which included, in addition to TCLP and SPLP, the EP Tox, WET, and MEP tests.

While standard retention values were recorded based on the tags attached to wood at the time of purchase, retention levels for the wood samples were confirmed using x-ray fluorescence (XRF) technology (ASOMA, model 100). XRF analysis was conducted by Koppers Inc. located in Gainesville, Florida. The first set of samples that were analyzed using XRF was sawdust used in the leaching tests. These samples were not dried prior to the XRF analysis (Koppers Inc., personal communication). The second set of samples used the same sawdust, but the samples were dried prior to analysis. The third set of samples were collect by drilling the outer 0.6 inches with a ¼ inch drill bit and collecting the sawdust for analysis. The second and third set of samples were dried and analyzed by Chemical Specialties Inc. located in Charlotte, NC. The results of the analysis are summarized in table IV.2. The results from XRF analysis show that there is a large variation between values indicated on the end tags and the measured retention values, and in some cases between the different measured values. The results from the wood sold as 0.25 pcf ranged from a metals content of 0.109 to 0.368 pcf with averages from 0.214 to 0.291 as presented in table IV.2. The results from the wood treated at 0.40 pcf ranged from 0.227 to 0.746 pcf with averages ranging from 0.227 to 0.557 pcf.

Sample Name	Brand	Size	Sealed	Retention Value Indicated at Retail Store (pcf)
Brand 1	A	2"x4"	NO	0.25
	B	2"x6"	NO	0.25
	C	2"x8"	NO	0.25
	D	4"x4"	NO	0.4
Brand 2	E	4"x4"	NO	0.4
Brand 3	F	2"x4"	YES	0.4
	G	2"x6"	YES	0.4
Brand 4	H	2"x4"	NO	0.4
	I	2"x6"	NO	0.4
Brand 5	J	2"x4"	NO	0.4

Table IV.1: New CCA-treated wood samples

Brand	Sample Name	Retention Value Indicated at Retail Store (pcf)	Measured Retention Value Using XRF (sawdust) (pcf)	Measured Retention Value Using XRF (sawdust) (pcf)	Measured Retention Value Using XRF (outer 0.6 in) (pcf)	Average Retention Value Using all XRF analysis (pcf)
Brand 1	A	0.25	0.229	0.276	0.368	0.291
	B	0.25	0.239	0.295	0.109	0.214
	C	0.25	0.161	0.336	0.232	0.243
	D	0.4	0.253	0.383	0.565	0.400
Brand 2	E	0.4	0.212	0.294	0.140	0.215
Brand 3	F	0.4	0.413	0.513	0.746	0.557
	G	0.4	0.236	0.181	0.407	0.275
Brand 4	H	0.4	0.309	0.481	0.139	0.310
	I	0.4	0.294	0.310	0.505	0.370
Brand 5	J	0.4	0.187	0.227		0.227

Table IV.2: Results of XRF Analysis



## *Mulch*

Of the 20 mulch samples (table IV.3), 13 were samples of processed C&D debris wood. Twelve of these samples were collected in 1997 and 1 was collected in 1999. The collection and processing methodology for the C&D wood samples collected in 1997 have been described in previous documents (Tolaymat et al. 1999; Solo-Gabriele et al. 1998). During the time period between sample collection in 1997 and the leaching analysis in 1999/2000, the wood samples were stored in plastic containers in a cold room at 4 °C. Two additional C&D mulch samples were obtained from retail establishments (original source of wood unknown). These samples were dyed red in color and were suspected of containing some C&D waste wood because of noticeable pieces of plywood, particleboard, and small pieces of painted wood. The remaining five mulch samples consisted of two samples of vegetative waste wood collected from two recycling facilities and three non-C&D mulch controls. These controls were also purchased at local retail establishments and consisted of either pine bark or cypress mulch.

Category	Sample <sup>1</sup>	Sample Source Description
C&D Recycled Wood Waste	A1, A2	Processing wood waste: Source separated C&D and pallets (1997)
	B1	Processed C&D wood waste from recycling facility. Wood separated up front in manual recovery system. (1997)
	C1, C2	Processing wood waste: Source separated C&D and pallets (1997)
	D1, D3	Processed C&D wood waste from recycling facility. Wood separated up front in mechanical recovery system. (1997)
	E1, E2	Processed C&D wood waste from recycling facility. Wood separated up front in manual recovery system. (1997)
	F1	Processed C&D wood waste from recycling facility. Wood separated up front in manual recovery system.(1997)
	G1	Processed C&D wood waste from recycling facility. Wood separated up front in manual recovery system. (1997)
	H1, H2	Processed C&D wood waste from recycling facility. Wood separated up front in manual recovery system. (1997)
	I1, I2	Processed C&D wood waste from recycling facility. Wood separated up front in manual recovery system. (1997)
	J2	Processed C&D wood waste from recycling facility. Wood separated up front in manual recovery system. (1997)
	K1	Processed C&D wood waste from recycling facility. Wood separated up front in manual recovery system. (1997)
	M1	Processed C&D wood waste from recycling facility. Wood separated up front in mechanical recovery system. (1997)
	N1, N2	Processed C&D wood waste from recycling facility. Wood separated by hand up front followed by processing. (1999)
Colored Mulch	P1	Bagged colored mulch product from garden supply store in North Florida. (1999)
	Q1, Q2	Commercial colored mulch product from garden supply store in South Florida. (1999)
Vegetative Waste	R1	Vegetative mulch from yard waste (1999)
	D2, D4	Processed land clearing debris from C&D recycling facility (1997)
Horticultural Mulch (non C&D controls)	S1	Pine bark mulch from mulching operation in North Florida (1999)
	T1	Cypress mulch purchased from garden supply store in North Florida. (1999)
	U1	Pine mulch purchased from garden supply store in North Florida. (1999)

<sup>1</sup>Samples A - M were SPLP extracted in triplicate, and samples N - U were SPLP extracted in duplicate.

Table IV.3: Mulch Samples Tested

#### IV.4.b Chemical Leaching Tests

Leaching tests consist of a series of steps which include sample preparation, chemical extraction, filtration, digestion, and analysis (figure IV.1). Sample preparation usually requires sample size reduction so that the waste tested passes a specified sieve size. In the set of experiments described herein, however, size reduction to the specific sieve size for the new CCA-treated wood samples was not performed in every case given that the impact of surface area to volume was to be evaluated. A minimal amount of size reduction was performed on the mulch samples. This size reduction was designed to mix the wood and to break up large pieces (Tolaymat et al., 2000).

A description of the chemical extraction steps used in the different leaching methods (TCLP, SPLP, EP Tox, WET, and MEP) is described in subsequent paragraphs. All these extraction methods are similar in that the sample is in contact with the chemical leaching fluid for a specified period of time. All of the extractions require a contact time between 18 to 48 hours except for the MEP which requires sequential extraction steps. Following the chemical extraction step, the leachate is filtered to separate it from the solid waste. The filtration step requires the use of a pressure filter apparatus and immediate acidification of the collected liquid to a pH below 2. This leachate is then digested. In some cases the leachate samples were split and subjected to two different digestions depending upon the analysis method used for quantifying metals. Digestates were analyzed in duplicate for chromium, copper, and arsenic on either an Inductively Coupled Plasma – Atomic Emission Spectrometer (Thermo Jarrel Ash Enviro 36) or an atomic absorption spectrophotometer (Perkin Elmer 5100) fitted with either a flame or a graphite furnace atomizer. A listing of the EPA methods used for digestion and metals analysis is provided in table IV.4. Quality assurance and quality control for these analyses were consistent with the University of Florida Environmental Engineering Sciences Solid and Hazardous Waste Research Program's Comprehensive Quality Assurance Plan #960218.

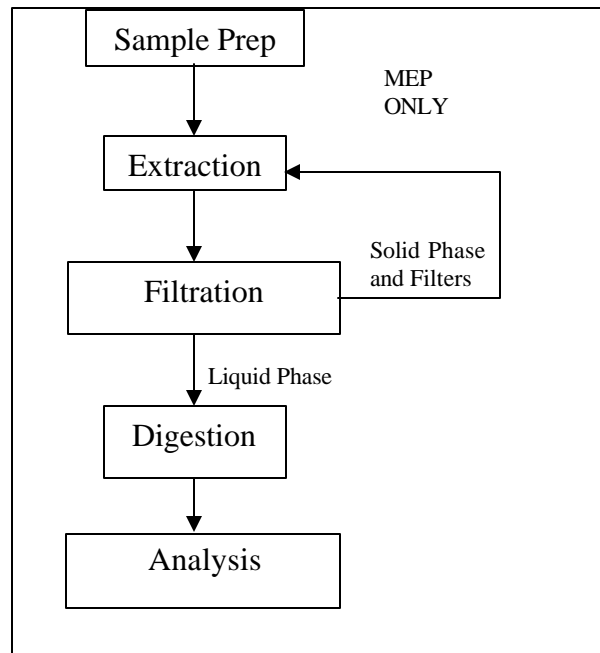


Figure IV.1: Basic Steps of Batch Leaching Tests

Type of Analysis	Metal Analyzed		
	As	Cu	Cr
Liquid Digestion (New CCA wood samples) To be Analyzed on ICP	3010A	3010A	3010A
Liquid Digestion (New CCA wood samples) To be Analyzed on Flame AAS	NONE	3010A	3010A
Liquid Digestion (C&D Wood Waste) To be Analyzed on GF-AAS	7060A	3020A	3020A
ICP-AES Analysis	6010B	6010B	6010B
Flame AAS Analysis	None	7210	7190
GF-AAS Analysis	7060A	7191	7211

Table IV.4: EPA Method Numbers Used for Various Analyses (SW-846, 1996)

#### *TCLP (Toxicity Characteristic Leaching Procedure)*

The TCLP (SW-846 Method 1311, USEPA 1996) involves extracting contaminants from a size-reduced mass of waste material using a buffered acetic acid solution. A 20-to-1 liquid-to-solid ratio was employed and the mixture was rotated for  $18 \pm 2$  hours. The specific composition of the acetic acid solution used for the extraction was dependent upon the pH of the sample, which was determined by immersing 5 grams of sample into 96.5 ml of deionized water. If the pH of the solution was less than 5, extraction fluid #1 was utilized. If the pH was greater than 5, then extraction fluid #2 was used. All samples evaluated in this study were characterized by a pH less than 5. Extraction fluid #1 was prepared by adding 11.4 ml of glacial acetic acid ( $\text{CH}_3\text{OOH}$ ) to approximately 1000 ml of reagent water in a 2 L volumetric flask. This was followed by an addition of 128.6 ml of one normal sodium hydroxide (1N NaOH). This mixture was then brought up to volume with reagent water. The resulting pH of this fluid was  $4.93 \pm 0.05$ . A representative 100.0 g sub-sample was then placed in a 2 L polyethylene container and 2 L of extraction fluid were added. An extraction fluid blank and a duplicate sample were prepared for each rotational period. The samples were then placed in the extractor (figure IV.2) and rotated for  $18 \pm 2$ -hrs. The leachate was filtered at the end of the rotation period and analyzed for its metal content.

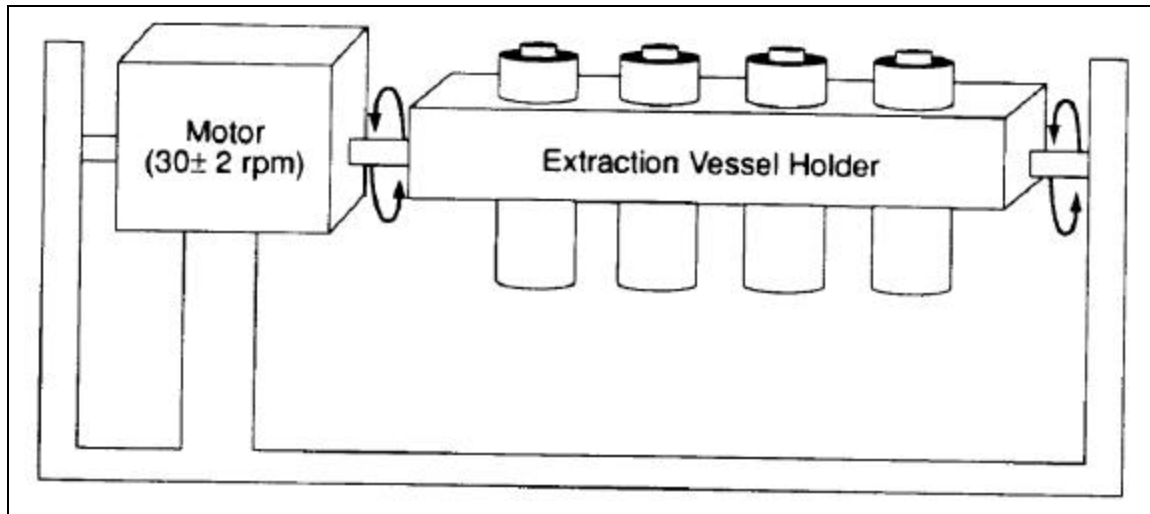


Figure IV.2: Extraction Apparatus (from SW-846, USEPA1996)

### *SPLP (Synthetic Precipitation Leaching Procedure)*

The SPLP (SW-846 Method 1312, USEPA 1996) is performed in the same manner as the TCLP, but a simulated acid rainfall is employed. The test consists of utilizing two inorganic acids (nitric and sulfuric acids). East of the Mississippi River the fluid is slightly acidic at a pH 4.22 that reflects the air pollution impact of heavy industrialization and coal utilization. A pH of 5.0 is used west of the Mississippi reflecting less industrialization and smaller population densities. 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 reagent water. The resultant pH was  $4.22 \pm 0.05$ . In a similar fashion as for the TCLP, a 100 g sample was placed in a 2 L polyethylene extraction vessel containing 2 L of SPLP extraction fluid. An extraction blank and a duplicate were included in analysis set. The samples were then rotated for  $18 \pm 2$  hours. The leachate was then filtered and analyzed for its metal content.

### *EP Tox*

The EP Tox (SW-846 Method 1310, USEPA 1996) requires that a 100 g solid sample be placed in 1.6 L of deionized water. If the pH of the solution was greater than 5.0, the pH of the solution was decreased to  $5.0 \pm 0.2$  by slowly adding 0.5 N acetic acid. If the pH was less than 5.0, no acetic acid was added. The pH of the solution was checked periodically, and, if necessary, 0.5 N acetic acid was manually added to the extractor in specified time intervals (15-, 30-, and 60-minutes) until the pH reached  $5.0 \pm 0.2$ . The maximum amount of 0.5 N acetic acid added to the solution was 400 ml. The mixture was then rotated for 24 hours. If, at the end of the 24-hour extraction period, the pH of the solution was not below 5.2 and the maximum amount of acid had not been added, the pH was adjusted to  $5.0 \pm 0.2$  and the extraction continued for an additional 4 hours, during which the pH was adjusted at 1 hour intervals, if needed. At the end of the extraction period, water was added, if needed, to bring the total volume of the extraction fluid to 2 L. The leachate was filtered, acidified (to a pH less than 2), and analyzed for metals concentrations as described earlier.

### *Waste Extraction Procedure (WET)*

The WET (CCR 1998) is standardized by the State of California to determine the amount of extractable substances in waste or other materials. This test is similar to TCLP in that it uses a buffered organic acid solution as the extraction fluid. The main difference lies in the choice of the acid. TCLP uses an acetic acid mixture, while WET uses a buffered citric acid solution. The pH of the TCLP (4.98) test and the WET (5.0) test are similar. The WET extraction fluid is prepared by titrating a 0.2 M citric acid solution with 4.0 N NaOH to a pH of  $5.0 \pm 0.1$ . One liter of this fluid were added to a 100 g sample and rotated for a period of 24 hours. Please note that CCA 1998 required a 48 hour extraction period. So while the WET solution was used, the extraction time was different. An extraction blank and a duplicate were prepared for each rotational period. After rotation, samples were filtered through a 0.7 um glass fiber filter using a pressure filtration system. After this initial filtration, the leachates were then re-filtered in the same manner through 0.45 um membrane filter. The filtrate was collected in plastic bottles and nitric acid was added until the pH of the solution was below a pH of 2. Extracts were then digested and analyzed for their metals concentrations.

### *Multiple Extraction Procedure (MEP)*

The extraction fluids used in the MEP (SW-846 Method 1320, USEPA 1996) consist of both an organic (acetic acid) used to simulate MSW leachate and an inorganic acid mixture (nitric and sulfuric acids) designed to simulate acid rain. The repetitive nature of the extraction procedure allows for maximum leaching of chemical constituents. This extraction method is therefore used to predict long term leaching characteristics of wastes placed in a landfill. Extraction was initially performed on 60 g of each sample using an acetic acid solution. The method of adding the acetic acid was the same as that for the EP Tox method. After the 24-hour rotation period and filtration of the leachate, seven additional extractions were performed on the solids captured on the filter. The solvent used for these extractions was a nitric/sulfuric acid solution (i.e. synthetic rain), which was prepared the same way as the SPLP leaching fluid except that the pH of the fluid was  $3.0 \pm 0.2$ . During each subsequent extraction, the synthetic rain extraction fluid was added to the waste at a 20:1 ratio, the samples were rotated for 24 hrs, and the leachate was filtered. After each filtration step the leachate was collected in plastic bottles and preserved by adding nitric acid until the pH of the solution was below 2. Samples were subsequently digested and analyzed for their metals concentrations.

## **IV.5 RESULTS ON TESTS CONDUCTED USING NEW CCA-TREATED WOOD**

Results from new CCA-treated wood include data obtained from 10 different samples, each characterized by different initial dimensions and/or brands. These samples were separated into four different particle sizes (sawdust, chipped wood, 5 20-g blocks, and 1 100-g block) and analyzed via SPLP and TCLP (section IV.5.a). This section also includes a discussion concerning the impact of particle size on SPLP and TCLP results (section IV.5.a) and describes the results of EP Tox, WET, and MEP conducted on one of the 10 new CCA-treated wood samples (section IV.5.b).

### **IV.5.a SPLP and TCLP Results for New CCA-Treated Wood**

Figures IV.3 through IV.6 present results of As, Cr, and Cu concentrations measured in the SPLP leachate while Figures IV.7 through IV.10 present results for the TCLP leachates. Each figure represents all results for one sample size only. Figures comparing the role of particle sizes are presented separately in Appendix C as Figures C.1 and C.2.

#### *Leachate Metal Concentrations*

The three metals leached measurable concentrations in all samples. None of the metals were found to be below their appropriate detection limit. As a whole, arsenic concentrations measured the highest, followed by copper, with chromium leaching the lowest concentrations. The highest As concentration measured in any sample was 12.5 mg/l (brand 1 4x4 saw dust, TCLP ) while the lowest As concentration was 0.31 mg/l (brand 3 2x4 100g block, SPLP). The highest Cr concentration measured in any sample was 5.14 mg/l (brand 4 2x6 5-20g blocks, SPLP) while the lowest Cr concentration was 0.10 mg/l (brand 3 2x4 100g block, SPLP). The highest Cu concentration measured in any sample was 21.2 mg/l (brand 1 2x8 chipped wood, TCLP) while the lowest Cu concentration was 0.26 mg/l (2 4x4 100g block, SPLP).

XRF results as presented in table IV.3 do not reveal any correlation between the retention value and metal leachability. The variability between reported and measured values and between different measurements, made interpretation with regard to retention levels difficult.

#### *Comparison of TCLP and SPLP Results*

The TCLP and SPLP each simulate different environments. The TCLP is often thought to represent a more aggressive leaching test for heavy metals (i.e. it releases more metals into solution) than SPLP as presented in appendix C figure C.3. The figure shows that TCLP tends to extract more copper than SPLP. However, both tests extract the similar amount of arsenic and chromium. For comparison sake, the concentrations resulting from the leaching of the smallest particle size samples are discussed here. The smaller particle size also reflects the requirement of the testing procedures. The average arsenic leachate concentration of all sample types was 6.7 mg/l for TCLP and 5.1 mg/l for SPLP. For chromium, TCLP leachates averaged 2.6 mg/l and the SPLP leachates averaged 1.4 mg/l. For copper, the TCLP leachates averaged 11.3 mg/l and the SPLP leachates averaged 2.3 mg/l.

In general, the TCLP resulted in more metal leaching than the SPLP. The type of leaching fluid used had the least impact on arsenic and the greatest impact on copper. On average, copper leached 3 times greater in the TCLP than the SPLP. Several characteristics of the leaching fluid impact the amount of heavy metal that leaches. The solution pH is of prime importance. Metals tend to solubilize at pH extremes (low and high pHs). It should be noted that it is not the initial pH of the leaching solution that controls the leaching process, but the pH present during the bulk of the leaching test. The SPLP has a lower initial pH (4.2) than the TCLP fluid used here (pH = 4.8). Since the acids used in making the SPLP solution are strong acids, only a small amount of acid is added, and thus a small amount of buffering capacity in the waste increases the leaching solution pH. The weak acid used in the TCLP (acetic acid) has much more acid present, and thus the final pH of buffered waste samples tends to be lower. In the case of treated wood, the final pH measurements of both tests are relatively close and pH alone does not explain the differences, especially for copper. The type of acid used can play a role in terms of complexation of heavy metals. In these tests, the acetic acid used in TCLP acted to form metal-acetate complexes, (especially with copper), and resulted in greater amounts of metals being released into the leaching solution.

### *Impact of Particle Size*

As expected, the concentration of metals that leach from CCA-treated wood is dependent upon the particle size. The greater the particle size, the lower the concentration of heavy metal in the leachate. This is illustrated in Appendix C in Figures C.1 and C.2. As the size of a particle decreases, the surface area that is exposed to the leaching solution increases. As a consequence more metals are leached from sawdust than from chipped wood. Chipped wood leaches more than the 5, 20g blocks, whereas the 1, 100g blocks leached the least.

### *Comparison to Regulatory Levels*

Although CCA-treated wood is exempt from being a hazardous waste by federal rule, the results of the leaching tests are compared to the federal toxicity characteristic (TC) limits. Again, the results for leaching of the smallest particle size are discussed. Arsenic was the only metal that exceeded TC limits (5 mg/l). Chromium never exceeded its 5 mg/l limit and copper does not have a TC limit. The TCLP leachates exceeded 5 mg/l of arsenic in 8 of the 10 samples tested. The SPLP leachates exceeded 5 mg/l of As in 6 of the 10 samples collected. Again, the average TCLP As concentration was 6.7 mg/l and the average SPLP As concentration was 5.1 mg/l.

Results were also compared to applicable groundwater limits. The Florida DEP uses a set of Groundwater Cleanup Target Levels (GWCTLs). As previously stated, these values are 0.05 mg/l, 0.10 mg/l, and 1.0 mg/l for As, Cr, and Cu, respectively. The GWCTLs for As and Cr represent primary drinking water standards while the GWCTL for Cu represents a secondary drinking water standard. For sawdust, leachate from every sample exceeded the GWCTL for each metal for both the TCLP and SPLP. The heavy metal that exceeded the GWCTL by the greatest amount was As, which exceeded the existing primary drinking water standard by an average factor of 134 for the TCLP leachates and 102 for SPLP leachates. When looking at the largest particle size (one 100-g block), arsenic exceeded the GWCTL in every sample using both the TCLP and SPLP. The minimum arsenic concentration measured in any TCLP or SPLP leaching test (0.31 mg/l) was 6 times the current GWCTL. Again looking at the 100-g block



samples, chromium leached greater than GWCTL 100% of the time using TCLP and 100% of the time using SPLP. Copper leached greater than the GWCTL 100 % of the time using TCLP and 40% of the time using SPLP.

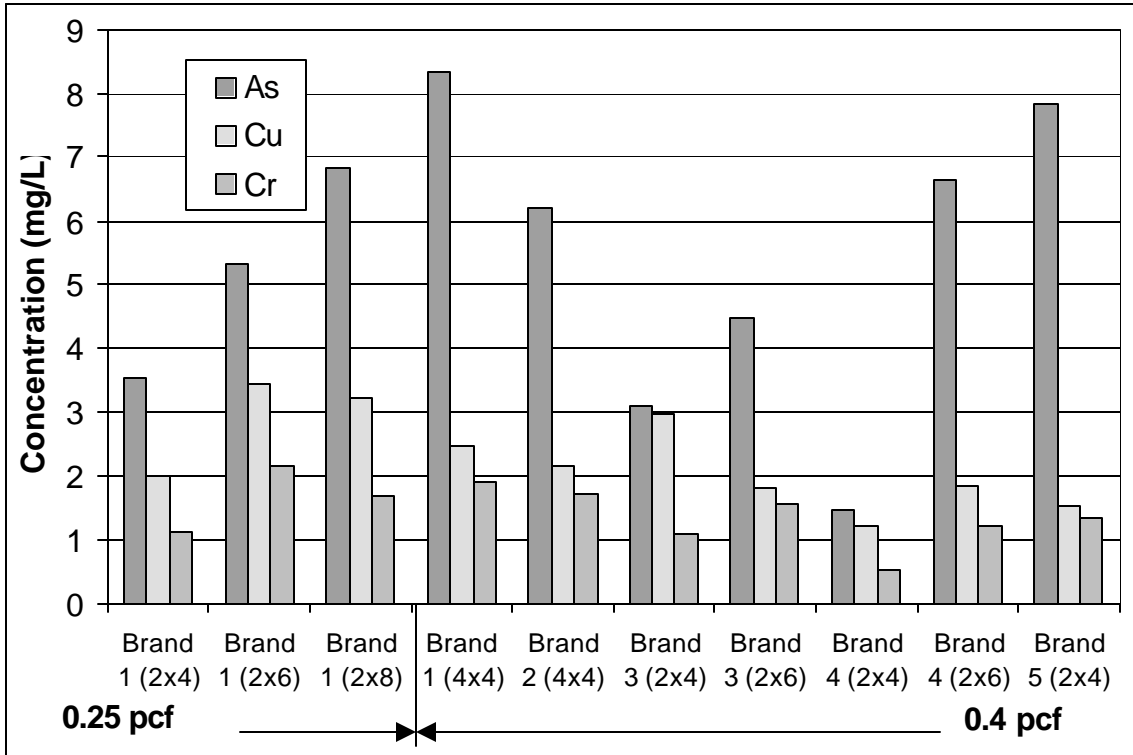


Figure IV.3: SPLP Extraction Results for As, Cu, and Cr from Saw Dust

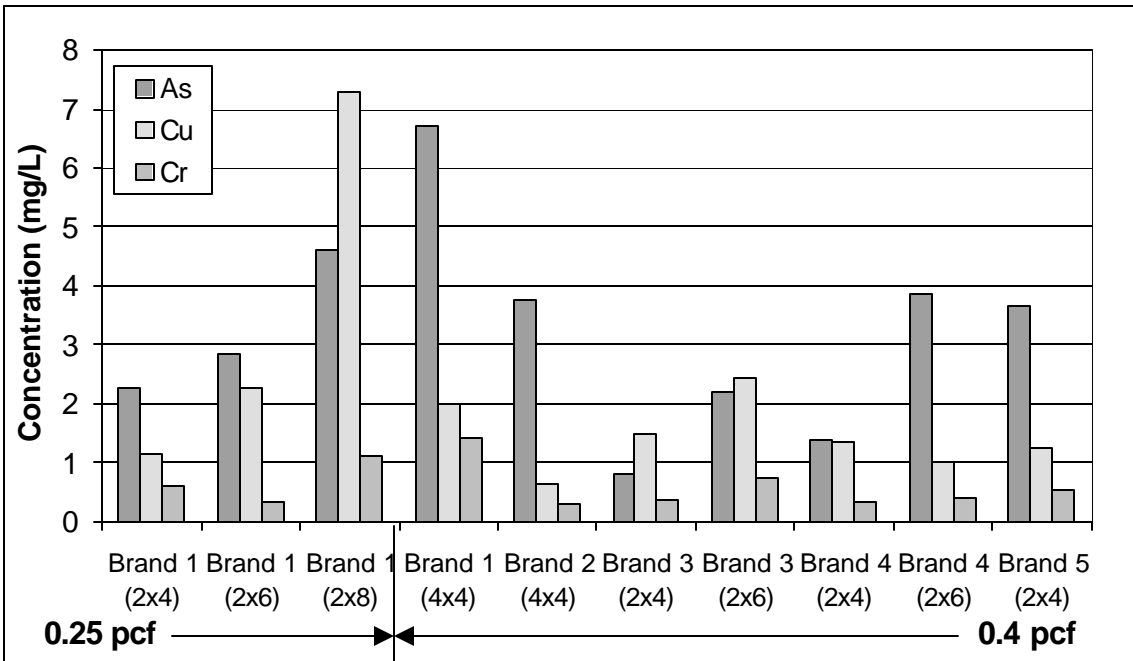


Figure IV.4: SPLP Extraction Results for As, Cu, and Cr from Chipped Wood

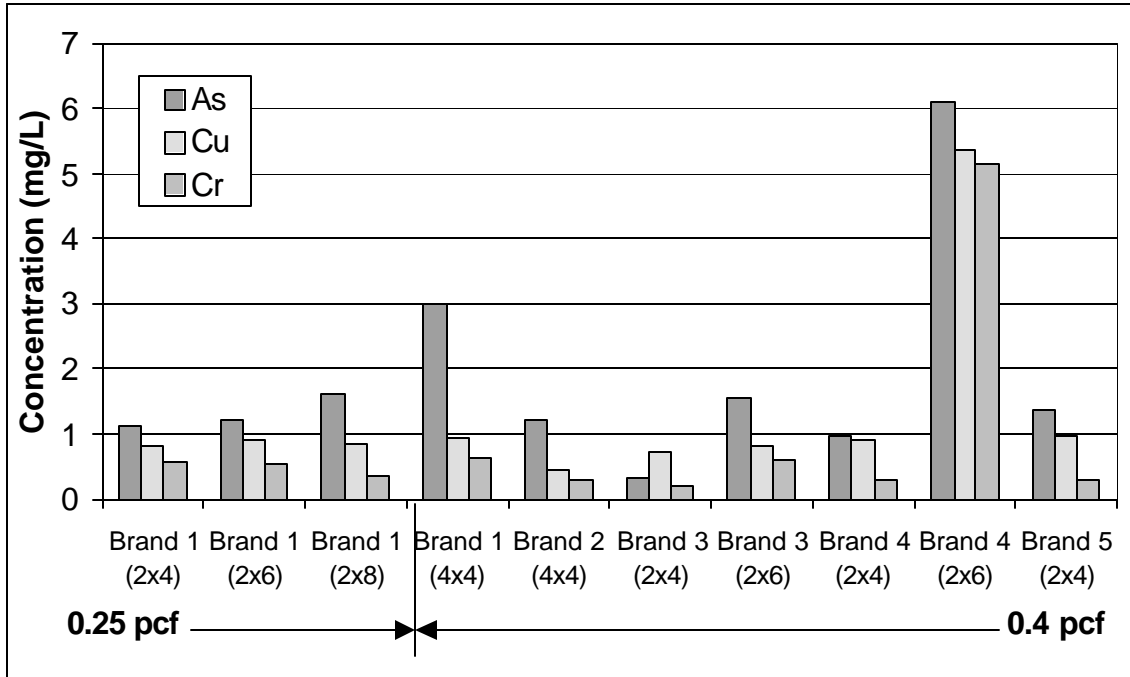


Figure IV.5: SPLP Extraction Results for As, Cu, and Cr from 5, 20-g Blocks

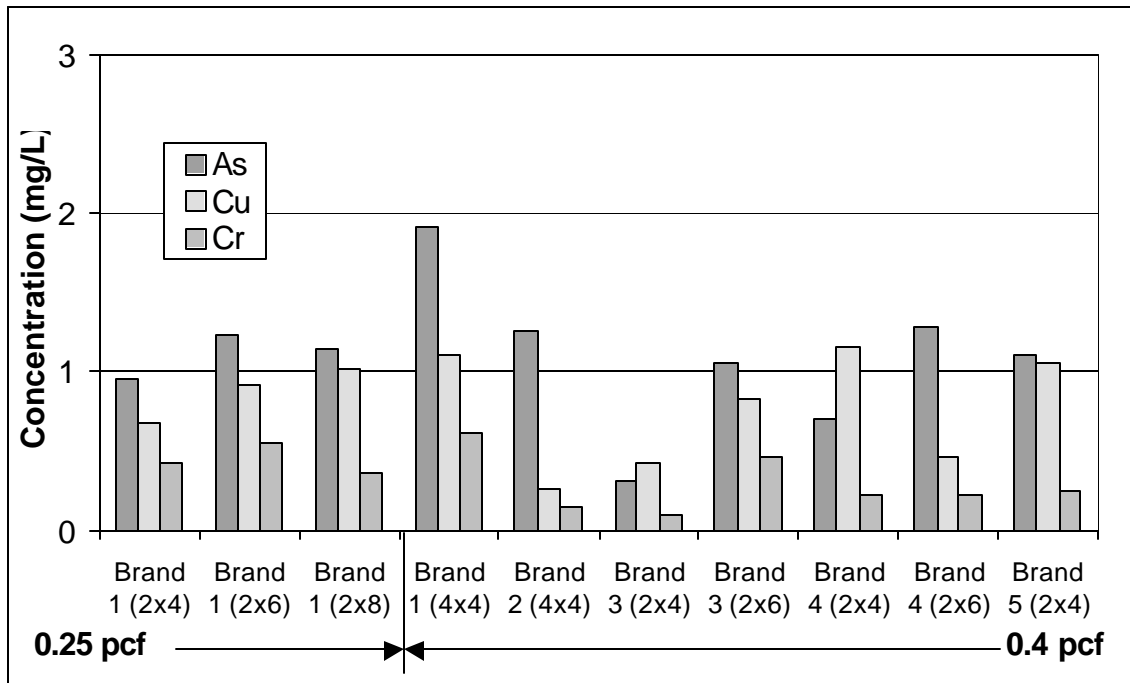


Figure IV.6: SPLP Extraction Results for As, Cu, and Cr from 1, 100-g Block

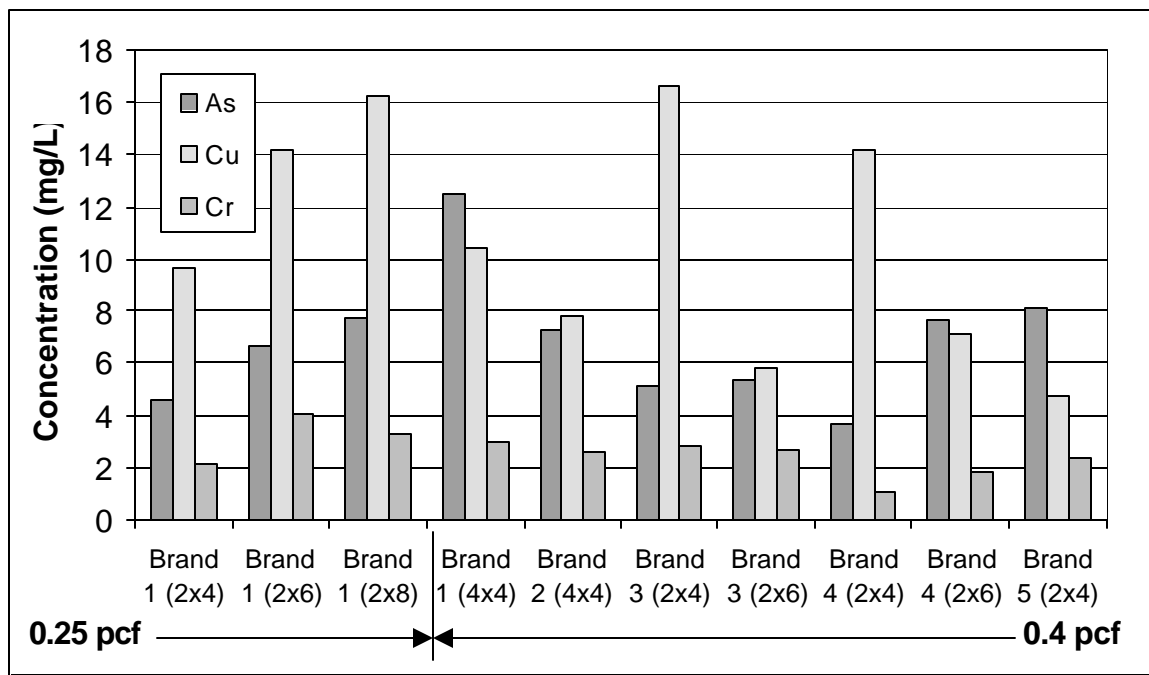


Figure IV.7: TCLP Extraction Results for As, Cu, and Cr from Sawdust

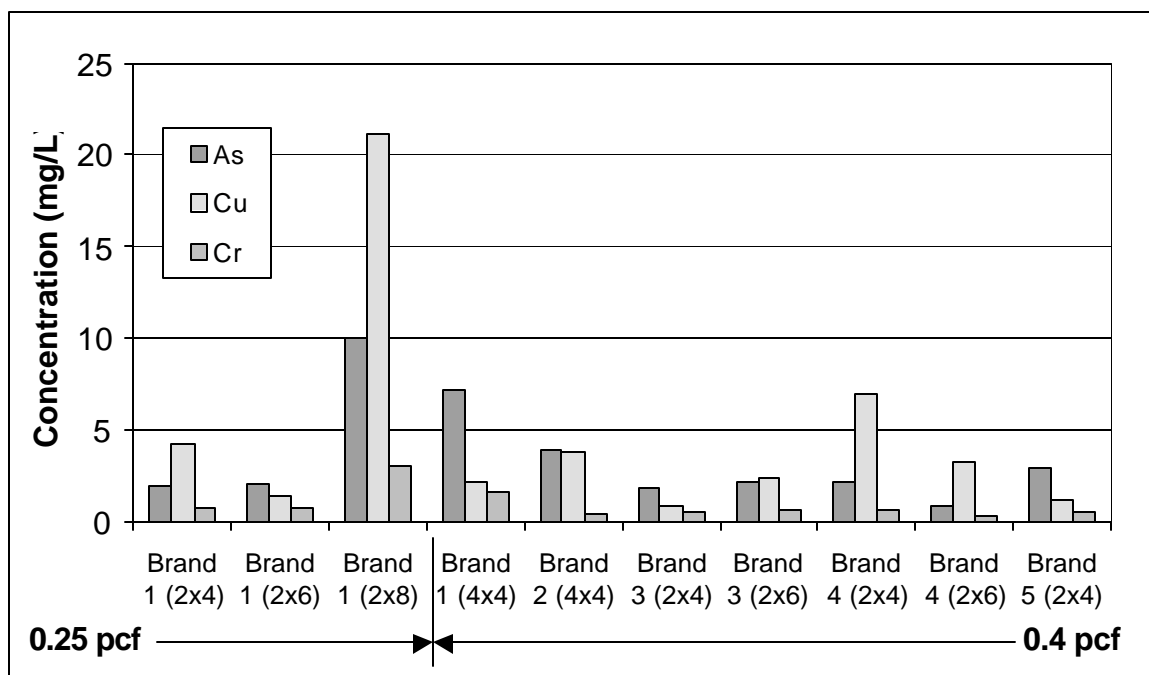


Figure IV.8: TCLP Extraction Results for As, Cu, and Cr from Chipped Wood

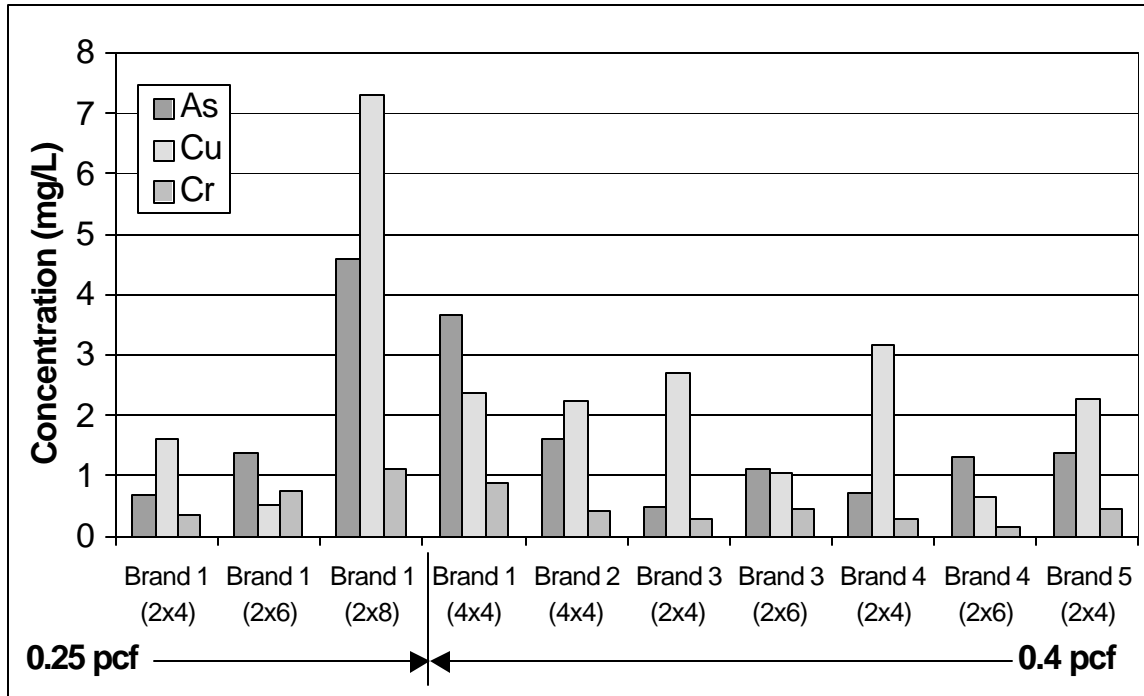


Figure IV.9: TCLP Extraction Results for As, Cu, and Cr from 5 20-g Blocks

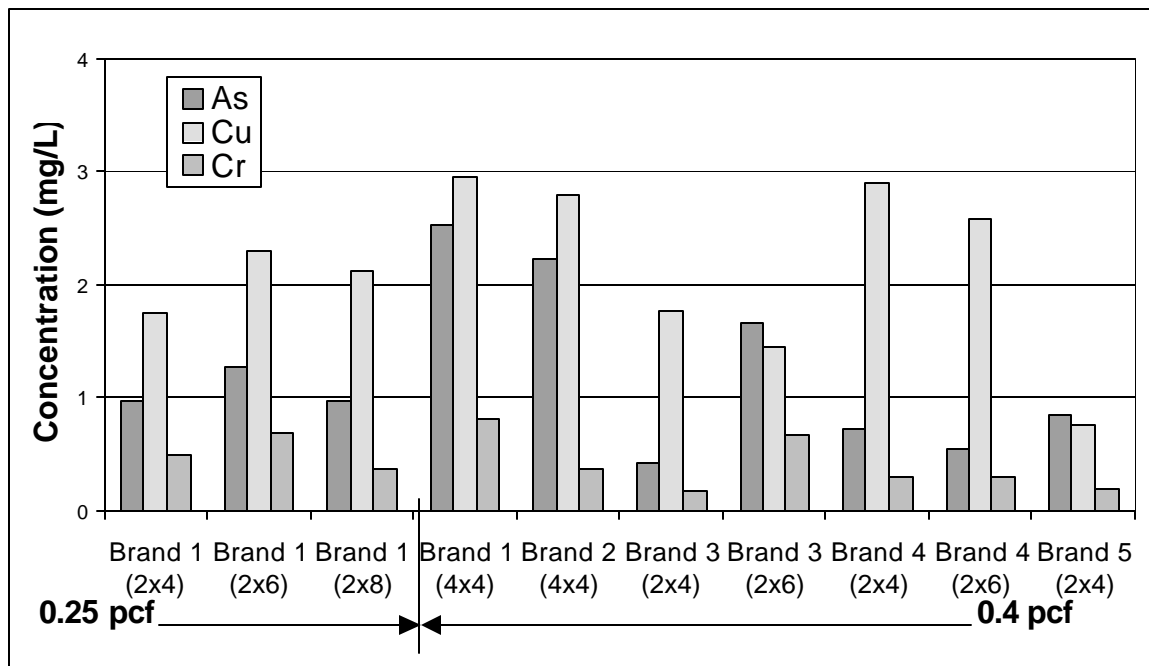


Figure IV.10: TCLP Extraction Results for As, Cu, and Cr from 100-g Block

### IV.5.b Batch Tests Comparison

Five different tests (TCLP, SPLP, EPTOX, WET and MEP) were conducted on brand 5 (2x4). Since the MEP test is different than the other four tests the results are presented separately. Figure IV.11 shows a comparison between the four tests for arsenic extractability for the four particle sizes examined. For each particle size arsenic is leached at approximately the same level for the TCLP and EPTOX tests. The SPLP resulted in similar but slightly lower concentrations and the WET resulted in much higher metals concentrations. The same trend is also observed with copper and chromium (Figures IV.12 and IV.13). The WET extracted an order of magnitude more chromium than the other four tests.

The results from the MEP show a decreasing trend throughout the extraction period for arsenic, chromium, and copper (figures IV.14 and IV.15). The copper concentrations were more variable. The largest decreases occurred during the first 4 days. It is apparent from figures IV.14 and IV.15 that during the first extraction day arsenic leached more than copper and chromium. But during subsequent days the leaching trend changed where copper leached more than arsenic and chromium. Indicating that arsenic is readily leachable from CCA-treated wood while copper leaches less but at a more constant level.

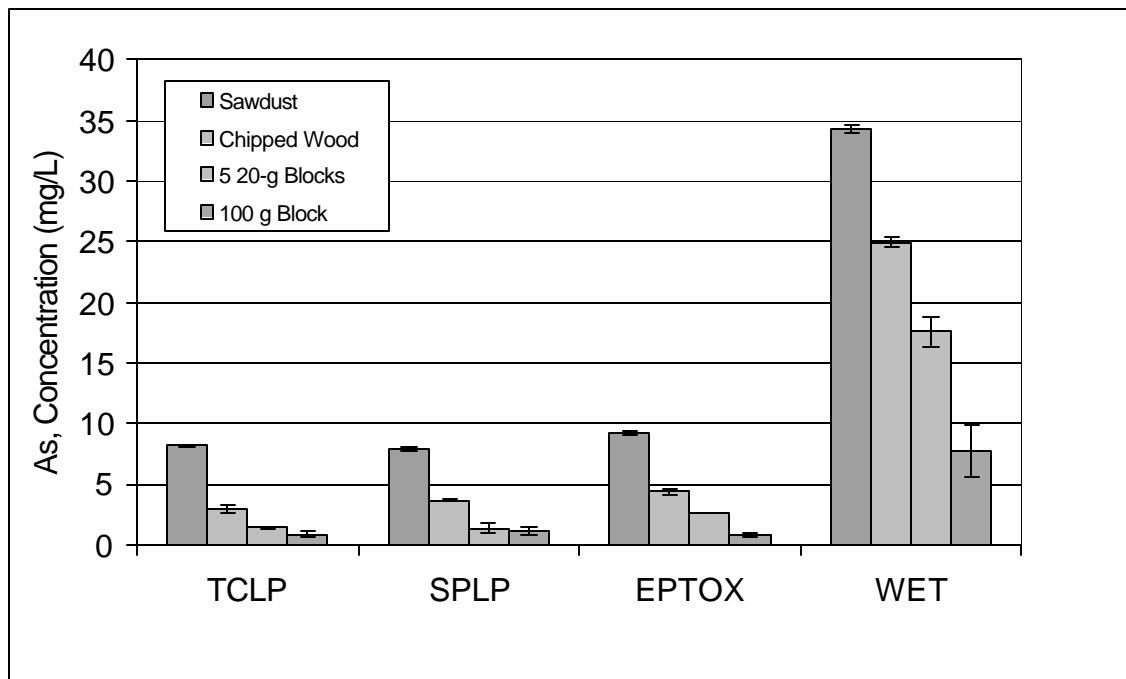


Figure IV.11: Arsenic Concentration in Extracts from TCLP, SPLP, EPTOX, and WET

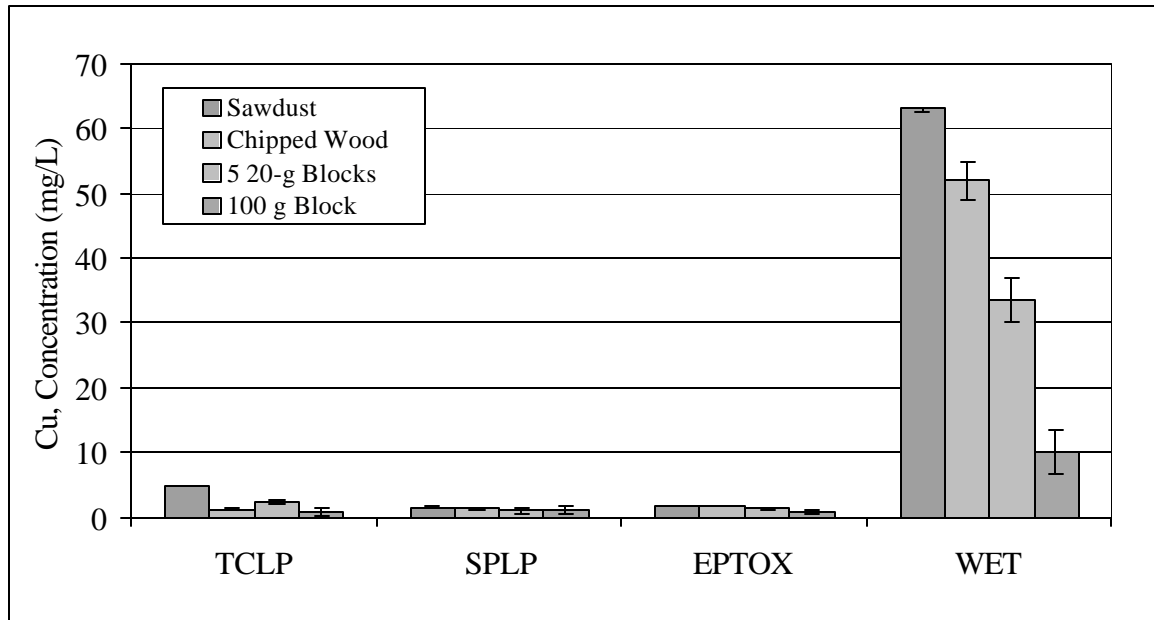


Figure IV.12: Copper Concentration in Extracts from TCLP, SPLP, EPTOX, and WET

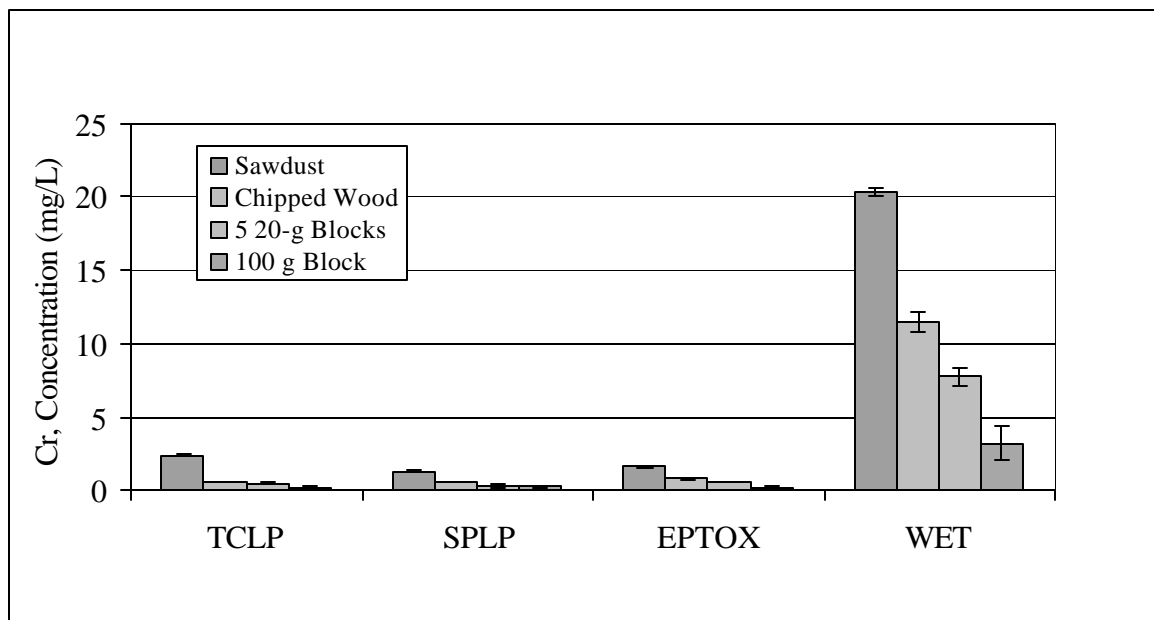


Figure IV.13: Chromium Concentration in Extracts from TCLP, SPLP, EPTOX, and WET

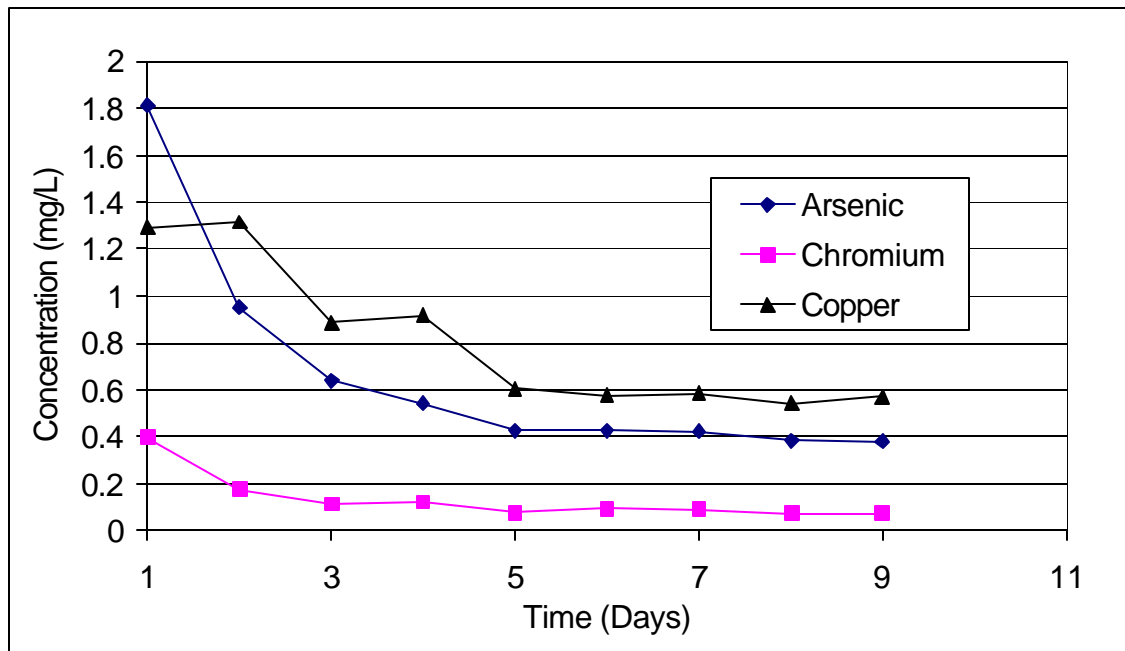


Figure IV.14: MEP Test Results for Arsenic, Copper, and Chromium Using 3 20-g Blocks

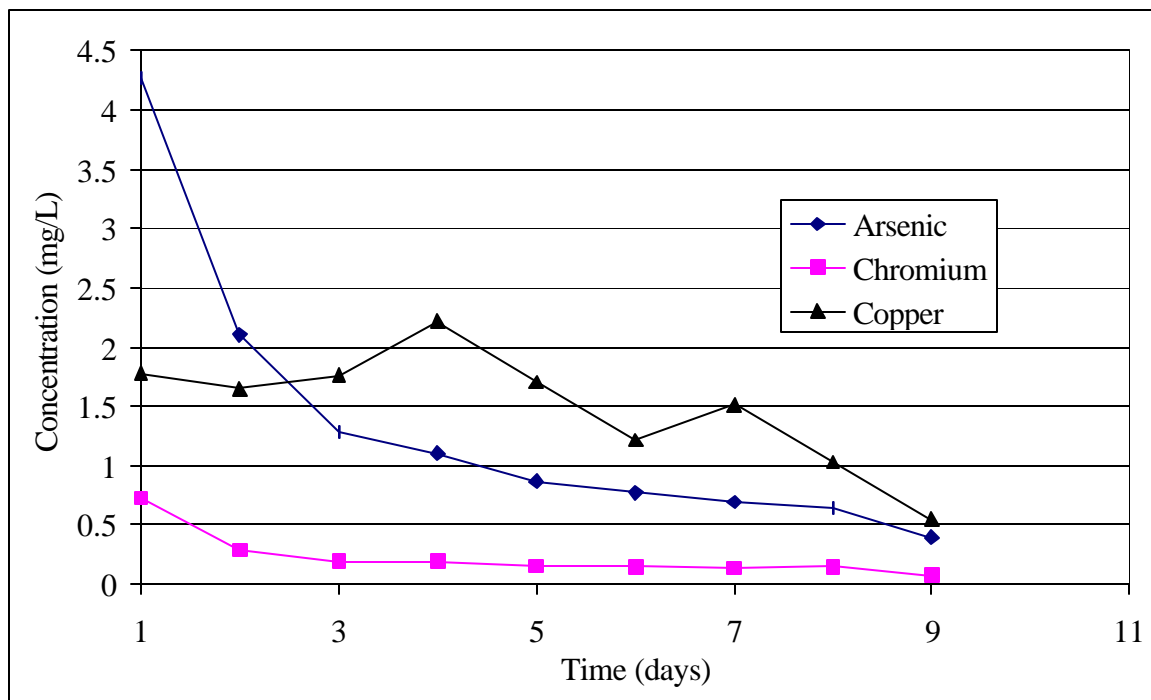


Figure IV.15: MEP Test Results for Arsenic, Copper, and Chromium Using Chipped Wood



#### **IV.5.c Discussion**

While leaching tests such as the TCLP and SPLP provide insight into the science of leaching behavior from waste materials, they were designed as regulatory tests and the results of these tests have very specific regulatory implications. The most commonly applied regulatory leaching is the TCLP. If a solid waste leaches concentrations of pollutants in the TCLP at concentrations greater than the toxicity characteristic limits in the RCRA regulations, the waste is considered a hazardous waste. The designation of hazardous waste carries much greater requirements and costs with the management of that waste. For example, a hazardous waste must be tracked from cradle to grave, and it must be stabilized before it can be disposed, and disposal can only occur in specific disposal facilities. Both As and Cr are toxicity characteristic metals. Of the tests conducted in this study, the ones that would be most representative of required regulatory testing for hazardous waste determination would be the TCLP performed on the sawdust samples. The TCLP requires size reduction of the waste prior to analysis. The results of these tests showed that 8 out of the 10 samples tested exceeded the toxicity characteristic limit of 5 mg/l for arsenic. None of the samples exceeded the 5 mg/l toxicity characteristic level for chromium. Again, copper is not a regulated toxicity characteristic metal. As previously discussed, CCA-treated wood is exempt from being a hazardous waste under U.S. federal regulations if it is discarded after its intended use. The results indicate that if this exemption was not in place, in many cases, CCA-treated wood would be required to be managed as a hazardous waste. A different waste with the same leaching characteristics would be required to be managed as a hazardous waste.

The issue of particle size is often cited as a criticism of the TCLP. It is argued that the small particle size (less than 0.95 cm) required by the test is unrepresentative of the condition in which the material is disposed. It must be noted that the TCLP was not designed to be a predictive tool for simulating actual leachate concentrations from a landfill, but rather it was designed to be a rapid test to provide a conservative estimate of maximum potential leachability and to thus distinguish wastes that must be managed with greater care than most. The test does not assume that the waste will be disposed in a size-reduced condition. The size reduction step is one of a number of conservative steps (others being the agitation and the aggressive leaching medium) that allow one test to serve to appropriately characterize which wastes warrant special management requirements to prevent possible environmental contamination, both in the short and long term. It is true that CCA-treated wood samples of larger particle size do leach less than the 5 mg/l Toxicity Characteristic, but this is more of an issue for assessing actual environmental impact than it is for determining regulatory status.

The use of the SPLP is not written into the solid waste regulations in the same manner as the TCLP. A solid waste cannot be a hazardous waste for failing the SPLP. The SPLP is used a tool for assessing when a solid waste can be applied in an environment where rainfall is the likely leaching medium and where there is no protection of the underlying groundwater (unlined landfill, land application). In this manner, the SPLP is used and required by regulatory agencies as part of the decision making process for management of wastes in these scenarios. The typical application is to perform an SPLP on the waste, measure the concentration of pollutants in the leachate, and then compare the concentrations of detected pollutants to groundwater standards in the aquifer that might be impacted by the proposed waste management. It should be noted, that unlike the Toxicity Characteristic list that encompasses only a relatively small number of

pollutants (e.g. only 8 heavy metals), most groundwater standards include concentrations levels for hundreds of chemicals.

In Florida, the groundwater guidance cleanup target levels (GWCTLs) are 0.05 mg/l, 0.10 mg/l, and 1 mg/l for As, Cr, and Cu respectively. The As and Cr GWCTLs represent primary drinking water standards set by the U.S. EPA and Cu represents a secondary drinking water standard. (Please note that the primary drinking water standard for arsenic has been proposed to be decreased to 10 ug/L, U.S. EPA, 2001) When comparing the sawdust results for SPLP, every sample exceeded the appropriate GWCTL for each metal. Even at the largest particle sizes, all samples exceeded the GWCTL for arsenic and chromium. A waste with these characteristics would not be allowed to be disposed in an unlined landfill. In Florida, however, CCA-treated wood is allowed to be disposed as part of the C&D debris. The implications of these results on the reuse of C&D debris wood as mulch are less clear. It is recognized that new CCA-treated wood is not being ground and used as mulch by itself. CCA-treated wood is present along with untreated wood. If one were to take the chipped sample results for the SPLP conducted, the minimum As leachability was approximately 1 mg/l. At this concentration, treated wood present at 5% of the total mulch would be equal to the arsenic groundwater guidance concentration of 0.05 mg/l. As stated in previous sections, the amount of CCA-treated wood observed in the C&D debris wood stream in recent years ranges from a low of 6% up to a high of 30%. So while a definite conclusion can not be drawn to the leachability of mulch from C&D debris wood, the results here indicate that it is likely that if SPLP were conducted, many mulch samples would exceed the GWCTL for As.

One additional point of discussion as related to the regulatory implications of these leaching tests is that the U.S. EPA's primary drinking water standard for arsenic has been proposed to be lowered from 0.050 mg/l to 0.010 mg/l (USEPA 2001). The lowering of the drinking water standard (which would be subsequently adopted as part of the Florida GWCTLs) only increases the degree to which the leachates measured in this study exceed the relevant regulatory health-based concentration limits. It should also be noted, that since the toxicity characteristic concentrations in RCRA were derived from the drinking water standards, the Toxicity Characteristic value for As could in theory be lowered from 5 mg/l to 1 mg/l. At a Toxicity Characteristic regulatory level of 1 mg/l, the whole pieces of CCA-treated wood tested would have failed nearly half of the time.

## **IV.6 RESULTS ON TESTS CONDUCTED USING C&D DEBRIS WOOD MULCH**

Results are first presented for the metal concentration data (section IV.6.a), and then a discussion of the results as compared to the Florida Groundwater Guidance Concentrations (section IV.6.b).

### **IV.6.a Leachate Heavy Metal Concentrations**

The arsenic, chromium, and copper results are presented in table IV.5. The concentration values presented for samples A through M represent the average of three leaching tests and the values for samples N through U represent the average of two leaching tests. When looking at the

entire sample data set, the concentration of arsenic ranged from below detection limit (10 µg/L) to 558 µg/L. The chromium concentrations ranged from below detection limit (10 µg/L) to 229 µg/L while the copper concentrations ranged from below detection limit (10 µg/L) to 340 µg/L. When the results are grouped by category (table IV.6) results show that wood that is generated from C&D recycling operations leaches arsenic, copper, and chromium at higher levels than any other type of wood.

The hypothesis of this study was that arsenic, chromium, and copper would leach from C&D debris wood mulch as a result of CCA-treated wood present in the material. Arsenic, copper and chromium were all observed to leach from the C&D debris wood mulches. The results indicate that for the most part, arsenic leaches at greater concentrations than the other metals. The relatively poor correlation between the metals is not surprising. Previous research indicates that all three metals leach at different rates and concentrations depending on factors such as solution pH, presence of other chemicals in the leachate, the type of wood, and the degree of leaching that has occurred already. In the research on new CCA-treated wood presented in the prior section of this report, arsenic leached more under the SPLP test than chromium and copper.

Category	Sample	As Concentration (ug/L)		Cr Concentration (ug/L)		Cu Concentration (ug/L)	
		Sample Average	Site Average	Sample Average	Site Average	Sample Average	Site Average
C&D Debris Samples (1997)	A1	52.3	54.25	49.4	51.7	41.9	43.25
	A2	56.2		54		44.6	
	B1	182	182	82.2	82.2	96.1	96.1
	C1	274.7	225.2	117.8	113.75	340.2	238.05
	C2	175.7		109.7		135.9	
	D1	41.9	103.6	103.6	74.19	71.45	80.48
	D3	165.3		39.3		94.9	
	E1	73.8	72.4	55.3	49.25	35.5	42.7
	E2	71.0		43.2		49.9	
	F1	68.5	68.5	38.3	38.3	25.8	25.8
	G1	160.2	160.2	112	112	66.2	66.2
	H1	80.6	116.85	35.8	40.45	42.8	53.5
	H2	153.1		45.1		64.2	
	I1	158	126.4	68.1	53.6	43.3	33.75
	I2	94.8		39.1		24.2	
J2	49.0	49.0	30.1	30.1	34.5	34.5	
K1	558.4	558.4	229	229	217.1	217.1	
M1	347	347	169.7	169.7	633.2	633.2	
C&D Debris Samples 1999	N1	172.7	164.35	85.9	79.85	35.1	45.65
	N2	156.0		73.8		56.2	
Colored Mulch	P1	BDL	BDL	BDL	BDL	11.1	11.1
	Q1	65	65.4	24	25.05	17.7	17.25
	Q2	65.8		26.1		16.8	
Commercial Mulch	S1	BDL	BDL	BDL	BDL	19.7	19.7
	T1	BDL	BDL	BDL	BDL	BDL	BDL
	U1	BDL	BDL	BDL	BDL	BDL	BDL
Yard Waste	R1	56.7	56.7	117.1	117.1	36.1	36.1
	D2	BDL	BDL	BDL	BDL	94.4	47.24
	D4	BDL		BDL		BDL	

Table IV.5: Metal Concentrations in SPLP Leachates

<b>Sample</b>	<b>As (mg/l)</b>	<b>Cr (mg/l)</b>	<b>Cu (mg/l)</b>
1997 C&D Debris Samples (Sites A through M, except D2 and D4)	153.5	73.4	113.0
1999 C&D Debris Mulch Sample (Site N)	164.4	79.8	45.7
Yard Waste Facility (Site R, D2, D4)	56.7	117.1	36.1
Commercial Mulch (pine bark, cypress) (Sites S, T, U)	BDL	BDL	6.56
Colored Mulch 1 (Site P)	BDL	BDL	11.1
Colored Mulch 2 (Site Q)	65.4	25.0	17.2

Table IV.6: Mean Metal Concentrations in SPLP Leachates

#### IV.6.b Comparison to Groundwater Guidance Concentrations

The metal concentrations in the SPLP leachates were compared to the Florida Groundwater Cleanup Target Levels (GWCTL) for arsenic, chromium, and copper. The GWCTLs for As, Cr, and Cu are 50 µg/l, 100 µg/l, and 1,000 µg/l, respectively. The GWCTLs for As and Cr represent risk based concentrations that were adopted from the Safe Drinking Water Act (SDWA) Primary Drinking Water Standards. The copper GWCTL was adopted from the SDWA secondary drinking water standard (due to aesthetic impact on drinking water). It is a common practice to compare the results of a batch leaching test such as the SPLP directly to groundwater standards to determine whether a contaminated soil or land-applied waste will present a risk of groundwater contamination. When this comparison is made, arsenic presented the largest risk to groundwater.

Table IV.7 presents the number of samples that exceeded the arsenic and chromium GWCTLs by sample category. No samples exceeded the copper GWCTL. The arsenic GWCTL was exceeded in the majority of the 1997 C&D debris wood samples (16 out of 18) and the 1999 C&D debris sample. The average arsenic concentration in all 22 C&D debris wood samples was 0.146 mg/l which is 3 times greater than GWCTL. Figure IV.16 presents a histogram of all of the leachate arsenic concentration data for the C&D debris wood samples. The histogram includes all of the individual SPLP leachate results, and not the averages presented in table IV 5. Arsenic was not detected in any of leachates from the pine bark or cypress mulch samples. Again, these samples were analyzed to assess whether arsenic would naturally leach from commonly used mulch products. Arsenic was detected above the GWCTL in the one sample of yard waste collected. This sample was collected to represent a control for natural vegetation. It is possible that CCA-treated wood could be mixed with yard waste. The authors have observed CCA-treated wood (e.g. fences) in piles of yard waste waiting to be mulched. It is possible for CCA-treated wood to be present in piles of yard waste under such circumstances.

The commercial colored mulches behaved differently. The sample purchased from a store in South Florida did leach arsenic above the GWCTL, while the one purchased in North Florida showed no detectable arsenic. This indicates that the South Florida sample was derived at least in part from C&D debris wood, while the North Florida one was not. This is not surprising considering the large number of C&D debris recycling facilities in South Florida. The pH results also corroborate this observation. The North Florida colored mulch was in the same range as the pine bark and cypress mulches, while the South Florida mulch was in the range with the C&D debris wood.

The comparison with the GWCTL may or may not reflect a realistic risk to the environment. The actual concentration in the groundwater will depend on factors such as how much mulch is applied, how often, the type of soil underneath the mulch, the depth to the groundwater table, and the degree of dilution in the groundwater. Thus, the actual impact on the groundwater would require additional investigation. It can be said, however, that arsenic does leach from C&D debris wood mulch at concentrations that would prohibit its application if current policy practices for waste materials were applied. It is also likely that the continued application of this type of mulch will result in increased soil arsenic concentrations.

<b>Samples</b>	<b>Number of Samples</b>	<b>Number of Samples Exceeding As GWCTL</b>	<b>Number of Samples Exceeding Cr GWCTL</b>
1997 C&D Debris Samples (Sites A through M, except D2 and D4)	18	16	5
1999 C&D Debris Mulch Sample (Site N)	2	2	0
Yard Waste Facility (Site R, D2, D4)	3	1	1
Commercial Mulch (pine bark, cypress) (Sites S, T, U)	3	0	0
Colored Mulch 1 (Site P)	1	0	0
Colored Mulch 2 (Site Q)	2	2	0

Table IV.7: Samples Exceeding the GWCTL

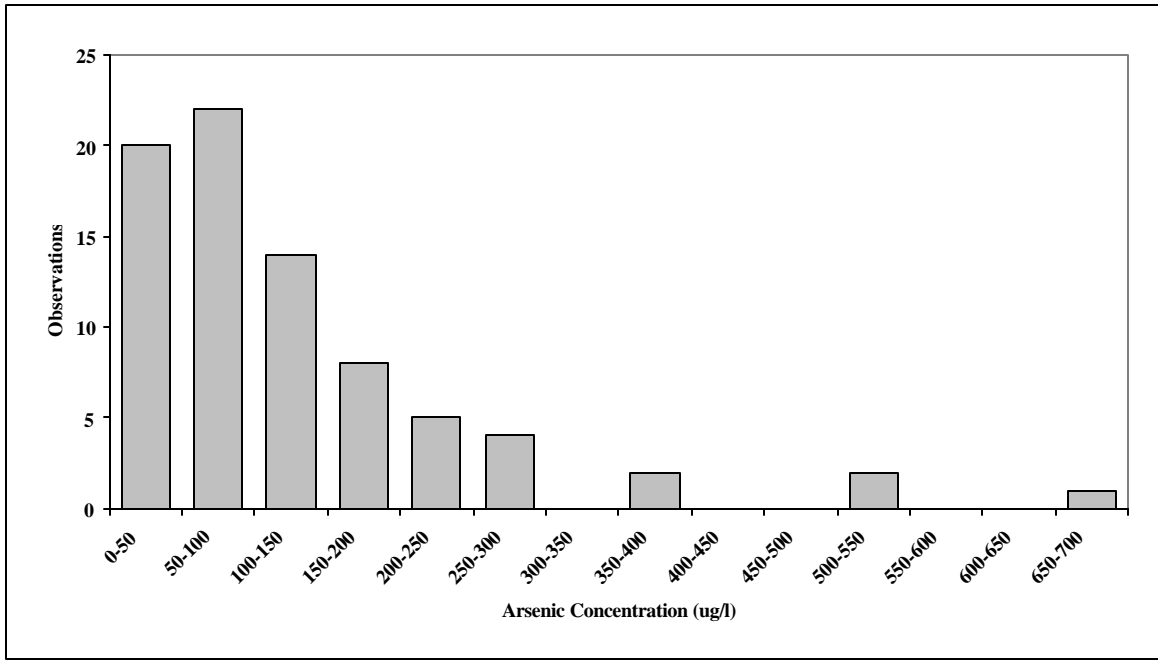


Figure IV.16: Distribution of Arsenic Concentrations in Leachates from Processed C&D Debris

## IV.7 DISCUSSION AND CONCLUSIONS

### *New CCA-Treated Wood*

Analysis of new treated wood indicates that the metals As, Cr, and Cu do leach from the wood. While they may not leach at levels that impact the efficacy of the treated wood products, they do leach at levels that have a potential regulatory and environmental impact. The TCLP results indicated that over half of the CCA-treated wood samples exceeded the toxicity characteristic limit for arsenic (5 mg/l) and would thus be characterized as a hazardous waste if the exemption were not in place. The results of the SPLP indicate that concentrations of all three metals exceeded Florida's GWCTL for each sample. Applying current policy, this indicates that CCA-treated wood should not be disposed in unlined landfills, a recommendation already supported by the wood treatment industry.

The TCLP and SPLP results discussed above were conducted on size-reduced wood, per the requirement of the tests. Additional experiments were performed on the same mass of sample but at larger particle sizes. The results indicated that as expected, samples with smaller particle sizes do leach greater concentrations of As, Cr, and Cu. While it is often argued that the TCLP unfairly characterizes wastes as hazardous because of this size reduction, the TCLP was not designed to represent actual waste disposal conditions, but rather to provide a conservative estimate of which wastes should require special management. In terms of the SPLP results, even at the largest particle size, As and Cr still leached greater than the GWCTLs.

### *C&D Debris Wood Mulch*

Samples of mulch from C&D debris recycling facilities and from horticultural mulch were tested using the SPLP to determine if As, Cr, and Cu did indeed leach as predicted by the tests on new treated wood. The results did indicate that C&D debris wood did leach all three metals. The metal representing the biggest limitation to the reuse of wood mulch was arsenic. Arsenic leached at levels greater than the current GWCTL in the majority of the wood mulch samples. If the policies in place for other types of solid wastes that are proposed to be land applied as a disposal option were enforced for C&D debris wood mulch of the type examined here, the mulch would not be allowed to be land applied. This takes into consideration the current As drinking water standard. If the As drinking water standard is lowered as expected, the reuse of this mulch will be even more limited.



**CHAPTER V**

**LITERATURE REVIEWS FOR FUTURE RESEARCH**

## **CHAPTER, V**

### **LITERATURE REVIEWS FOR FUTURE RESEARCH**

This chapter provides a review of the analytical methods available for: quantifying chromium species (section V.1), arsenic species (section V.2), and the chemicals found in alternative-chemical treated wood products (section V.3). The purpose of these reviews is to develop the analytical techniques within the UF/UM laboratories so that research efforts can be expanded in the future.

#### **V.1 ANALYTICAL METHODS FOR CHROMIUM SPECIATION**

Chromium is one of three heavy metals used in the wood preservative CCA. In previous research reports (Solo-Gabriele et al. 1998 & 1999) and in chapter IV of this report, chromium measurements were reported for different environmental media including CCA-treated wood itself, CCA-treated wood ash, and the leachates from these samples. In this earlier work, it is important to note that the chromium concentrations reported were “total” concentrations of chromium (in mg/kg or mg/l), and did not distinguish between the forms of chromium present in the samples. Chromium is unique in that the two primary species encountered in the environment possess very different properties. Hexavalent chromium, Cr(VI), is much more toxic than trivalent chromium, Cr(III). Hexavalent chromium compounds also tend to be much more mobile than most forms of trivalent chromium. These differences suggest that determining which form of chromium is present in an environmental sample (wood, ash, soil, or leachate) is extremely important. Environmental regulatory agencies recognize the difference and often provide mechanisms for managing the two chemical forms differently in terms of assessing hazard or risk. For example, U.S. hazardous waste regulations exempt a solid waste that would otherwise be hazardous for chromium from being hazardous if the chromium is in the trivalent form.

One of the objectives of this phase of the project was to review methods commonly used to measure the concentration of hexavalent chromium in environmental samples. The methods for measuring total chromium concentration are well established and have been used previously by the research team. Chromium III concentrations are most often measured as the difference between total chromium and chromium VI concentrations. This approach will be employed in future research efforts to measure the chromium species in various samples of environmental media that have been impacted by CCA-treated wood (e.g. soil, water). The following sections provide background of pertinent chromium chemistry (section V.1.a), the methods used to measure total chromium (section V.1.b), the methods used for hexavalent chromium analysis (section V.1.c), and a summary of the proposed methods to be used in future research (section V.1.d).

##### **V.1.a Basic Chromium Chemistry**

Chromium is a heavy metal with an atomic weight of 52. Chromium exists in several oxidation (or valence) states, including 0, +2, +3, +4 and +6. The most common forms in the environment and chemical processes are the 0, +3, and +6 forms. At each valence state, chromium may exist in several different mineral forms. Some of the common mineral forms are

listed in Table V.1.

Valence State	Chemical Name(s)	Chemical Formula
Zero Valent (Cr)	Chromium	Cr
Trivalent (Cr <sup>3+</sup> ) (a.k.a. Cr(III))	Chromic Chloride Chromic Oxide Chromic Nitrate	CrCl <sub>3</sub> Cr <sub>2</sub> O <sub>3</sub> Cr(NO <sub>3</sub> ) <sub>3</sub> • 9H <sub>2</sub> O
Hexavalent (Cr <sup>6+</sup> ) (a.k.a. Cr(VI))	Ammonium Chromate Chromium Trioxide Chromyl Chloride Sodium Chromate Sodium Dichromate	(NH <sub>4</sub> ) <sub>2</sub> CrO <sub>4</sub> CrO <sub>3</sub> CrO <sub>2</sub> Cl <sub>2</sub> NaCrO <sub>4</sub> Na <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub> • 2H <sub>2</sub> O

Table V.1: Examples of Chromium Chemicals

The chemical forms of chromium in the environment are dictated by the surrounding conditions such as pH, oxidation-reduction potential, and other chemicals present. The distribution and occurrence of different chromium species under varying environmental conditions is well illustrated through the use of an Eh-pH diagram (see figure V.1 ). The figure presented represents chromium in a water system. The addition of other chemical species (e.g. iron, sulfide) will change the exact placement of the lines within the graph and may include the addition of more chemical compounds. The hexavalent species of chromium, located in Figure V.1, are HCrO<sub>4</sub><sup>-</sup> and CrO<sub>4</sub><sup>2-</sup>, while the trivalent species are CrOH<sup>2+</sup>, Cr<sub>2</sub>O<sub>3</sub>, and CrO<sub>2</sub><sup>-</sup>. From this figure, general observations regarding the conditions where trivalent and hexavalent chromium occur can be made. Hexavalent chromium occurs under highly oxidized conditions and is more prevalent at high pH values. Trivalent chromium occurs under moderately oxidizing and reducing conditions. At low pH values trivalent chromium is the predominant form.

In the natural environment chromium exists predominantly in the trivalent form. Hexavalent chromium tends to be reduced to trivalent chromium by organic matter, divalent iron, and sulfides. This feature plays a large role when sampling and analyzing environmental samples for Cr(VI). Trivalent chromium rarely becomes oxidized to hexavalent chromium in the natural environment. One exception to this has been discovered, however, as manganese oxides in soil have been shown to oxidize Cr(III) to Cr(VI) (Eary and Ral 1987). Hexavalent chromium is present in many chemical products (e.g. CCA-treating solutions) and when these chemicals are spilled or disposed of in the environment, Cr(VI) may remain in the environment for an extended period of time. Hexavalent chromium may also be produced as a result of the manner in which a material or waste is handled. Examples include 1) oxidation of Cr(III) in CCA-treated wood to Cr(VI) as a result of chemical oxidants (e.g. deck cleaners), 2) formation of Cr(VI) during combustion of wastes containing chromium; and 3) formation of Cr(VI) during the cleaning of industrial boilers.

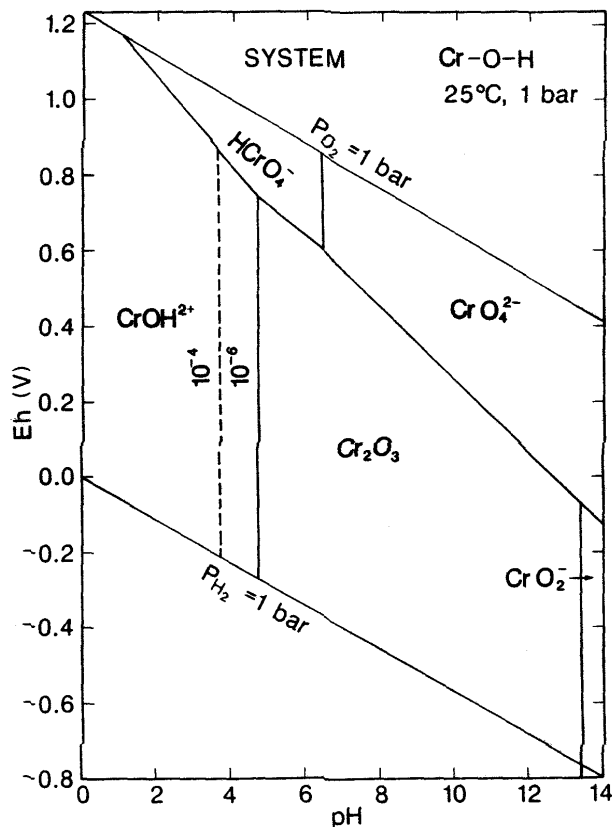


Figure V.1: Eh-pH diagram for part of the system Cr-O-H (Brookins 1988)

### V.1.b Measurement of Total Chromium

The measurement of total chromium is conducted in a manner similar to most heavy metals, using atomic absorption spectroscopy (AAS) or inductively coupled plasma atomic emission spectroscopy (ICP-AES). Environmental samples are first extracted or digested to free chromium bound to organic and inorganic matter. The very act of the digestion procedure (performed under extremely acidic conditions) may cause the chemical species to change from that present in the original environmental sample. AAS and ICP procedures involve the atomization of the metals in the liquid sample or digestate using an energy source (e.g. flame, plasma). In this process all chemical species are converted to their atomic form. AAS or ICP analysis of chromium thus provides the total concentration of all forms of chromium (trivalent, hexavalent, and others) present in the sample.

### V.1.c Measure of Hexavalent Chromium

#### *Overview*

The marked difference in toxicity between the two predominant forms of chromium has led to the development of analytical methodologies for the measurement of hexavalent chromium. Many different methods can be found in the scientific literature and several of the methods that have been widely accepted by the scientific and regulatory community have been

standardized. The U.S. EPA's *Test Methods for the Analysis of Solid Waste (SW-846)* published in 1996 list several methods for the analysis of hexavalent chromium in environmental samples. These methods include a procedure for the extraction of the hexavalent chromium from a waste or soil (Method 3060A), and five methods for analytical detection (Methods 7195, 7196A, 7197, 7198, 7199). The SW-846 methods are summarized in table V.2.

<b>SW-846 Method</b>	<b>Method Title</b>
<b>Method 3060A:</b>	Alkaline Digestion for Hexavalent Chromium
<b>Method 7195:</b>	Chromium, Hexavalent (Coprecipitation)
<b>Method 7196A:</b>	Chromium, Hexavalent (Colorimetric)
<b>Method 7197:</b>	Chromium, Hexavalent (Chelation/Extraction)
<b>Method 7198:</b>	Chromium, Hexavalent (Differential Pulse Polarography)
<b>Method 7199:</b>	Determination of Hexavalent Chromium in Drinking Water, Groundwater and Industrial Wastewater Effluents by Ion Chromatography

Table V.2: EPA SW-846 Methods for Hexavalent Chromium Digestion & Analysis

Two of the methods (7195 and 7197) involve the extraction or separation of hexavalent chromium from trivalent chromium followed by analysis of the hexavalent chromium fraction on an atomic absorption spectrophotometer. Method 7196A involves adding a chemical that causes a color change when hexavalent chromium is present. Methods 7198 and 7199 are more advanced techniques for the specific detection and measurement of hexavalent chromium. It should be noted that all the methods suggest that samples be analyzed as soon as possible after collection because of the tendency of hexavalent chromium to become reduced to trivalent chromium. Both the extraction methods and the analytical methods are reviewed in more detail.

#### *Alkaline Digestion (Method 3060A)*

The extraction of metals using an acidic digestion procedure is a common step for the analysis of most heavy metals prior to analysis by AAS or ICP. In the case of hexavalent chromium, the acid digestion would tend to reduce all of the Cr(VI) to Cr(III). Methods have thus been developed that extract Cr(VI) from soil or waste in a manner that does not cause reduction to Cr(III). It is also important that these methods do not oxidize Cr(III) to Cr(VI).

A comparison of five such methods was conducted and reported by James et al., 1995. The five solutions included distilled water (pH 5.7), phosphate buffer (5mM K<sub>2</sub>HPO<sub>4</sub>/5mM KH<sub>2</sub>PO<sub>4</sub>, pH 7.0), carbonate hydroxide extractant (0.28M Na<sub>2</sub>CO<sub>3</sub>/0.5M NaOH; pH 11.8) with and without heat, and hydroxide solution (0.1 M NaOH; pH 13) with sonication. The most effective extractant of Cr(VI) was found to be the heated carbonate-hydroxide solution which is

the basis for SW-846 Method 3060A.

Method 3060A is an alkaline digestion procedure for extracting Cr(VI) from soluble, adsorbed, and precipitated forms of chromium compounds in soils, sludges, sediments, and similar waste materials. This method uses an alkaline digestion to solubilize both water-insoluble and water soluble Cr(VI). The digestion is performed by using 0.28M Na<sub>2</sub>CO<sub>3</sub>/0.5M NaOH solution and heating at 90-95 °C for 60 minutes to dissolve the Cr(VI) and stabilize it against reduction to Cr(III). Minimal reduction of Cr(VI) or oxidation of native Cr(III) occurs under the alkaline conditions of the extraction. The pH of digestion may be adjusted to 7.5 depending upon the method used for quantification of Cr(VI) in the digestate.

#### *Coprecipitation (Method 7195)*

Method 7195 is a method used to determine the concentration of dissolved Cr(VI) in toxicity characteristic leaching procedure (TCLP) extracts and ground waters. This method is based on the separation of Cr(VI) from solution by coprecipitation of lead chromate with lead sulfate in an acetic acid solution. After separation by using a centrifuge, the supernatant (containing Cr(III)) is drawn off and the precipitate is washed to remove occluded Cr(III). The Cr(VI) in the precipitate is then reduced and resolubilized in nitric acid and quantified as Cr(III) by either flame or furnace atomic absorption spectroscopy or ICP (USEPA, 1996).

#### *Colorimetric Diphenylcarbazide Method (Method 7196A)*

Method 7196A is used to determine the concentration of dissolved Cr(VI) in TCLP extracts and groundwaters. In the absence of interference from substances such as molybdenum, vanadium, and mercury, this method is able to determine dissolved Cr(VI) colorimetrically by its reaction with diphenylcarbazide. The addition of an excess of diphenylcarbazide yields a red-violet product, and its absorbance is measured photometrically at 540 nm. The detection limits for this method range from 0.5 to 50 mg of Cr(VI)/liter (USEPA, 1996). This method is also described in *Standard Methods for the Examination of Water and Wastewater* (APHA 1995). The colorimetric method is frequently reported in the literature (Rudel and Terytze 1999; Kozuh et al. 2000).

#### *Chelation/Extraction (Method 7197)*

Method 7197 is used to determine the concentration of dissolved Cr(VI) in TCLP extracts, alkaline digestion extracts, and ground water samples. This method is based on the chelation of Cr(VI) with ammonium pyrrolidine dithiocarbamate (APDC) and the extraction of Cr(VI) with methyl isobutyl ketone (MIBK). The extract is analyzed by AAS or ICP (USEPA, 1996).

#### *Differential Pulse Polarography (Method 7198)*

Method 7198 uses differential pulse polarography. In this method, the peak current produced from the reduction of Cr(VI) to Cr(III) is measured using a dropping mercury electrode. This procedure requires that the method of standard additions be used to quantify the Cr(VI) concentration in the samples. The presence of copper ions causes interference and requires method modification.

### *Ion Chromatography (Method 7199)*

Method 7199 determines Cr(VI) in drinking water, groundwater, and industrial wastewater effluents using ion chromatography. The method is also applied to alkaline digestates and leachates. An aqueous sample is filtered through a 0.45 µm filter and the filtrate is adjusted to a pH between 9 and 9.5 with a buffer solution. A 50 to 250 µl aliquot is introduced into an ion chromatograph. The hexavalent chromium is separated by the ion chromatographic column and the Cr(VI) is read as a peak using a Ultraviolet/Visible detector. The peak area is compared to a series of peak areas from standard solutions used to form a calibration curve, and the concentration of Cr(VI) in the sample is calculated. The detection system consists of post-column derivatization of the Cr (VI) with diphenylcarbazide followed by detection of the colored complex at 530 nm. Samples containing high levels of organics or sulfides cause rapid reduction of soluble Cr(VI) to Cr(III). A guard column removes organics from the sample before the Cr(VI) as  $\text{CrO}_4^{2-}$  is separated on an anion exchange separator column. Samples containing high levels of anionic species such as sulfate and chloride may cause column overload.

#### **V.1.d Summary and Proposed Method**

Different extraction methods of hexavalent chromium in solid samples have been discussed. Method 3060A using heated carbonate-hydroxide solution is known as the most effective extraction method. Five analytical methods for hexavalent chromium were examined. The method proposed for use in future studies is Method 3060A for extraction of hexavalent chromium from soils and wastes with subsequent analysis using ion chromatography (Method 7199). The colorimetric method will be used as a backup analytical technique (Method 7196A). These methods represent the best available technology for the analysis of hexavalent chromium in environmental media.

## V.2 ANALYTICAL METHODS FOR ARSENIC SPECIATION

Arsenic represents roughly 22 % of the CCA chemical (type C) by weight. Thus for wood treated at 0.25 pcf there is approximately 25 grams of arsenic ( $0.25 * 0.22 * 1000/2.204$ ) per cubic foot of treated wood product resulting in a net arsenic concentration in the wood of 1,900 mg/kg. For wood treated at 2.50 pcf, the concentration of arsenic increases by a factor of 10 to 250 grams per cubic foot or 19,000 mg/kg. Given these high concentrations in the wood and the evidence of leachability observed in the previous chapters, there is reason to suspect that the disposal of CCA-treated wood waste into MSW and C&D landfills may result in elevated concentration of arsenic in leachate from these landfills. This phenomenon has been observed in simulated landfills where CCA-treated wood was known to be present (Townsend et al. 2000). The environmental impact associated with arsenic, however, depends upon its chemical form or species, given that some forms are much more toxic than others. Therefore, to accurately assess the toxicity of an arsenic bearing waste sample, the arsenic species of the samples must be measured.

The objective of this section of the project was to review the literature concerning analytical methods available to measure arsenic species. The intent of this work was to identify suitable analytical methods to measure arsenic species in leachates from CCA-treated wood. This section of the report: summarizes basic arsenic chemistry (which includes a discussion of arsenic toxicity) (section V.2.a), describes the analytical methods available (section V.2.b), and provides a summary of the methods that will be employed in subsequent research (section V.2.c).

### V.2.a Basic Arsenic Chemistry

The major forms of arsenic in natural waters are inorganic, arsenite, As(III) and arsenate, As(V), which can be biomethylated by bacteria, fungi, algae, invertebrates and man to yield the organic methylated (monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA)) forms. Other organic forms include, arsenobetaine (AsB) and its reduced form, arsenocholine (AsC) (both found in marine invertebrates, fish and human urine) and trimethylarsine oxide (TMAO) also found in marine samples (table V.3).

In its natural state, arsenic is usually associated with sulfide ores, with frequent occurrence in the pentavalent state, arsenate (As(V)), and in the trivalent state, arsenite (As(III)), in soils. In environmental systems, the arsenic species of significance include arsenous acids or arsenites ( $H_3AsO_3$ ,  $H_2AsO_3^-$ ,  $HAsO_3^{2-}$ ), arsenic acids or arsenates ( $H_3AsO_4$ ,  $H_2AsO_4^-$ ,  $HAsO_4^{2-}$ ), monomethylarsonic acid ( $H_2AsO_3CH_3$ ), dimethylarsinic acid ( $(CH_3)_2AsO_2H$ ), and arsine ( $AsH_3$ ). Acute toxicity of arsenic decreases in the following order: arsines > inorganic arsenite (As(III)) > arsenoxides (organic, trivalent) > inorganic arsenate (As(V)) > monomethylarsonic acid (MMAA) > dimethylarsinic acid (DMAA) > arsenobetaine (AsB) and arsenocholine (AsC), suggesting that the acute toxicity of arsenic compounds diminishes with the progress of methylation. Arsenic as As(III) is much more toxic than the oxidized form of arsenic, As(V), and the organic forms, AsB and AsC are considered virtually non-toxic. Methylated arsenic compounds are far less acutely toxic than the inorganic compounds, with the trimethylated compounds being the least toxic (Yamauchi and Fowler 1994). Therefore, the total concentration of arsenic present in the sample is not an accurate indicator of its toxicity.



Compound	Formula
Arsenous acid As(III) (a.k.a. arsenite)	$\begin{array}{c} \text{OH-As-OH} \\   \\ \text{OH} \end{array}$
Arsenic acid As(V) (a.k.a. arsenate)	$\begin{array}{c} \text{OH} \\   \\ \text{OH-As=O} \\   \\ \text{OH} \end{array}$
Monomethylarsonic acid MMAA	$\begin{array}{c} \text{OH} \\   \\ \text{CH}_3\text{-As=O} \\   \\ \text{OH} \end{array}$
Dimethylarsonic acid DMAA	$\begin{array}{c} \text{CH}_3 \\   \\ \text{O=As-OH} \\   \\ \text{CH}_3 \end{array}$
Arsenobetaine AsB	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{-As}^+\text{-CH}_2\text{-C=O} \\   \quad \quad   \\ \text{CH}_3 \quad \quad \text{OH} \end{array}$
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	$\begin{array}{c} \text{CH}_3 \\   \\ \text{CH}_3\text{-As-O} \\   \\ \text{CH}_3 \end{array}$
Arsine AsH <sub>3</sub>	$\begin{array}{c} \text{H} \\   \\ \text{H-As} \\   \\ \text{H} \end{array}$

Table V.3: Formulas of the principal arsenic species  
(modified from, Benramdane et al. 1999)

Humans have been found to be more sensitive to arsenic than most laboratory animals. For example, a dose of 0.05 - 0.1 mg/kg/day of inorganic arsenic has been shown to be toxic to humans, whereas, a dose of 0.72 - 2.8 mg/kg/day of As(III) or As(V) given to monkeys, dogs, and rats was not. Experimentation on rats has shown that the lethal oral dose, LD<sub>50</sub>, for arsenic ranges from 15 to 293 mg/kg, whereas for other invertebrates it ranges from 10 to 150 mg/kg. As little as 0.25 ppm inorganic arsenic have been reported to cause symptoms of poisoning in humans (Naqvi et al. 1994). Table V.4 shows results from studies conducted to estimate the toxicity of arsenic compounds in mice and rats.

Arsenic Compound	LD <sub>50</sub> (mg/kg)	Animal/Mode of Administration
Arsenite: arsenic trioxide <sup>1</sup>	34.5	mouse / oral
Arsenite: sodium arsenite <sup>1</sup>	4.5	rat / intraperitoneal
Arsenate: sodium arsenate <sup>1</sup>	14 - 18	rat / intraperitoneal
MMAA <sup>1</sup>	1,800	mouse / oral
DMAA <sup>1</sup>	1,200	mouse / oral
Arsenobetaine <sup>1</sup>	10,000	mouse / oral
Arsenocholine <sup>2</sup>	6,000	mouse / oral
Trimethylarsine oxide <sup>1</sup>	10,600	mouse / oral
Trimethylarsine <sup>1</sup>	8,000	mouse / subcutaneous
Trisdimethylaminoarsine <sup>1</sup>	15	mouse / subcutaneous
Tetramethylarsonium iodide <sup>2</sup>	890	mouse / oral

<sup>1</sup>Yamauchi and Fowler 1994

<sup>2</sup>Shiomi 1994

Table V.4: LD<sub>50</sub> for mice/rat of arsenic compounds

The E<sub>H</sub> - pH diagram for arsenic in the environment (figure V.2) shows that under oxidized conditions the arsenate species predominate with H<sub>3</sub>AsO<sub>4</sub> observed at extremely low pH (<2); where from a pH of 2 to 11, it is replaced by H<sub>2</sub>AsO<sub>4</sub><sup>-</sup>, and HAsO<sub>4</sub><sup>-2</sup>. Under mildly reduced conditions the arsenite species predominate where at low pH H<sub>3</sub>AsO<sub>3</sub> appears but as the pH increases to 12, it is replaced by H<sub>2</sub>AsO<sub>3</sub><sup>-</sup>, which is then replaced by HAsO<sub>3</sub><sup>-2</sup> above a pH of 12. In the presence of sulfide and at low pH, HAsS<sub>2</sub> can form and under extreme reducing conditions arsine and its derivatives, as well as metallic arsenic can occur.

It is also important to note that arsenic solubility increases with diminishing E<sub>H</sub> and increasing pH with As(III) species being more soluble and more mobile than As(V) species (Masscheleyn et al. 1991). Sorption is the principal means by which arsenic is removed from solution. Arsenic is strongly sorbed onto soils and sediments and the factors that affect sorption include redox conditions, pH, competing anions, salinity, clay content, and hydrous oxide content. In anaerobic and aerobic sediments, As(V) is more strongly sorbed than MMAA and DMAA and it can be remobilized if conditions become sufficiently reduced so that As(III) is formed. Studies have also shown that under alkaline conditions, arsenic appears to be more mobile. As(III) sorption on a variety of materials decreases above a pH of 9, while for As(V), the decrease occurs when the pH is above 7. The presence of other ions also affect arsenic sorption because they compete for sorption sites or complex with arsenic; and sorption unto alumina, bauxite and carbon decreases with increased salinity (Bodek et al. 1988).

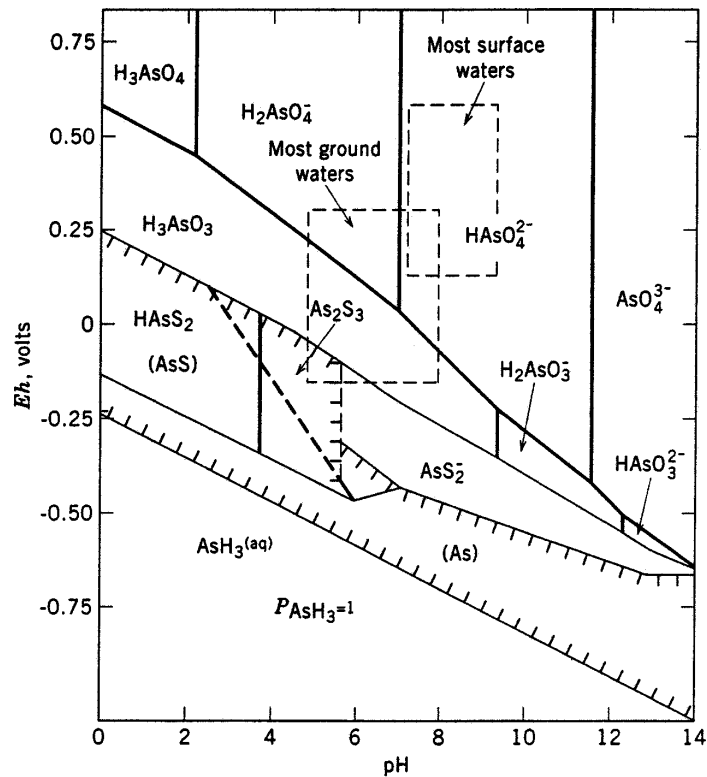


Figure V.2:  $E_H$ -pH diagram for arsenic at 25 °C and 1 atm with total arsenic  $10^{-5}$  M and total sulfur  $10^{-3}$  M. Solid species are enclosed in parentheses in cross-hatched area, which indicates solubility less than  $10^{-5.3}$  M (Schnoor 1996)

## V.2.b Laboratory Methods of Analysis

Analytical methods for arsenic analysis are generally based upon “hyphenated techniques” which are techniques that combine different instruments for pre-processing, separation of different species, and detection. These methods are categorized according to the separation method that is used.

### HPLC

High performance liquid chromatography (HPLC) is useful for separating nonvolatile species, making it a good method for the analysis of arsenic compounds. The most common type of HPLC method used for separating the arsenic species is ion exchange (IC). The primary component of an HPLC is its analytical column which serves to separate the arsenic species based upon a chemical species’ affinity for the column packing material. Once separated the arsenic in the sample can then be detected using one of several different highly sensitive detection methods. Detectors include inductively coupled plasma-atomic emission spectrometry (ICP-AES), inductively coupled plasma-mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS). ICP-MS is considered the most sensitive. By coupling HPLC with hydride generation (HG) matrix interference is reduced and the sample can be more efficiently introduced into the detector to help further separate

species and enhance sensitivity. HG is a technique that converts the aqueous arsenic species to a gas. AFS detectors, for example, require that the sample be introduced as a gas and therefore HG is required if such a detector is to be used. Table V.5 summarizes the detection limits using HPLC directly coupled with various detectors.

Although, HPLC is the most common and versatile method for separation of arsenic species, it is restricted in its separation capabilities. HPLC requires a large quantity of the mobile phase which in turn contains large quantities of organic solvent which may 1) cause carbon deposits on the sampling cone, 2) cause plasma instability, and 3) quench the plasma. This results in a decrease in the signal and an increase in noise levels. Also, at times when sample volumes are limited, HPLC cannot be used because it requires large sample volumes. To overcome these problems capillary zone electrophoresis (CZE) has been explored as an alternative to HPLC for the identification and quantification of metal species in very small sample volumes and has demonstrated separation within a short period of time (10 minutes) with extremely high sensitivity (Tian et al. 1999).

### *Hydride Generation*

Hydride generation (HG) is a common separation technique used in the analysis of different arsenic species. Chemical hydride generation (CHG) is the conventional method which involves the use of chemicals (usually sodium borohydride,  $\text{NaBH}_4$  and a strong acid) to control the pH and generate the hydrides from the hydride-forming arsenic species (As(III), As(V), MMAA and DMAA). It is important to note that HG methods cannot quantify non-hydride forming species such as arsenobetaine and arsenocholine (which are significantly less toxic). Electrochemical hydride generation (EHG) can also be used to generate arsine gas. Though it has been around since 1969, it is not used much because of restrictions. EHG does not obtain the low detection limits and eliminate matrix interference as well as CHG.

As previously mentioned, HPLC/IC can be coupled successfully with chemical hydride generation (CHG) to further enhance sensitivity for arsenic species and reduce interferences. However, HG need not be combined with HPLC and can be directly coupled with the AAS, ICP-AES, and ICP-MS. If an HPLC is not used, the method involves reducing the arsenic species, (As(III), As(V), MMAA and DMAA) to their corresponding volatile hydrides or arsines using HG methods. Speciation is accomplished by adjusting the pH which controls the ability of different species to convert from their dissolved form to their gaseous or hydride form. Usually As(III) is converted first at a pH between 6 and 8 and As(V), MMAA, and DMAA are converted to their corresponding arsine gases at low pH (approximately pH = 1). Separation of As(V), MMAA, and DMAA is accomplished by capturing the arsines on chromatographic packing in a cold trap. The arsines are then thermally desorbed allowing for each of the arsine species to be separated in time. These arsines are then introduced into a detector, such as a gas or liquid chromatograph or into a spectroscopic detection system such as an AAS, ICP-AES, or ICP-MS (Rauret and Padro, 1991) for detection and quantification. Precision and recovery are strongly dependent on experimental conditions and detection limits are generally very low (0.05 to 2 ng As) (Masschelyn et al. 1991; Andreae 1977).

Technique	Sample	Species	Reference
<b>HPLC Separation Methods, without HG</b>			
HPLC/IC-ICP-AES	Seaweed	30 µg/l As(III) 30 µg/l As(V) 19 µg/l MMAA 41 µg/l DMAA	Morita et al. 1981
HPLC/IC-USN-ICP-AES		1300 µg/l As(III) 2300 µg/l As(V)	Furuta & Shinofuji. 1998
HPLC/IC –ICP-MS	urine, earthworm extract and groundwater	0.2 µg/l As(III) 0.6 µg/l As(V) 0.06 µg/l MMAA 0.12 µg/l DMAA 0.09 µg/l AsB 0.04 µg/l AsC	Zheng et al. 1998
HPLC/IC –ICP-MS	Soil	0.033 µg/l As(III) 0.217 µg/l As(V) 0.064 µg/l MMAA 0.035 µg/l DMAA 0.046 µg/l AsB 0.069 µg/l AsC	Pongratz 1998
HPLC/IC –ICP-MS	fly ash, poultry litter and sewage sludge	0.028 µg/l As(III) 0.161 µg/l As(V) 0.051 µg/l MMAA 0.031 µg/l DMAA	Jackson & Miller 1999
HPLC/IP-ICP-MS	-	6.7 - 16.7 µg/l As 5 - 7.5 µg/l As	Shibata & Morita 1989
HPLC/IC-ICP-MS	dogfish muscle	0.25 - 1.5 µg/l As	Beauchemin et al 1989
HPLC/IC-AAS	Groundwater	0.6 µg/l As	Rassler et al. 1998
HPLC-AFS		140 µg/l As(III) 200 µg/l As(V) 80 µg/l DMAA 80 µg/l MMAA	Woller et al. 1995
<b>HPLC Separation Methods, with HG</b>			
HPLC/IC-HG-ICP-AES		70 µg/l As(III) 170 µg/l As(V)	Furuta & Shinofuji. 1998
HPLC/IC-HG-ICP-AES		17 µg/l As(III) 640 µg/l As(V) 100 µg/l DMAA	Schlegel et al. 1994
HPLC/IC-HG-ICP-AES	aquatic	3.5 µg/l As(III) 9.2 µg/l As(V) 3.8 µg/l MMAA 21.3 µg/l DMAA	Rauret & Padro 1991
HPLC/IP-HG-ICP-AES	well water	50 µg/l As(III) 50 µg/l As(V) 105 µg/l DMAA	Bushee & Krull 1984
HPLC/IC-HG-AFS	urine	0.17 µg/l As(III) 0.38 µg/l As(V) 0.30 µg/l MMAA 0.45 µg/l DMAA 0.38 µg/l AsB	Gomez-Ariza et al. 1998
HPLC/IC-HG-AAS	sediment coal fly ash	0.8 µg/l As(III) 0.8 µg/l As(V)	Manning & Martens 1997
HPLC/IC-HG-ICP-MS	sediment	0.46 µg/l As(III)	Story et al. 1992

Table V.5: Summary of detection limits using direct HPLC

### *Capillary Zone Electrophoresis (CZE)*

Capillary zone electrophoresis (CZE) is another separation process that has the advantage over HPLC methods in that it can quantify arsenic species in very small samples (1 to 30 nl) and can overcome some interference problems. CZE is based on the different electrophoresis mobilities of different arsenic species. For successful species separation, CZE requires that species not be altered by the CZE conditions, such as, pH buffer, salt concentrations, complexing agents or high voltage. CZE has been successfully interfaced with HG and ICP-MS for arsenic speciation (Magnuson et al. 1997). The detection limits in distilled water for CZE-HG-ICP-MS were 25, 6, 9, and 58 ppt for As(III), As(V), MMAA, and DMAA, respectively.

### *SDDC*

The silver diethyldithiocarbamate (SDDC) spectrophotometric procedure (APHA 1995) is a relatively inexpensive analytical method capable of measuring As(III) and As(V) species. DMAA and MMAA can not be measured using this method. The SDDC method is a chemical hydride generation method in which As(III) is reduced by a solution of aqueous NaHB<sub>4</sub> to arsine, AsH<sub>3</sub>. The analysis of As(III) and As(V) is a two step process. AsH<sub>3</sub> is generated only from As(III). Thus the first step in the process is to convert the As(III) present in the sample by the addition of NaHB<sub>4</sub>. The solution is buffered at a pH of 6 to assure that the As(III) in the solution is not converted to As(V) during the formation of arsine. Once the arsine is formed it is transported through a scrubber, containing glass wool impregnated with lead acetate, into an absorber tube containing a yellow solution of SDDC and morpholine dissolved in chloroform. The yellow silver solution turns red in the presence of arsine and the intensity of the color is proportional to the amount of As(III) originally present in the sample. The intensity of this color is measured at 520 nm with a bench-top spectrophotometer. The second step of the analytical procedure is the addition of HCl to the same sample, which reduces As(V) to As(III) over a pH range of 1 to 4, and further addition of NaBH<sub>4</sub> is used to generate arsine from the As(III) that is formed. The minimum detection limit using this method is 1 µg arsenic which for a typical sample size of 80 ml would result in a detection limit of 12.5 µg/l.

### **V.2.c Summary and Proposed Method**

Arsenic speciation is best accomplished by hyphenated techniques, which are separation processes coupled with detection methods to provide concentrations of individual arsenic species. High performance liquid chromatography (HPLC) has become the most powerful analytical tool for separation of elemental species because of its capability to overcome interference of unwanted ions present within the complex sample matrix. The detectors usually coupled with HPLC include ICP-AES, ICP-MS, AAS, and AFS to yield low detection limits in the microgram, nanogram and even the picogram per liter levels.

The sensitivity of the method may be further enhanced if the sample is pre-concentrated and an on-line hydride generation (HG) step added. HG is limited to the hydride forming arsenic species, As(III), As(V), DMAA and MMAA, and does not include AsB, AsC, and TMAO determination without further sample treatment. CZE is a relatively recent separation technique that can be used when HPLC is restricted. CZE separates species based on their electrophoretic mobilities and can be effectively interfaced with other separation and detection methods,

including HG, ICP-MS and UV. HG can also be used without HPLC to effect specie separation. The conventional method for hydride generation is chemical, which utilizes the reducing agent, sodium borohydride ( $\text{NaBH}_4$ ) to convert As(III) to arsine gas. Speciation is controlled by adjusting the pH of the sample and noting the timing of the release of corresponding arsine gases captured on a chromatographic column.

Subsequent analytical work will focus on the SDDC method given that it is less instrument intensive and supplies are already available for running this method within the environmental engineering laboratories at the University of Miami. Efforts will also focus on utilizing resources available within other Departments and nearby Universities. The Marine and Atmospheric Chemistry Division of the University of Miami's Marine School has an ICP/MS available for use. The Chemistry Department at Florida International University has HPLC-ICP/MS and HPLC-HG-AFS systems tailored towards arsenic speciation analysis.

### V.3 LABORATORY METHODS FOR THE ANALYSES OF ALTERNATIVE CHEMICALS

One of the objectives of the supplemental year three study was to compile analytical methods for measuring the chemical constituents found in the alternative wood treatment preservatives. Promising alternative wood preservatives to CCA, which were identified during the “year 3” study, included copper boron azole (CBA), copper citrate (CC), copper dimethyldithiocarbamate (CDDC), and alkaline copper quat (ACQ). In addition to the analysis of copper, a preservative constituent also found in CCA, all of the alternatives contain organic co-biocides, each with its own method of detection and measurement. Analytical methods for determining the concentrations of these organic chemicals (i.e. the azole, citrate, dimethyldithiocarbamate, and quat) are needed to conduct leaching studies on the alternative preservatives. This section of the report summarizes analytical methods for the organic co-biocides, as well as any inorganic analysis that may be required.

Analytical methods have been compiled for the following wood preservatives: ACQ, CBA, CDDC, and CC. The analysis methods described have been assembled from the American Wood-Preservers’ Association (AWPA) *Book of Standards*, 1999, and from the United States Environmental Protection Agency (USEPA) *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods*, SW-846 (1996).

The analytical methods have been separated into two categories: inorganic chemicals (section V.3.b) and organic chemicals (section V.3.c). A summary of methods that will be utilized in future research is provided in section V.3.d. The methods for inorganic chemical analysis include testing for copper and boron, while the organic chemical analysis includes methods for the determination of azole (tebuconazole), dimethyldithiocarbamate (DDC), citrate, and didecyldimethyl ammonium chloride (DDAC) concentrations. DDAC is also known as quat, quaternary ammonium compound, and alkyl ammonium compound. Table V.6 lists the organic and inorganic analytes present in each of the wood preservative chemicals.

For some of the analytes, the analytical methods differ somewhat when testing a liquid (aqueous) versus a solid matrix. Because liquid samples (leachates) will be analyzed as part of upcoming research, the methods for measuring alternative chemicals in liquid samples are provided in greater detail than those analytical methods that also require extracting chemicals from the wood matrix.

Wood Preservative	Inorganic Analytes	Organic Analytes
CCA	Chromium Copper Arsenic	NONE
ACQ	Copper	Didecyldimethyl ammonium chloride (DDAC)
CBA	Copper Boron	Tebuconazole
CDDC	Copper	Dimethyldithiocarbamate (DDC)
CC	Copper	Citrate

Table V.6: Inorganic and Organic Analytes in Various Wood Preservative Chemicals



### V.3.a Analysis of Inorganic Chemicals

The inorganic chemicals found in treated wood can be analyzed using both EPA and AWWA methods. The analytical methods recommended by both agencies are comparable, and utilize standard techniques and instrumentation. The AWWA methods are cross-referenced to the EPA methods in table V.7. The analytical method using x-ray fluorescence (XRF) spectroscopy does not have a direct equivalent method in USEPA SW-846, and is only listed as a standard method within AWWA *Standards*. The methods in table V.7 (with the exception of XRF) are conducted on aqueous solutions. Thus the analysis of inorganic chemicals in solid matrices requires a method to extract the chemicals into solution.

Analytical Method	US EPA SW-846 Method	AWWA Standard
Inductively Coupled Plasma Emission Spectroscopy (ICP)	6010B	A21-93
Atomic Absorption, Direct Aspiration (Flame-AAS)	7210	A11-93
Atomic Absorption, Furnace Technique (GF-AAS)	7211	A11-93
X-Ray Fluorescence Spectroscopy (XRF)		A9-99

Table V.7: EPA and AWWA Metals Analysis Methods

Although the analytical methods for the ICP, Flame-AAS and GF-AAS are the same within EPA and AWWA references, the methods differ for extracting the chemicals into solution. The EPA methods for extracting metals from a solid matrix into an aqueous matrix (digestion) are typically performed on matrices such as soil and waste, while the AWWA methods are designed for wood. USEPA SW-846 uses digestion methods based on the instrument used for analysis. USEPA SW-846 sample preparation methods include Method 3010A, which is an acid digestion of aqueous samples and extracts for total metals for analysis by Flame-AAS or ICP Spectroscopy, Method 3020A, which is an acid digestion of aqueous samples and extracts for total metals analysis by GF-AAS, and Method 3050B which is an acid digestion of solid (sediment, sludge and soil) samples for total metals analysis by GF-AAS, Flame-AAS or ICP. AWWA does not indicate which of the extraction methods listed in the *AWWA Book of Standards* is the most appropriate for different situations nor does it indicate why there are different methods listed.

### V.3.b Organic Chemical Analysis

While the methods for the analysis of inorganic chemicals in CCA and the alternative chemicals are similar, the analytical methods for the organic chemicals used as co-biocides all differ dramatically. Some chemicals require advanced instrumentation (GC, HPLC), while others require only simple spectrophotometry or chemical titrations. Table V.8 summarizes the methods used for the alternative chemicals. The methods listed are from AWWA *Standards 1999*. USEPA SW-846 does not have standard methods to analyze for these chemicals. Where applicable, method numbers are provided for both the analysis of the chemical from the wood (requiring some form of extraction) and for analysis of the chemical when found in solution. In some of the methods, dilution of the treating solutions may be needed and some of the analyses may require that the leachates be concentrated prior to analysis.

The following sections summarize the methods available for the analysis of the organic chemicals found in the alternative preservatives.

Chemical	Analytical Method	AWPA Standard Solids	AWPA Standard Solutions
CDDC	UV Spectrophometric	A25-94	None
DDAC	HPLC	A16-93	A17-97
Tebuconazole	HPLC, GC	A23-94/ A24-94	A23-94/ A24-94
Citrate	UV Spectrophometric	A2-98 (17)	A2-98 (17)

Table V.8: AWPA Analytical Methods for Organics Analysis

### *CDDC*

The analysis of CDDC utilizes the fact that the chemical absorbs ultra-violet (UV) light at a wavelength of 435 nm. The AWPA Standard A25-94 (Analysis of Copper Dimethyldithiocarbamate (CDDC) Treated Wood by Colorimetry) is specific to the analysis of CDDC in the wood (i.e. to determine the retention value). While a test method is not listed for aqueous samples, such as leachates, the information provided in the method does suggest that CDDC in aqueous samples can be analyzed following a similar methodology.

The standard method for wood extraction consists of preparing a calibration curve using analytical grade CDDC placed into an azeotropic mixture of methanol/chloroform at concentrations ranging from 3.55 to 21.31 µg/l. (Note: An azeotropic mixture is a liquid mixture of two or more substances which behaves like a single substance in that the vapor produced by partial evaporation of the liquid has the same composition as the liquid). The absorbance readings are taken and the curve is prepared by plotting absorbance versus concentration. For wood samples, ground borings are placed into an extraction flask along with 200 ml of the azeotrope, heated to 45 °C and allowed to reflux over a 30-minute period. After cooling, the extract is filtered and the borings rinsed with successive 100 ml washings of the azeotrope. A 3-ml aliquot of the filtrate is diluted with 200 ml of the azeotrope and then read at 435 nm on a spectrophotometer (AWPA 1999).

The adapted methodology for leachates will be to prepare the samples as stated above, with the exception of the use of the methanol/chloroform azeotrope, given that the purpose of the azeotrope is to extract the CDDC from the treated wood. Solutions of known concentrations of CDDC will be prepared using the same aqueous matrix as used in the given test (i.e. DI water, seawater, TCLP fluid, and SPLP fluid). The absorbance of the standard solutions will then be read at 435 nm using the spectrophotometer to create a calibration curve. The concentration of CDDC in leachate samples will be measured accordingly.

### *DDAC*

Four methods are available for DDAC analyses. One method uses an HPLC for analysis; the remaining three methods utilize titration techniques. The HPLC method corresponds to AWPA Standard A16-93 (Standard HPLC Method for Didecylmethyl-ammonium Chloride Determination in Treated Wood). This method consists of performing an HPLC separation using a cation exchange column (a Whatman SCX column, 5 µm particle size, 100 mm x 4.6 mm i.d.). The HPLC system uses a UV/Vis detector set to 262 nm. The mobile phase used is

water/methanol at a 1:5 ratio (v:v), modified with benzyltrimethyl ammonium chloride and acetic acid. The sample preparation consists of weighing 500 mg of wood meal into a screw cap polytetrafluoroethylene (PTFE) lined vial. An extraction solution (20 ml of denatured ethanol, adjusted to a pH of 5 with formic acid) is added to the vial and the sample is sonicated for 3 hours. An aliquot of the sample extract is injected onto the HPLC system using a syringe fitted with a filter. The calibration curve for this method is from 50 to 1000 ppm. This method consists of using a method of indirect detection which results in very low sensitivity and is therefore, the least optimum method for analysis of low level samples.

Of three titration methods available, two are AWWA standards (A18-99 and A17-97), whereas the manufacturers of ACQ developed the third method. AWWA Standard A18-99 (Standard for Determination of Quaternary Ammonium Compounds in Wood by 2-Phase Titration) is a titration method that is not compound specific (i.e. the method does not distinguish between various alkyl ammonium compounds) and therefore, may not be suitable for determination of trace levels of quaternary ammonium compounds in wood (AWWA 1999). Sample preparation begins with 1.5 g of wood meal added to 20 ml of 0.1 N hydrochloric acid (HCl) in a 20 ml screw cap vial. This is followed by placement in an ultrasonic bath. The samples are agitated for three hours. After removal from the bath the samples are then allowed to cool and settle prior to analysis. Before beginning the titration with the cationic surfactant (Hyamine 1622), the samples are treated with an anionic surfactant (sodium lauryl sulfate) and a mixture of dimidium bromide (cationic dye) and erioglaucline (anionic dye). Because quaternary ammonium compounds are cationic surfactants, the anionic dye (erioglaucline), when present in excess of the quaternary compounds, forms a pink chloroform soluble complex. Hyamine 1622 displaces the anionic surfactant/dye complex as well as the anionic surfactant/chloroform complex to form a more stable compound with the anionic dye. When excess Hyamine 1662 is present, a blue chloroform soluble compound is formed which signals complete titration. The titration is conducted on a blank sample as well as for all samples of treated wood. Calculations to determine the concentration of the compound in solution are given by the following equations:

$$\text{Molarity of Hyamine 1662} = \text{Mass of Hyamine 1662(g)} / 44.8.1 \quad \text{equation V.1}$$

$$\% \text{wt DDAC} = (V_0 - V)(\text{MW DDAC}) * (0.5) / \text{sample mass} \quad \text{equation. V.2}$$

where  $V_0$  is the volume of Hyamine 1622 used in the blank titration,  $V$  is the volume of Hyamine 1622 used for the sample titration and MW DDAC is the molecular weight DDAC which equals 362.08.

The second AWWA titration method (A17-97, Standard for Determination of Didecyltrimethylammonium Chloride in ACQ Solutions) uses a single indicator (2',7'-dichlorofluorescein). The endpoint is reached when the solution color changes from purplish pink to yellowish green. The titration is set up by standardizing the 2',7'-dichlorofluorescein with Hyamine 1622. An aliquot of 10 ml of Hyamine 1622 is placed into a 125 ml Erlenmeyer flask. An addition of 25 ml of DI water and seven drops of 2',7'-dichlorofluorescein are then added. The solution is then titrated with sodium tetrphenylboron until a lemon-green color is formed. The analysis begins by placing 2 g of treatment solution and 25 ml of DI water into a 125 ml flask. The pH should be neutralized with 20% phosphoric acid to a pH of approximately

7. Seventeen drops of 2',7'-dichlorofluorescein are then added to the solution. At this point, the solution should be light pink. The solution is then titrated with sodium tetraphenylboron until a lemon-green color is formed and the amount of tetraphenylboron is recorded. The concentration of DDAC in the solution is determined by the following equations.

$$M \text{ Hyamine (Hyamine Concentration)} = \text{Hyamine Mass (g)}/448.1 \quad \text{equation V.3}$$

$$M \text{ STPB (Conc. of Sodium Tetraphenylboron)} = \frac{(M \text{ Hyamine}) \times (\text{ml Hyamine})}{(\text{ml STPB added})} \quad \text{equation V.4}$$

$$\% \text{DDAC in solution} = \frac{(100) \times (\text{ml STPB}) \times (M \text{ STPB}) \times (362)}{(1000 \times (\text{sample mass(g)}))} \quad \text{equation V.5}$$

The non-standardized titration method, which is referred to herein as the methylene blue method, is similar to AWWA method A18-99, but only requires one visual identification of color change. As with method A18-99, a cationic surfactant (Hyamine 1622) and an anionic surfactant (sodium lauryl sulfate) are used to form complexes with the indicators, but in this method, the dye used is methylene blue. The same types of reactions occur with this method, but only one indicator is used. The sodium lauryl sulfate solution is standardized to 0.004M by titrating with a 0.004M Hyamine 1622 solution. The standardized sodium lauryl sulfate solution is then used to titrate the aqueous solution. The titration begins with a blue aqueous layer and a clear chloroform layer. The endpoint of the titration is reached when the chloroform (bottom) layer just begins to turn blue. If the aqueous phase turns white and the chloroform layer turns dark blue, the titration needs to be repeated. Calculations for the concentration of DDAC are as follows:

$$\% \text{DDAC} = \frac{(M_{\text{sodium lauryl sulfate solution}}) \times (\text{ml titrant}) \times (\text{MW DDAC}) \times (100)}{(1000 \times \text{g of sample})} \quad \text{equation V.6}$$

where  $M_{\text{sodium lauryl sulfate solution}}$  is the molarity of the sodium lauryl sulfate and MW DDAC is 362 g/mole.

### *Tebuconazole*

The azole compound used in CBA is tebuconazole. The type of azole for which a method has been developed within the AWWA *Book of Standards* is propiconazole. Tebuconazole is not listed in the standards book, but can be tested using the same methodology as propiconazole. There are two AWWA standards for the analysis of azole compounds: AWWA Standard A23-94 (Analysis of Wood and Solutions for Propiconazole by HPLC) and AWWA Standard A24-94 (Analysis of Wood and Solutions for Propiconazole by Gas Chromatography).

The sample preparation is the same for both the HPLC and GC standards for wood samples: 2.5-g of wood meal is added to 50mL of methanol in a flask, and the mixture is stirred for 2 hours. The sample is then filtered and injected into either the HPLC system or the GC system. The HPLC system uses a water/acetonitrile mobile phase with UV detection at a wavelength of 230 nm, while the GC method uses an OV-17 packed column with a Flame Ionization Detector

(FID), a Thermionic Specific Detector (TSD) or a mass spectrometer.

The sample preparation is different for the HPLC and GC methods when analyzing for azole concentrations in liquids. Sample preparation for the GC method begins with pipetting a known volume of sample into a 25-ml flask and diluting to volume with the solvent dichloromethane. The standard AWP method requires that a reference curve be constructed by preparing and analyzing standards of 108, 114, 120, 126 and 132 mg of azole per 25-ml of dichloromethane.

The HPLC method requires that a known volume of sample weighed to the nearest 0.1 mg be placed in a 10 ml volumetric flask and diluted to 10 ml with tetrahydrofuran (THF). Then, 2 ml of this solution is placed into a 50 ml volumetric flask and diluted to volume with THF. The method states that the final concentration in the solution should be approximately 200 µg/l of azole. Standardization is achieved by preparing and analyzing standard solutions of 150, 200 and 250 µg/ml azole in THF. The standards are then used to construct a reference curve by plotting the mean peak areas of the solutions versus the concentration in µg/ml. Linear regression analysis is then used to determine the correlation coefficient (r), the slope (a) and the intercept (b) of the curve. The azole concentration is then calculated in µg/ml by using the following equation:

$$C_s = (\text{mean peak area in sample solution} - b)/a \quad \text{equation V.7}$$

Then, the weight (W) of the sample (in mg) in the sample solution can be calculated using the following equation:

$$\%w/w = (C_s * 50)/(W * 10) \quad \text{equation V.8}$$

Tebuconazole will be analyzed using GC/MS versus the traditional method of the GC with the FID. The GC/MS method provides two separate pieces of information, thereby allowing for a higher degree of accuracy in isolating the azole.

### *Citrate*

The method available for citrate determinations is AWP standard A2-98(17) (Standard Methods for the Analysis of Waterborne Preservatives and Fire-Retardant Formulations – UV Spectrophotometric Method for Citrate Determination in Wood and Solutions). This method is based upon citrate's ability to absorb light at a wavelength of 420 nm. The method begins by preparing citric acid standards of 0-500 ppm in 0.18 M trichloroacetic acid. One ml of a citrate standard (or sample) is placed into a test tube and 1.3 ml of pyridine followed by 5.7 ml of acetic acid are added and mix thoroughly. The test tubes are then placed into a water bath at 32°C ± 0.5 °C. The color development will be complete after 30 minutes. Once the standards are removed from the water bath, they are read on a spectrophotometer (within 30 minutes after removal from the water bath) at an absorbance of 420 nm. A 0 ppm citric acid standard is used as the baseline. For leachates, dilutions will be prepared as needed to bring the samples into the detection range of the spectrophotometer.

The concentrations of citric acid in leachates and from wood samples can be calculated using the following equation:

$$\% \text{ citrate} = (\text{ppm citrate}) * (9.79 * 10^{-5}) * 100 / \text{sample weight in grams} \quad \text{equation V.9}$$

The retention value of the citrate in wood in pounds per cubic feet (pcf) can be determined by:

$$\text{pcf Citrate} = (\% \text{Citrate}) * (\text{wood density, pcf}) / 100 \quad \text{equation V.10}$$

There is an alternative method to analyze for citrate in solutions. This method was developed by Dionex Corporation and is based upon the use of an ion chromatograph (IC). (Dionex Application Note No.123) to determine the citrate concentrations present in the extraction fluid. The IC in this method is fitted with a guard column and an anion exchange column (IonPac AS-AG11), which is equipped with a suppressed conductivity detector. This set-up results in an estimated detection limit of 400 µg/l citrate in deionized water. Stock solutions of citrate are prepared to estimate lower detection limits and linearity. The average retention time for citrate in this column is approximately 15.5 minutes.

#### **V.4.c Summary and Recommendations**

The previous sections in this chapter provided an overview of the methods currently available to test for the inorganic and organic chemical constituents of CCA and the alternative wood treatment chemicals in aqueous and solid phases. In future research (year 4), leachates will be analyzed to determine the concentrations of chemicals released from the wood during standardized leaching procedures.

The inorganic chemicals will be analyzed using standard US EPA SW-846 methods. Because the concentrations of the inorganic constituents present in the leachate are unknown, there are several instruments that may be used for analysis. These analytical instruments include GF-AAS for low level detection (or diluted high concentrations) and either ICP or Flame-AAS for higher concentrations. The organic constituents will be analyzed using modified AWWA methods. There are many options available and changes may be made during the test if there are difficulties encountered.

The method chosen to test for the concentration of CDDC in leachates is a modification of AWWA Method A25-94. This is the only method found that analyzes for CDDC in solution. Because the treatment process requires two separate applications of chemicals, the industry has not developed a standard method of analysis for the combined chemical. The method to analyze the concentrations in wood utilizes a spectrophotometer and a methanol/chloroform azeotrope to measure the concentration of the chemical. A calibration curve will be created using known concentrations of CDDC and sample analysis will be based on this curve.

There are several methods available to test for the alkyl ammonium compound DDAC. These methods include three AWWA standards and one methodology (the methylene blue method) developed by the industry, which has not been standardized. The methylene blue method of analysis has been chosen to analyze for DDAC. This method has not been standardized by the AWWA, but the method only involves one visual indication of color change. This method was selected because of the simplification (only one color change) and because it was recommended by a company that produces alternative wood preservatives.

Two methods for determining tebuconazole concentrations in solutions are available: a GC method and an HPLC method. The GC method is the recommended option for analyzing theazole concentrations in leachate. This method has been chosen for its availability and accuracy in analysis. A GC fitted with a mass spectrometer (GC-MS) will be the instrument utilized at the University of Florida laboratories.

Only one method for determining citrate concentrations in treatment solutions is standardized by AWWA. This method uses a spectrophotometer to detect the levels of citrate in leachate. An alternative IC method will be employed to improve the detection limits to approximately 400  $\mu\text{g/L}$ . This change in method is being utilized because leachate samples will contain significantly lower citrate concentrations than full strength treating solutions.

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**CHAPTER VI**

**SUMMARY, RECOMMENDATIONS, AND  
ACKNOWLEDGMENTS**

## **CHAPTER VI, SUMMARY, RECOMMENDATIONS, AND ACKNOWLEDGMENTS**

### **VI.1 SUMMARY & RECOMMENDATIONS**

A summary along with concluding remarks are provided for each of the investigative chapters (Chapter II through VI) of this report.

#### *Chapter II, Metals Concentrations in Soils Below Decks Made of CCA-Treated Wood*

Results from the deck soil study indicate that CCA-treated decks caused the surface soil arsenic concentrations below the decks to increase by over two orders of magnitude or 2000%, on average. Increases above background concentrations were also observed for chromium and copper. On average the concentrations of chromium in “below deck” soils was 3 and ½ times larger than the average of the control samples. For copper, the “below deck” soils were, on average, 6 times higher. Data also indicate that the impact of CCA-treated decks is not confined to the soil surface. Core data show that impacts are observed within the upper 3 inches for chromium and copper. For arsenic, the impacts are observed to a depth of roughly 8 inches of soil.

The increases in soil metal concentrations are significant. All of the surface soil samples collected from below decks (except those collected from Lake Talquin) exceeded the residential SCTL of 0.8 mg/kg of arsenic. Of these 65 samples, 62 also exceeded the industrial SCTL of 3.7 mg/kg. If it is assumed that all CCA-treated decks in Florida impact the surrounding soil it can be estimated that roughly 25,000 acres or 60 million tons of soil in Florida are impacted due to the use of CCA-treated decks.

Given the evidence in Chapters II and IV data indicate that the CCA chemical does in fact leach from the treated wood decks. There is the potential for an additional metal burden to the environment that has not been accounted for. This additional burden can be in the form of rainwater and runoff that has been contaminated and discharged into nearby surface water bodies and groundwater. It would be of interest to quantify the overall amount of metals discharged from CCA-treated products. It is therefore recommended that a set of experimental decks be constructed that will permit all potential metal discharges to be captured. In particular, the experimental decks should be fitted with a drainage system designed to capture rainwater that has been in contact with the deck, surface runoff, and potential infiltration to the groundwater system. Given the high retention levels associated with marine and freshwater docks, it is also of interest to determine the quantities of CCA leached from such products. It is likely that the quantity of metals released is greater for these products than for decks. Further research should therefore focus on quantifying all releases from CCA-treated products. An emphasis should be placed on wood treated at high retention levels.

### *Chapter III, Inventory of CCA-Treated Wood In Florida*

Production statistics indicate that the proportion of CCA-treated wood among all wood types used for construction can be as high as 40 to 50%. Such a high proportion of treated wood greatly limits recycling and reuse options for the waste. The disposal forecast model indicates that the majority of treated wood disposed in Florida is in the form of lumber, timbers, and fence posts. The disposal of these products is currently at roughly 4 million cubic feet per year. The peak in the disposal of these products (up to 32 million cubic feet per year) will be likely observed near the year 2020. Disposal of significant quantities of poles is yet to be observed given the longer service life of this product. Currently it is estimated that roughly 0.03 million cubic feet of utility poles are disposed per year. This disposal quantity is anticipated to increase by over a factor of 50 (to 1.55 million cubic feet per year) by the year 2040. The success of current utility pole re-use or “give-away” programs is therefore due, in part, to the relatively small amount of utility poles available and the fact that the poles that are discarded today have not yet reached their service life, thereby maintaining their structural integrity. It is likely that once major power lines are decommissioned that current “give-away” programs will not be able to handle the quantity nor the quality of the wood coming out of service.

The cumulative amount of arsenic imported into the State associated with CCA-treated wood is estimated at 28,600 tons. Of this quantity roughly 1,800 tons have been disposed and 26,800 tons are currently in service. The amount of arsenic associated with CCA-treated wood currently in service (26,800 tons) is enough to increase the arsenic concentration in the upper one inch of Florida soils by 4 mg/kg. The 4 mg/kg is 5 times greater than the residential soil clean-up target level of 0.8 mg/kg established for the state and 1.1 times greater than the industrial soil clean-up target level of 3.7 mg/kg. Evaluating the amount of arsenic with respect to potential water contamination, the 26,800 tons is enough to increase the arsenic concentration of a volume of water equal to 650 times the size of Lake Okeechobee by 10 ug/L, which is the proposed federal drinking water limit for arsenic.

A long-term management plan aimed at minimizing the impacts of arsenic from treated wood should be composed of two parts. It should a) focus on recovering as much of the arsenic that is associated with CCA-treated wood currently in service and b) focus on waste minimization. Approximately 5,600 tons or 20% of the arsenic currently in service can be recovered from wood used in marine/fresh water applications and utility poles. The remainder of the arsenic is associated with outdoor decks, fences, landscape timbers, highway construction, and other miscellaneous uses. The one advantage of most of these remaining uses is that non-arsenical waterborne wood treatment preservatives are available and can be substituted for CCA-treated wood. For example, the non-arsenical wood treatment preservatives ACQ, CBA, CC, and CDDC, have been standardized for the “light duty” uses, such as use in outdoor decks, fences, and landscape timbers. Use of these alternative chemicals for these “light duty” uses could therefore significantly decrease the amount of arsenic (associated with CCA-treated wood) requiring ultimate disposal.

*Chapter IV, Leaching of Chromium, Copper, and Arsenic from New CCA-Treated Wood and C&D Debris Wood Mulch*

Leaching tests confirmed observations gathered as part of the deck-soil study: the metals in the CCA preservative do leach from the wood under normal environmental conditions. It is frequently cited that the metals do not leach from CCA-treated wood because the chemical is “fixed.” While fixation is used to describe the treatment efficacy, something that is well fixed (e.g. 95% fixed) may still leach more than enough to exceed applicable environmental standards or risk-based goals. This was evidenced by the fact that a majority of samples leached using the TCLP exceeded the US EPA’s toxicity characteristic limit for arsenic. If not for the regulatory exclusion from being a hazardous waste, CCA-treated wood would routinely be characterized as a hazardous waste. If the exemption were not in place, the cost of disposing CCA-treated wood would likely be much higher.

The TCLP is conducted using a simulated landfill-acid and involves size reducing the waste to less than 9.5 mm. These test requirements are often cited as being unrealistic when assessing certain management scenarios. To address this concern, alternative leaching tests, as well as leaching tests at larger particle sizes were conducted. While copper did leach much less using a synthetic rainwater test (SPLP), arsenic and chromium leached similar amounts as TCLP. Over one-half of the SPLP tests performed exceeded the toxicity characteristic value of 5 mg/L for arsenic. As expected, particle size does have an impact on leaching, but even at the largest particle size (one-100 g block), the arsenic and chromium concentrations were over an order of magnitude above the appropriate ground water guidance concentrations. It was demonstrated that metals, especially arsenic and chromium, continued to leach from the wood in longer leaching tests.

The leaching tests indicate that new CCA-treated wood does not meet the definition of being “non-water soluble” included in the Florida C&D debris regulations. While CCA-treated wood is currently allowed to be disposed in C&D debris landfills, the results show that environmental regulations would be justified in banning the CCA-treated wood from unlined landfill disposal. Since the leaching tests were performed on new, but fixed, CCA-treated wood, one might argue that in service treated wood that had already leached substantial quantities of metals to the environment would not leach upon disposal. Three items indicate that even CCA-treated wood taken out of service would still present a problem for unlined landfill disposal. First, the magnitude by which the leaching tests exceeded the current drinking water standards for arsenic was very large. Second, the multiple extraction procedure (MEP) shows that arsenic continues to leach at appreciable concentrations (above GWCTL) after multiple leachings. Third, the C&D mulch in nearly all cases leached above the GWCTL when tested with the SPLP. The primary question that remains to be explored relative to leaching of “out-of-service” wood is whether it fails TCLP routinely or not.

The evidence of arsenic leaching from C&D debris wood mulch corroborates information collected in previous study years. CCA-treated wood is currently present as

part of the recovered C&D debris wood stream. While this may be inadvertent in most cases, it is still happening. If the same guidelines were applied to C&D debris wood mulch as were applied to other land-applied wastes, it would be excluded from land application. While the question of whether land applied mulch would ever cause groundwater problems is debatable, the continued application of such mulch would surely increase the concentration of arsenic in the soils, in a manner similar to that observed under the decks in chapter II. The fact that some of this mulch is being bagged and sold to the general public for home application adds an extra degree of concern to the issue.

#### *Chapter V, Literature Reviews for Future Research*

Analytical methods have been identified for chromium speciation analysis, arsenic speciation analysis, and for analysis of the organic co-biocides associated with alternative chemical treated wood products. The methods identified for chromium speciation analysis includes a carbonate-hydroxide extraction followed by analysis using ion chromatography. Initial work with arsenic speciation analysis will include use of the SDDC method which has the capacity to analyze for two arsenic species. Efforts will also focus on identifying readily available equipment (such as an HPLC-ICP/MS and HPLC-HG-AFS) for analyzing additional arsenic species. AWWPA standards will be utilized to analyze the organic co-biocides associated with CDDC, and ACQ. A GC method will be implemented to analyze the tebuconazole found in CBA and an IC method will be utilized to analyze for the citrate component found in CC.

#### *Overall Conclusion From This Study*

Overall, results indicate that CCA-treated wood does indeed leach arsenic, chromium and copper and thereby increases the metals concentrations in surrounding soil during its service life. The areal extent and volume of soil impacted are significant. The impacts of the increased concentrations on human and ecological health, however, are open to interpretation. While the current 1-in-a-million cancer risk level for arsenic in residential soils is 0.8 mg/kg in Florida, some have questioned the true risk resulting from such concentrations. Future work should focus on evaluating the health impacts associated with these increases.

This study also emphasizes the need to recapture the arsenic associated with CCA-treated wood during its disposal. The quantity of arsenic associated with CCA-treated wood currently in service is significant. Current methods of disposal such as use as mulch or disposal within unlined landfills would not be permitted if current policy practices for waste materials were applied. Efforts should focus on establishing a holistic disposal management plan for CCA-treated wood that would recapture the CCA and dispose of it in an environmentally acceptable manner. Future research should focus on economical options for ultimate disposal.

## VI.2 ACKNOWLEDGEMENTS

Funding for this project was received from the Florida Center for Solid and Hazardous Waste Management and from Florida Power and Light Company. The authors gratefully acknowledge the project's technical advisory group (TAG) for their guidance and feedback. A list of technical advisory group (TAG) members along with a list of TAG meeting attendees is provided in appendix D. The research team gratefully acknowledges Robbins Manufacturing for analyzing the retention levels of the decks used in the soil impact study and, Koppers Inc. and CSI Inc. for analyzing the retention levels of the new CCA-treated wood used in the TCLP and SPLP tests. We also thank Dave Bullock of Wood Protection Products who provided a sample of Penta-Check used to test the Lake Talquin deck for the presence of pentachlorophenol. Dave Mason and Steve Bean of the Southern Forest Products Association provided considerable insight concerning the statistics that their organization has compiled. The authors also thank John Schert of the FCSHWM and Dave Mason of the FDEP for their assistance in sampling the soil below CCA-treated decks. The following graduate students also assisted with various aspects of this project: Sean Bennie, Jenna Jambeck-Carlsen, Kim Cochran, Kelvin Gary, Monika Kormienko-Blassino, and Paul Thur de Koos.

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## **APPENDIX A**

### **ADDITIONAL GRAPHS AND FIGURES FOR DECK SOIL STUDY**

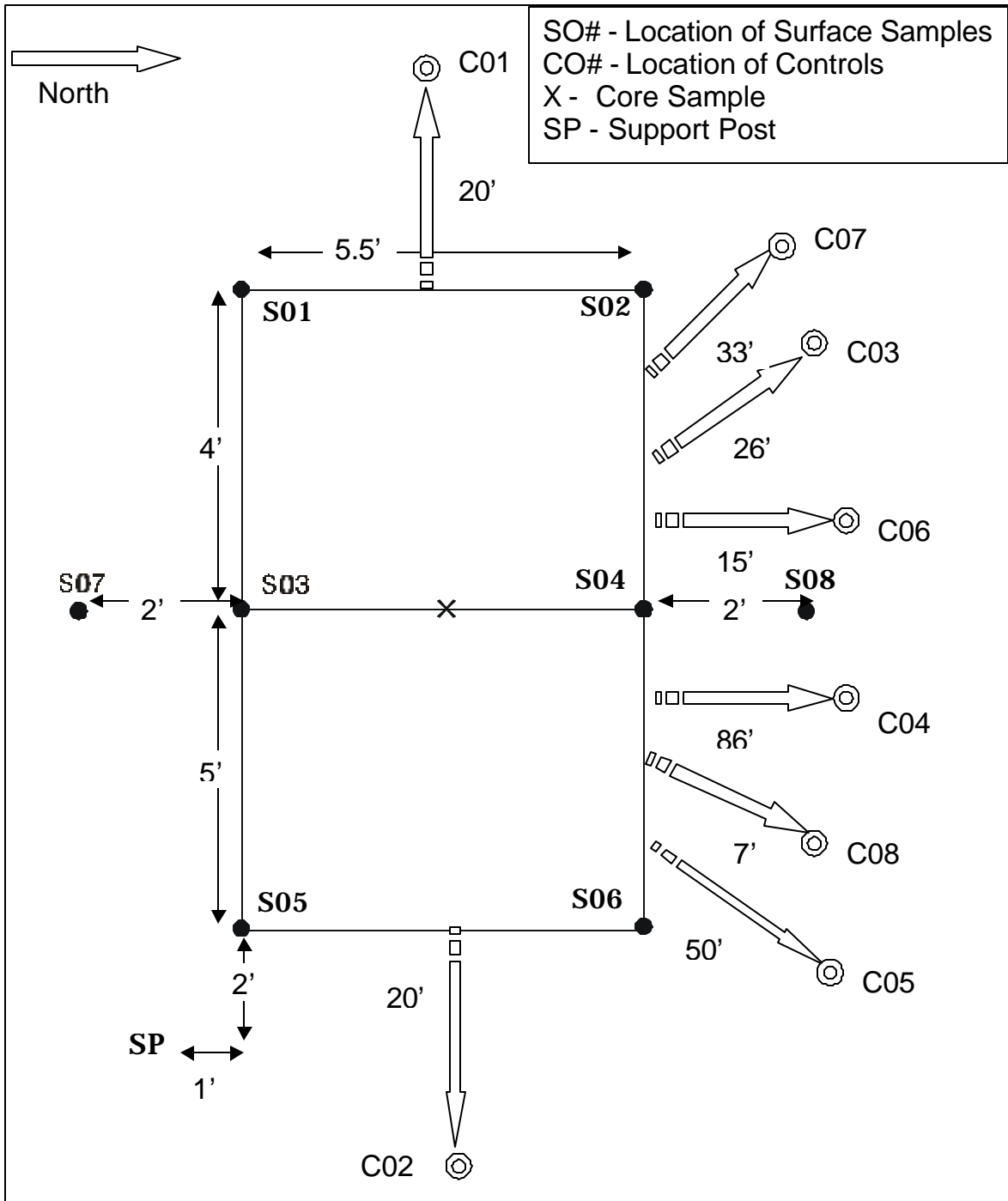


Figure A.1: Sampling Locations for Deck at Bivens Arm Park, BP

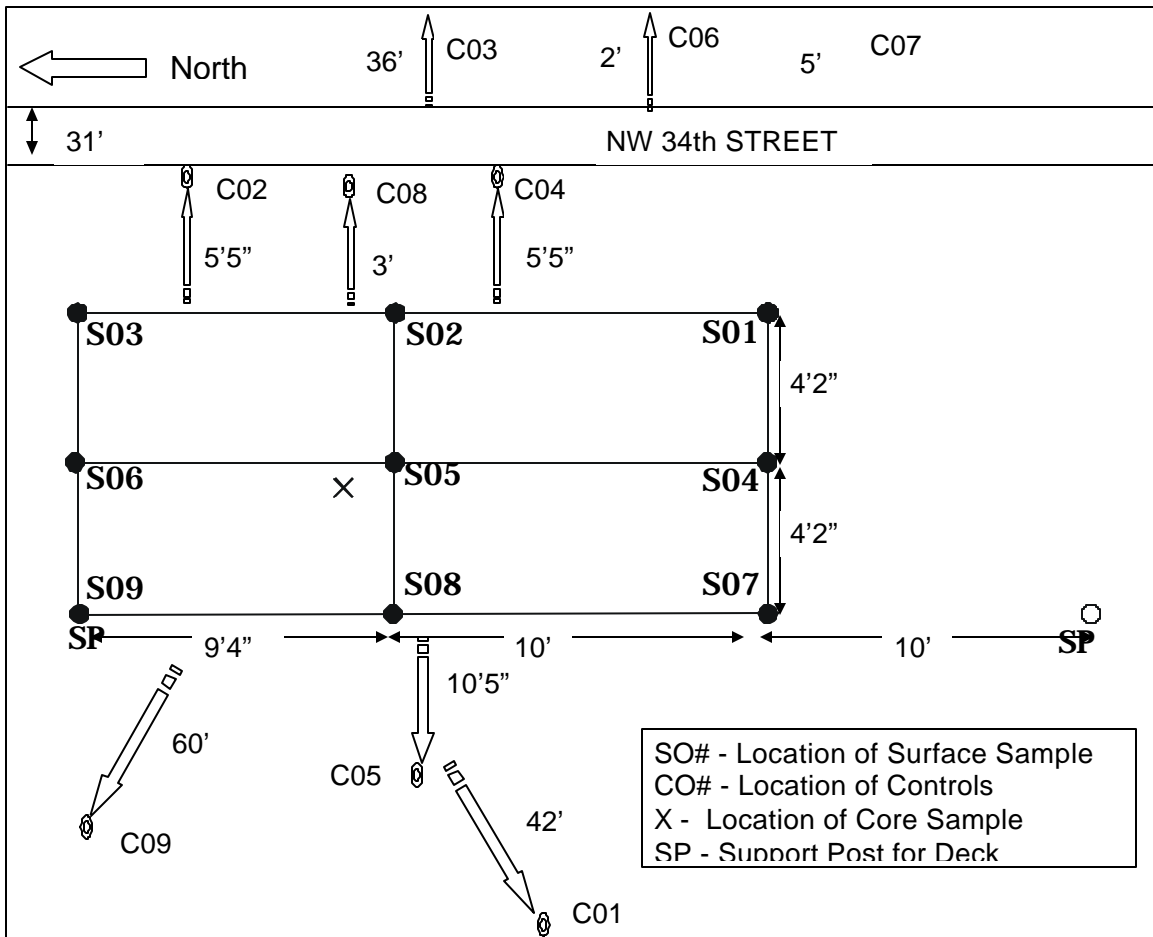


Figure A.2: Sampling Locations for Deck at 34<sup>th</sup> Street Bridge, BR

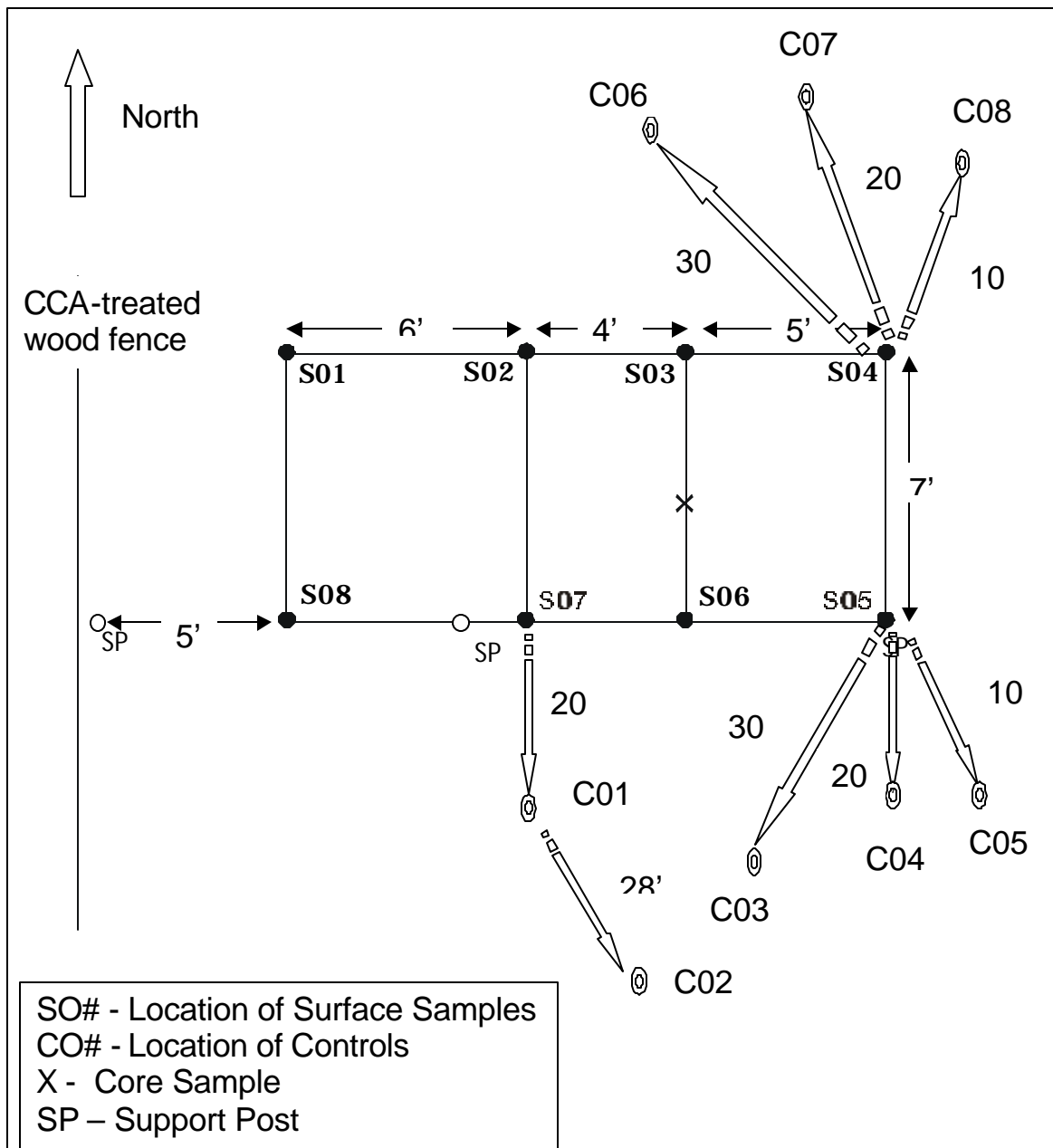


Figure A.3: Sampling Locations for Deck at Paynes Prairie, PP



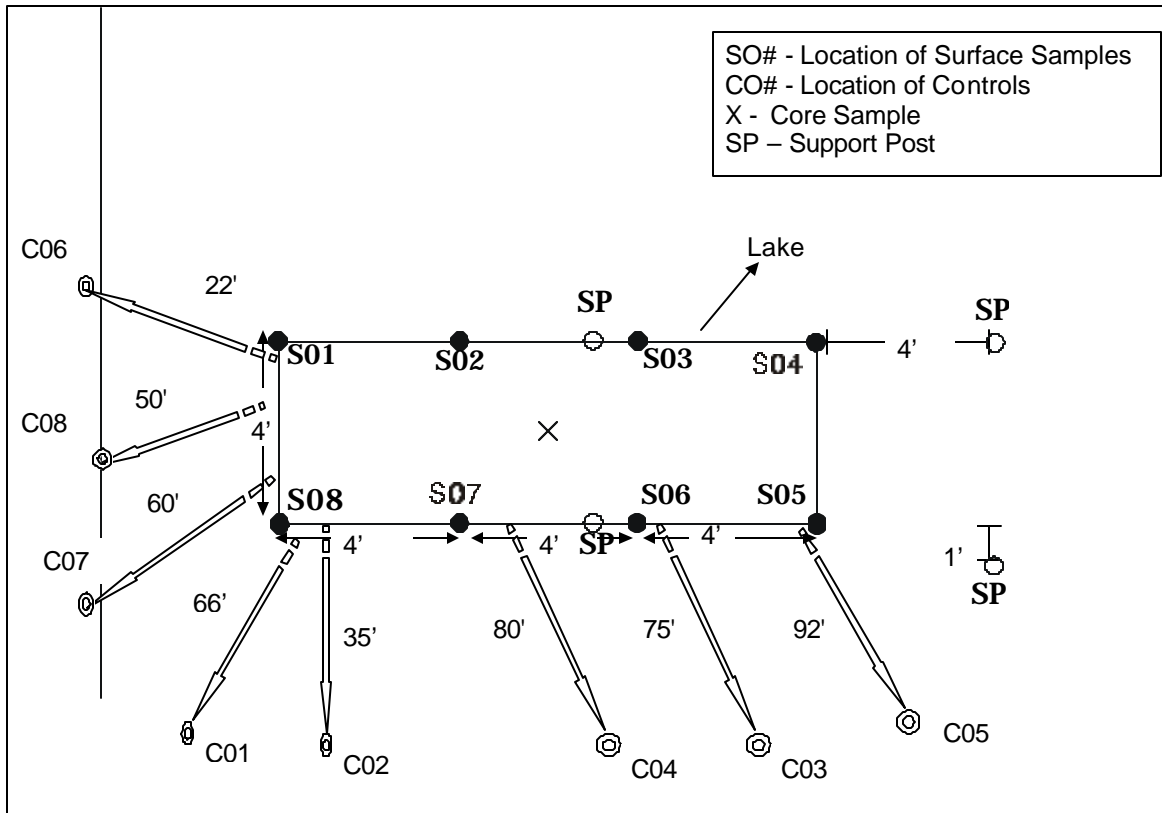


Figure A.4: Sampling Locations for Deck at Tom Brown Park, TB



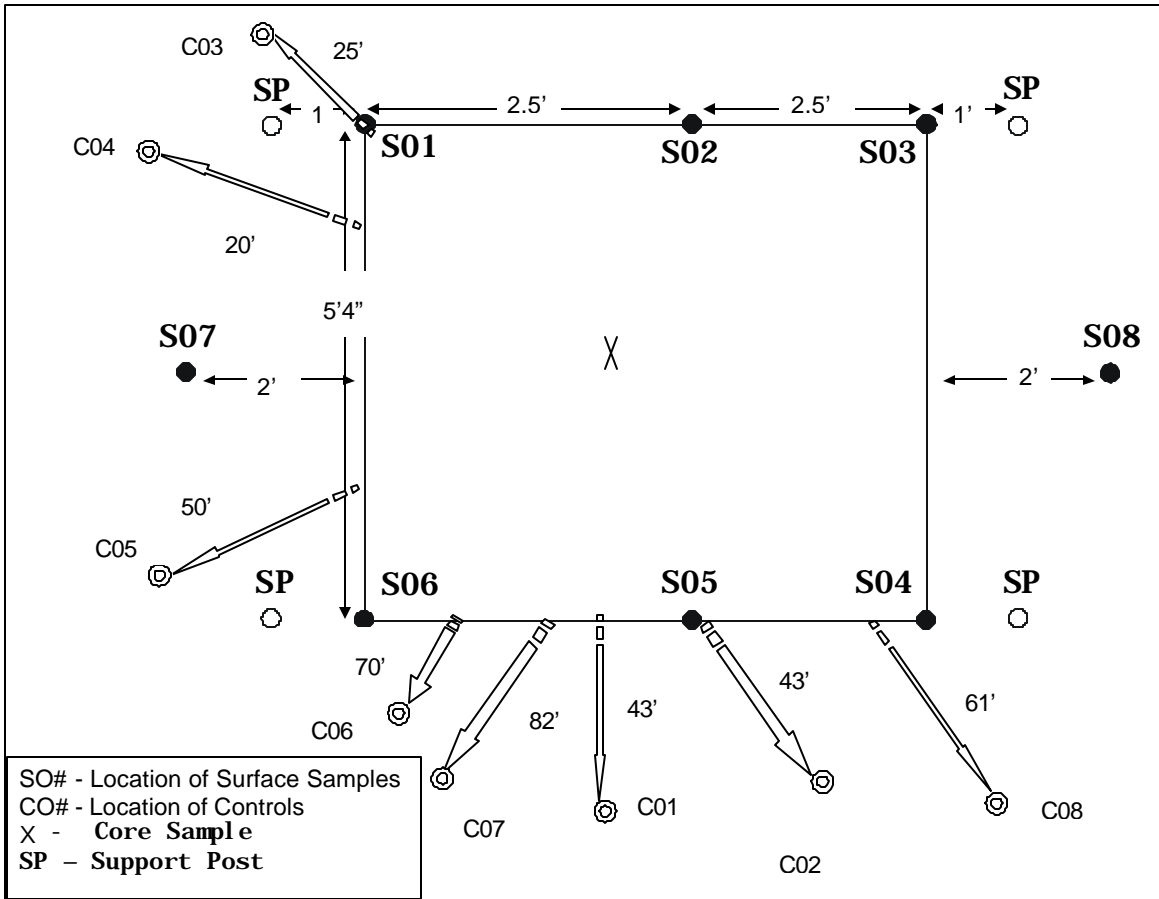


Figure A.6: Sampling Locations for Deck at Lake Talquin, LT



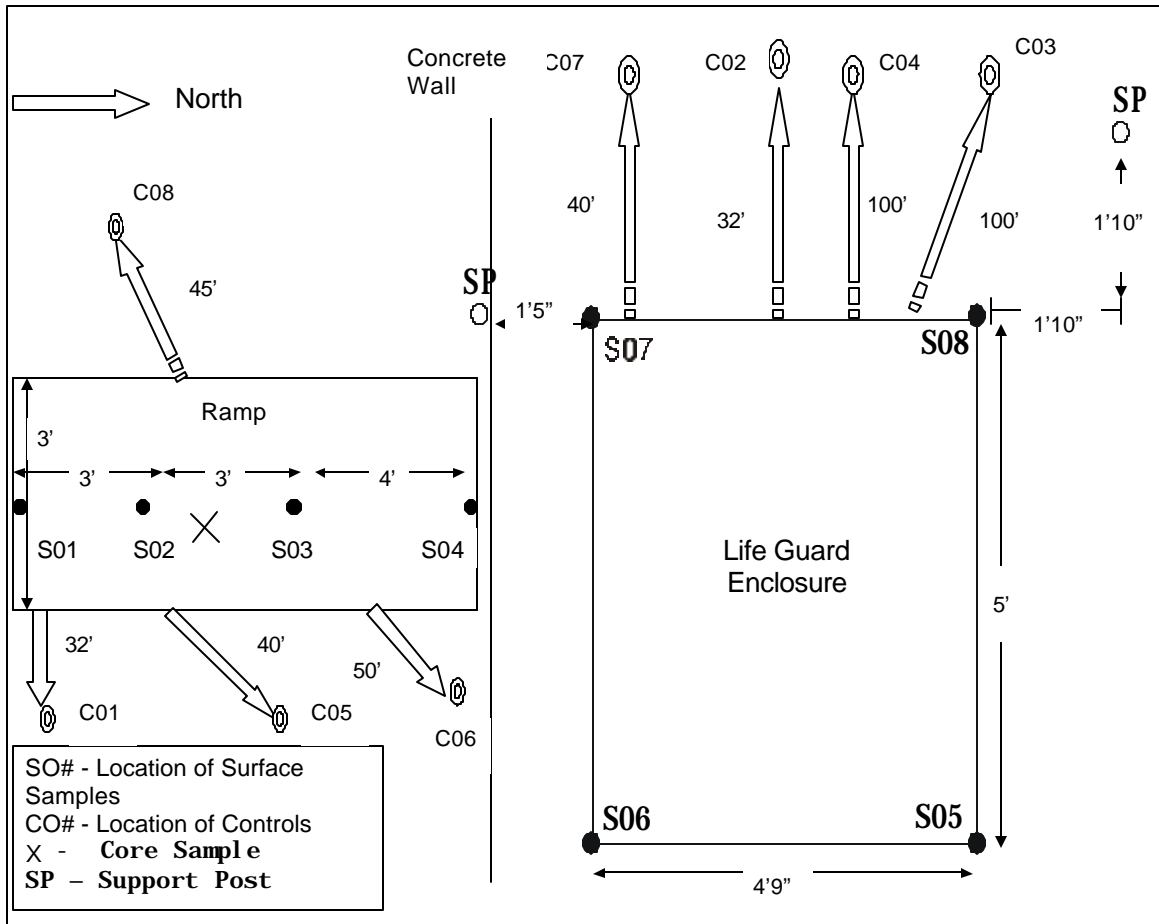


Figure A.8: Sampling Locations for Deck at Tropical Park, TP

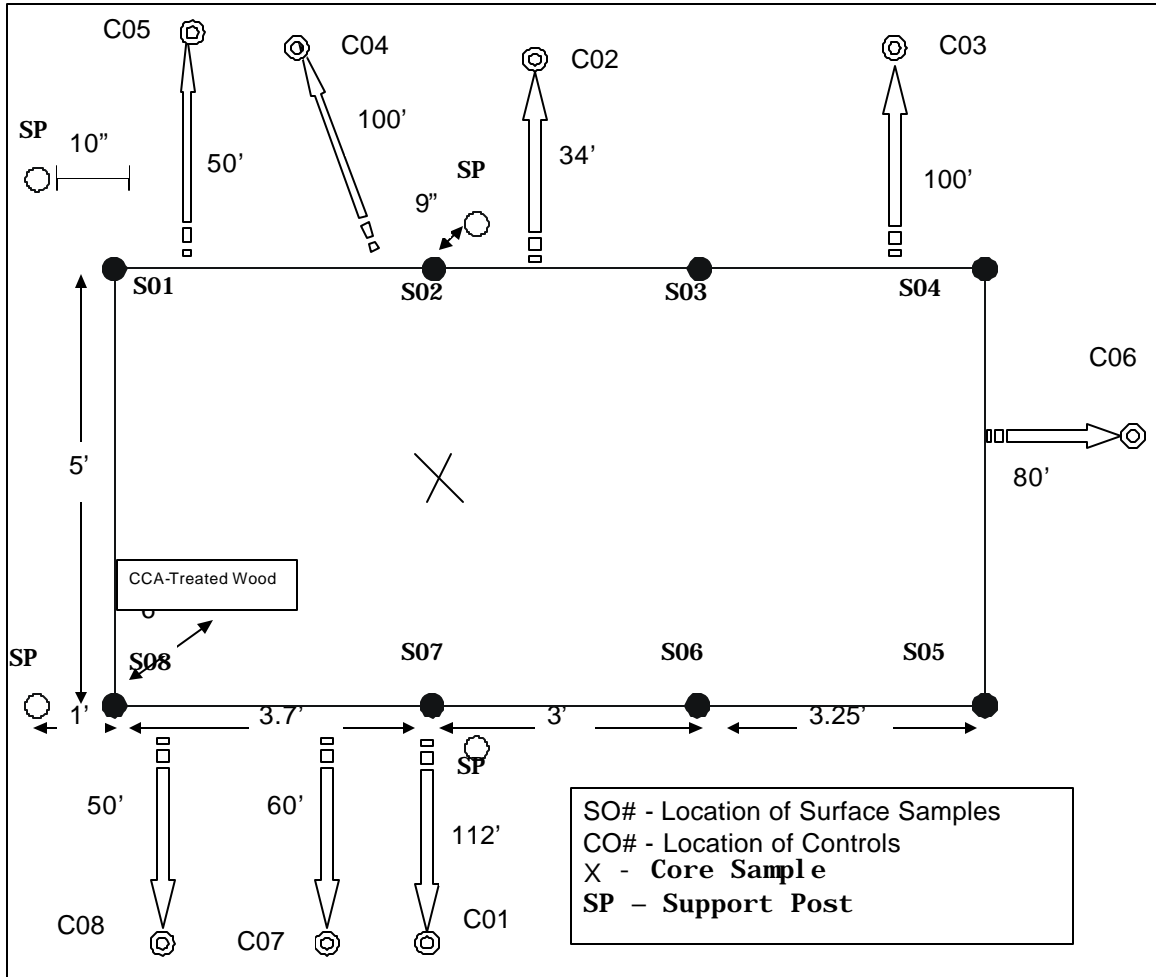


Figure A.9: Sampling Locations for Deck at Oleta River Park, OP

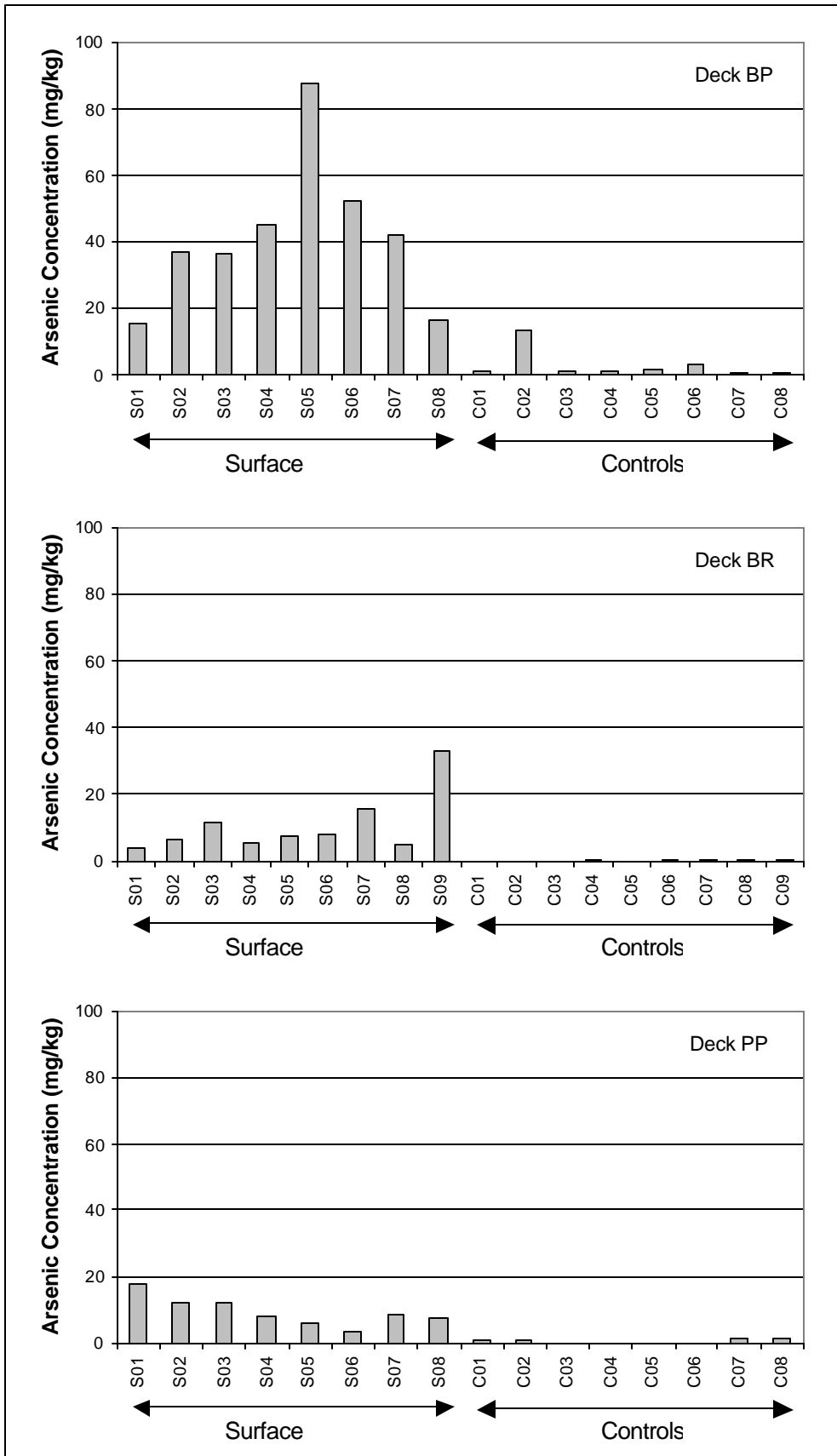


Figure A.10: Arsenic Concentrations Below the Gainesville Decks

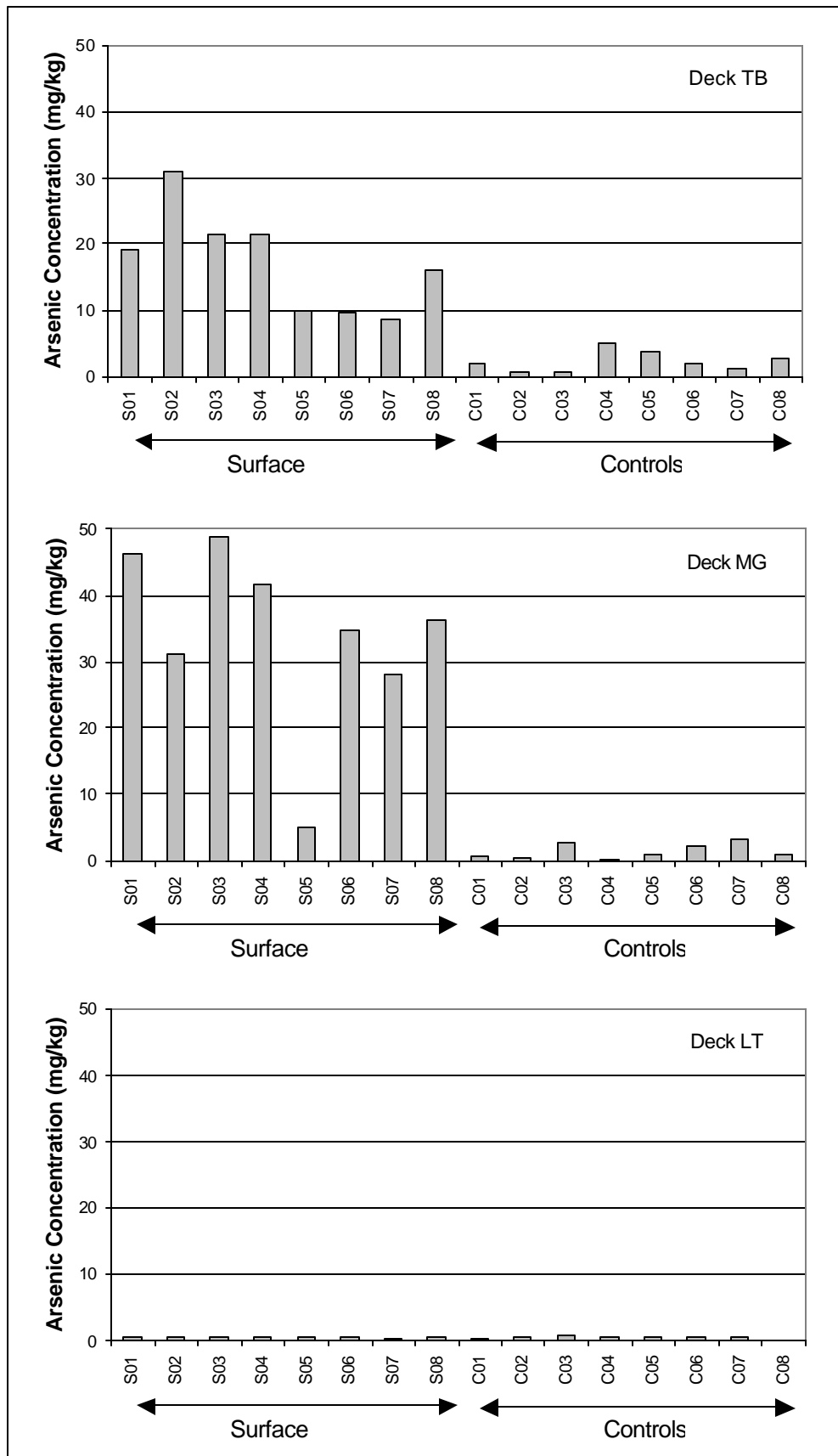


Figure A.11: Arsenic Concentrations Below the Tallahassee Decks



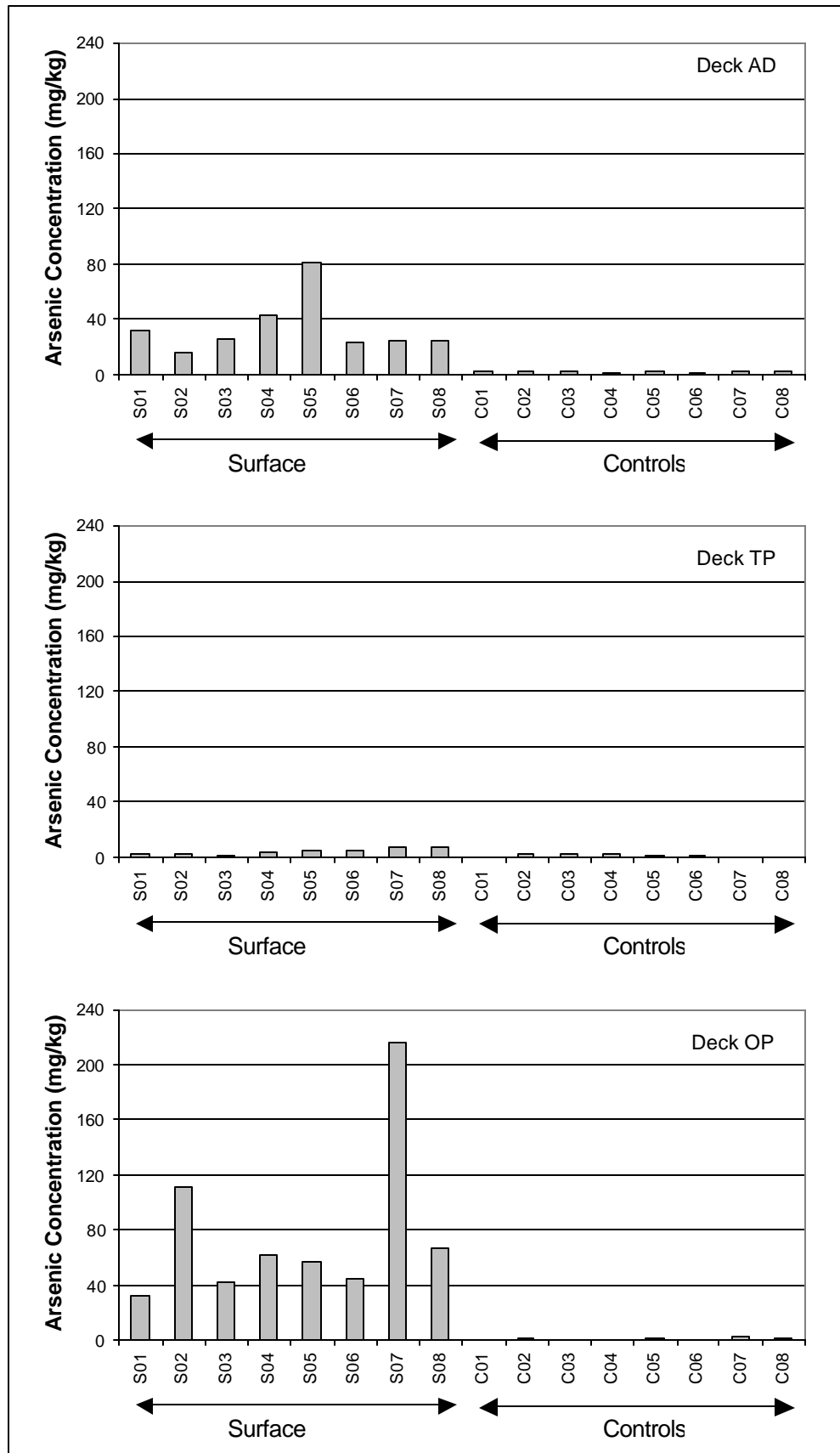


Figure A.12: Arsenic Concentrations Below the Miami Decks

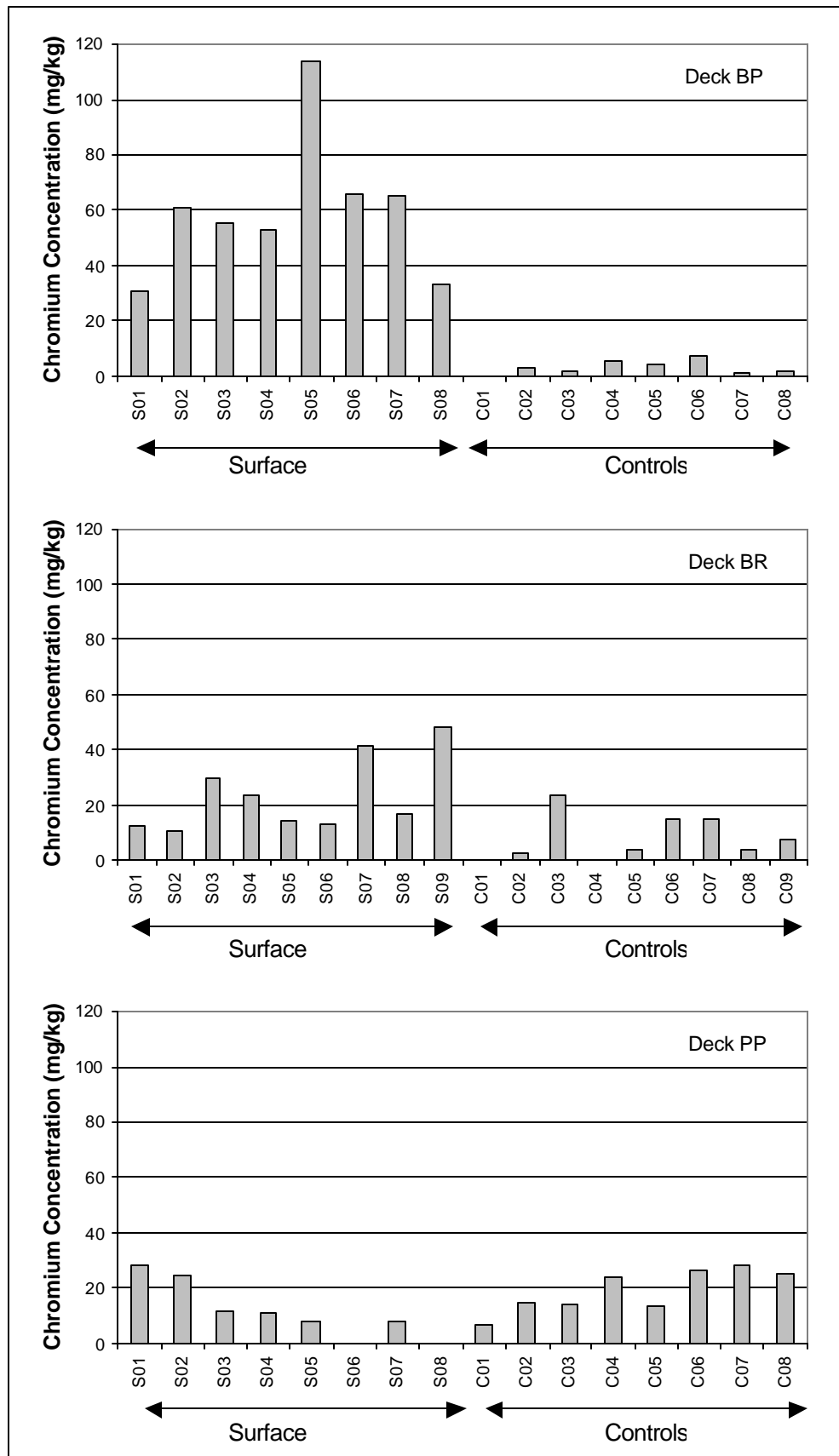


Figure A.13: Chromium Concentrations Below the Gainesville Decks

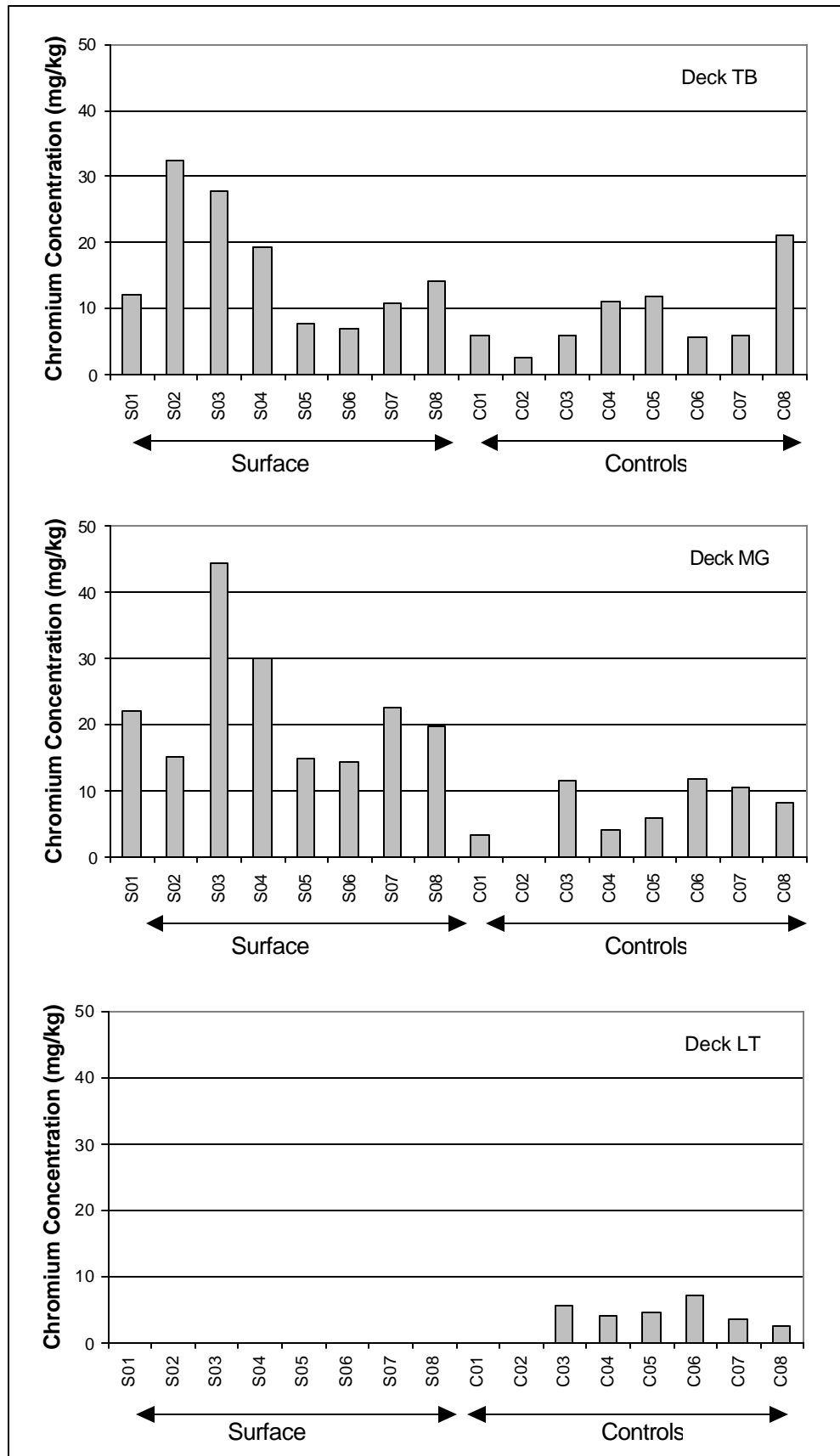


Figure A.14: Chromium Concentrations Below the Tallahassee Decks

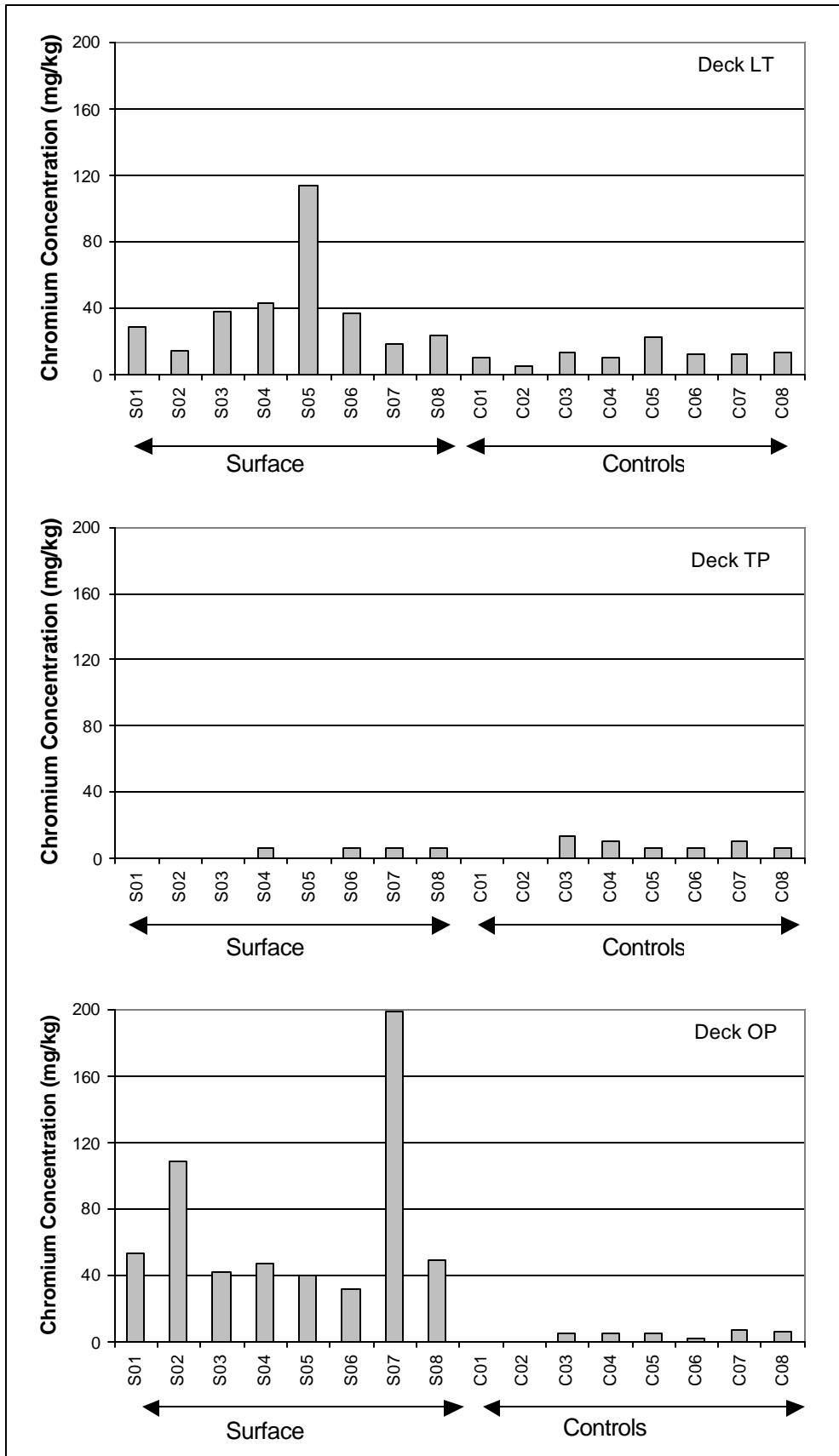


Figure A.15: Chromium Concentrations Below the Miami Decks

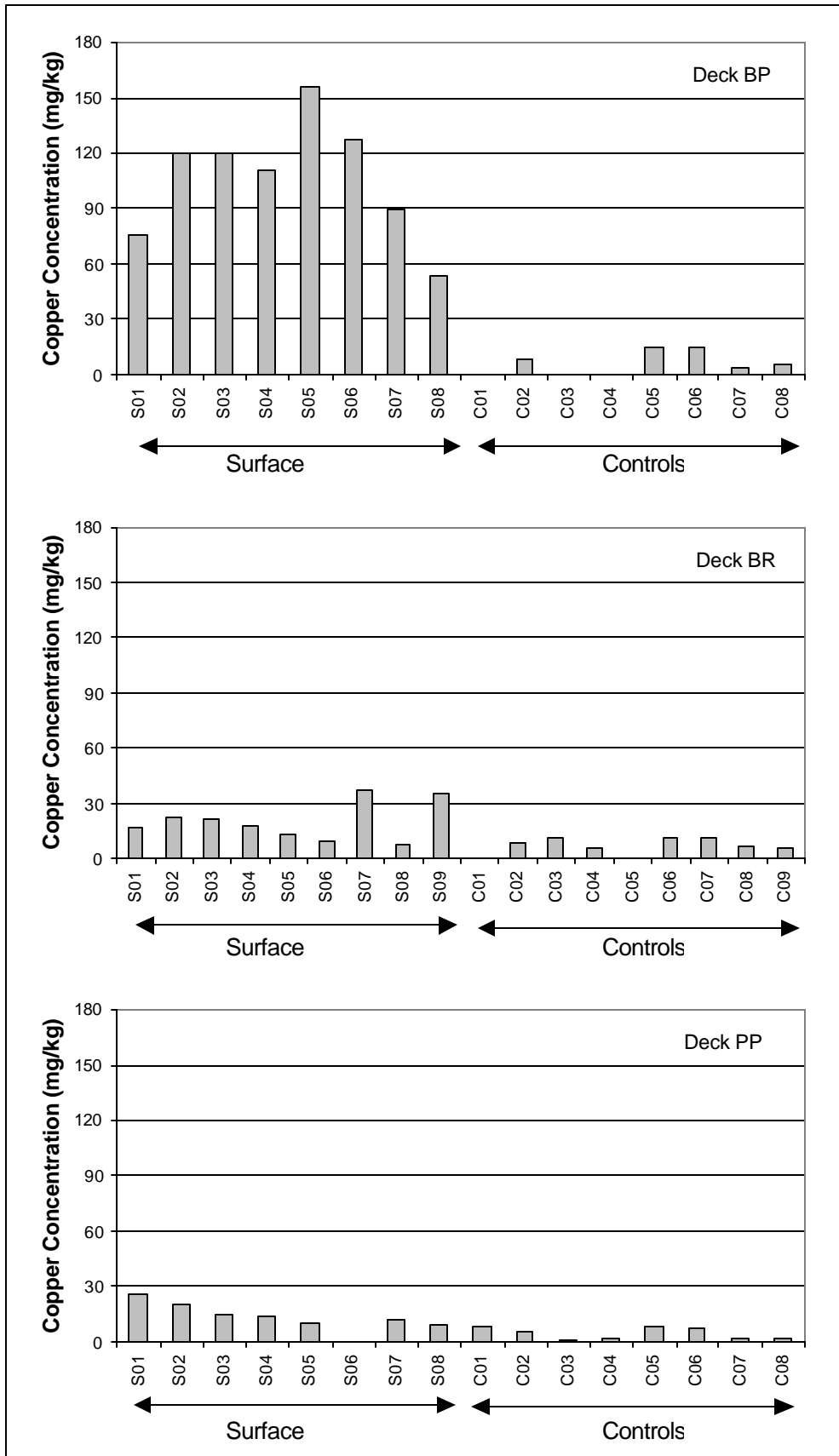


Figure A.16: Copper Concentrations Below the Gainesville Decks

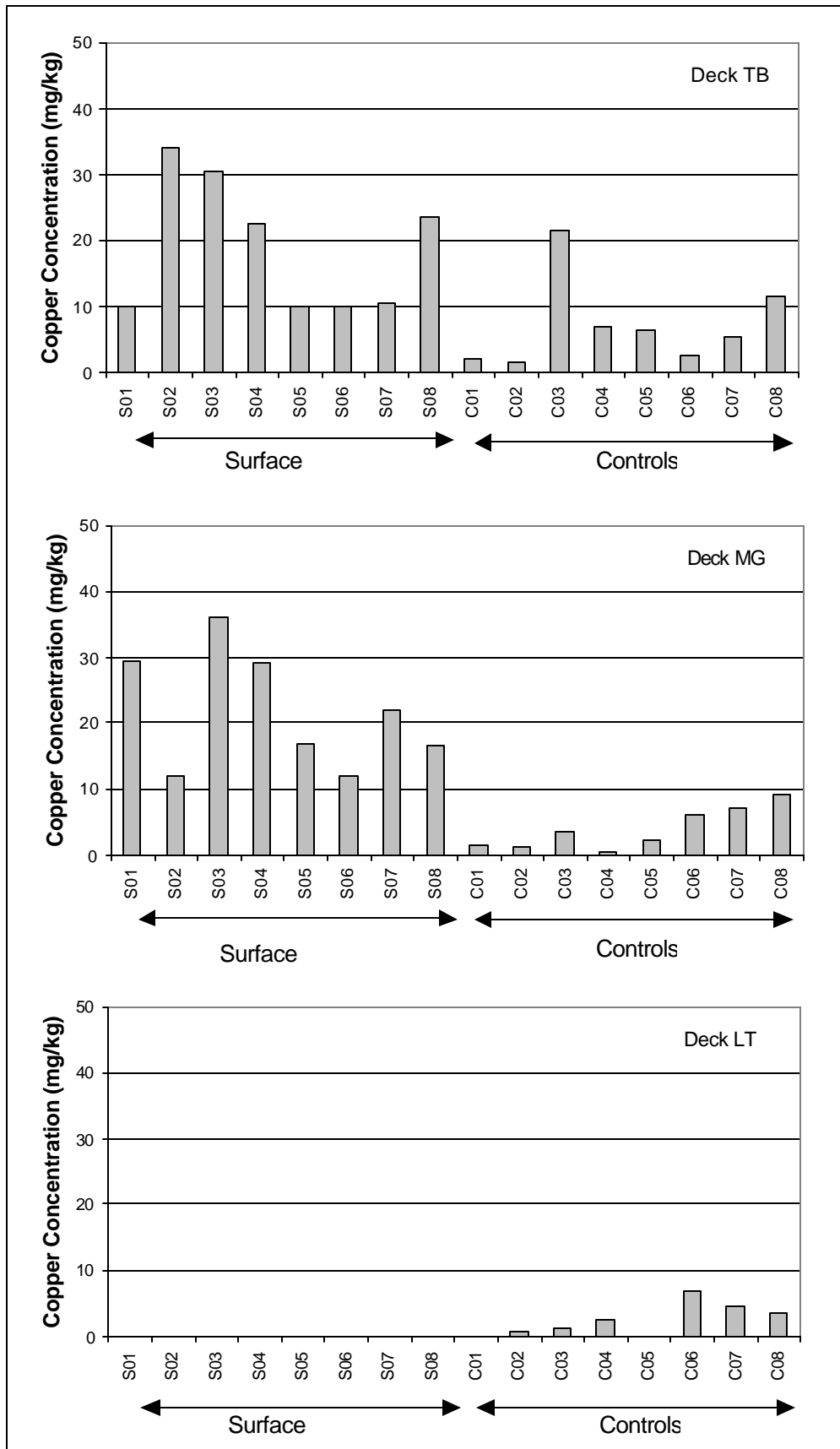


Figure A.17: Copper Concentrations Below the Tallahassee Decks

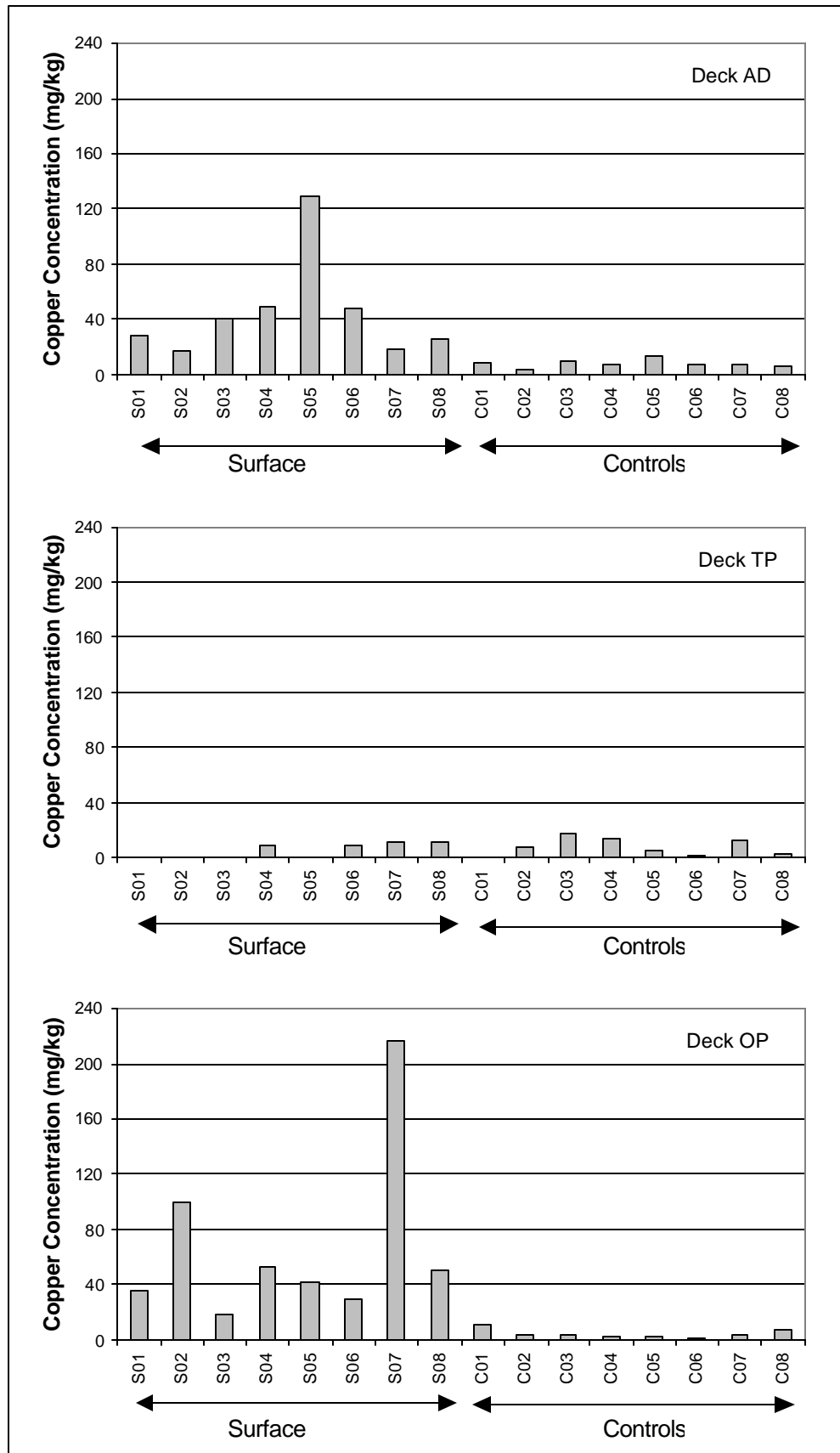


Figure A.18: Copper Concentrations Below the Miami Decks

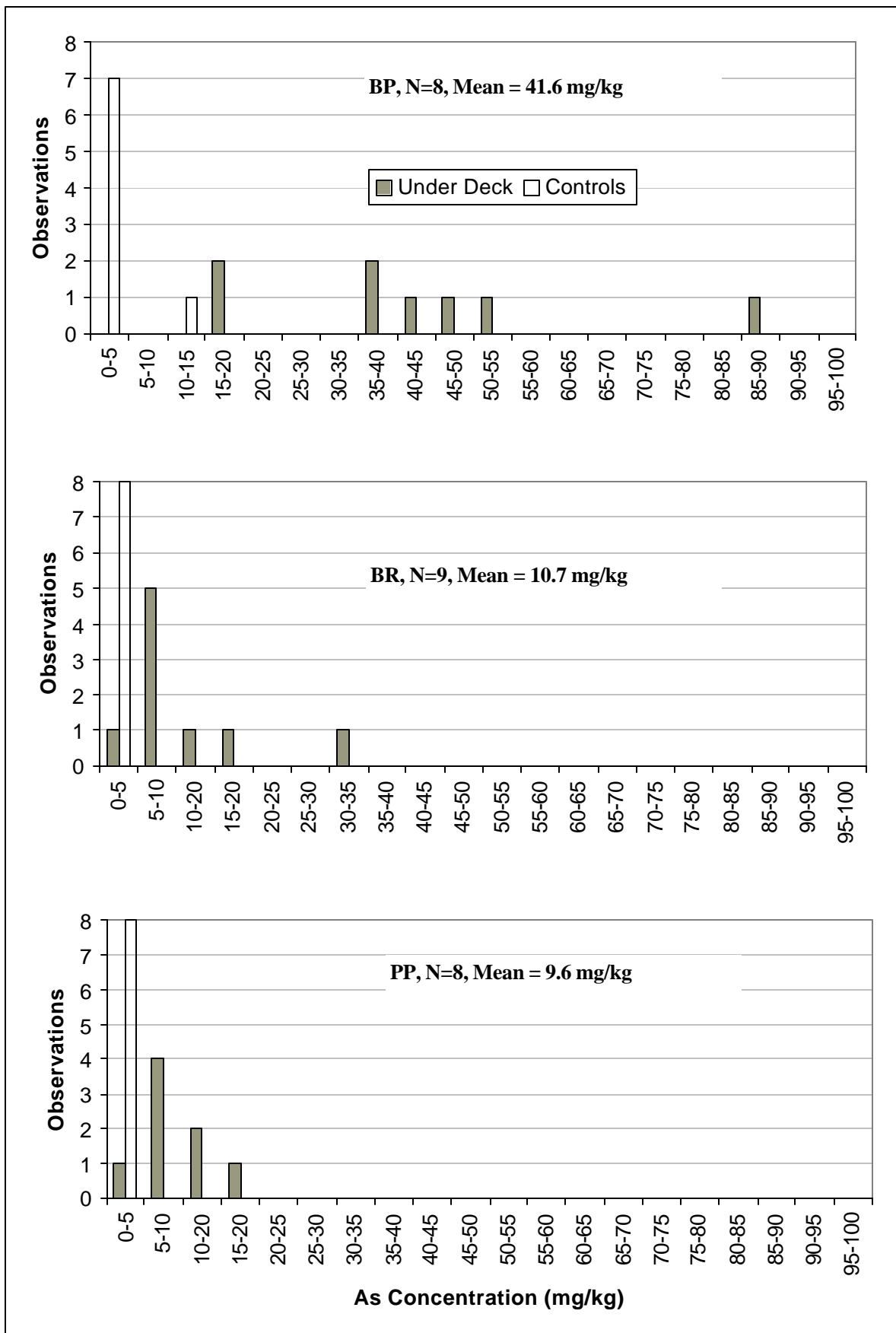


Figure A.19: Arsenic Distribution Below the Gainesville Decks



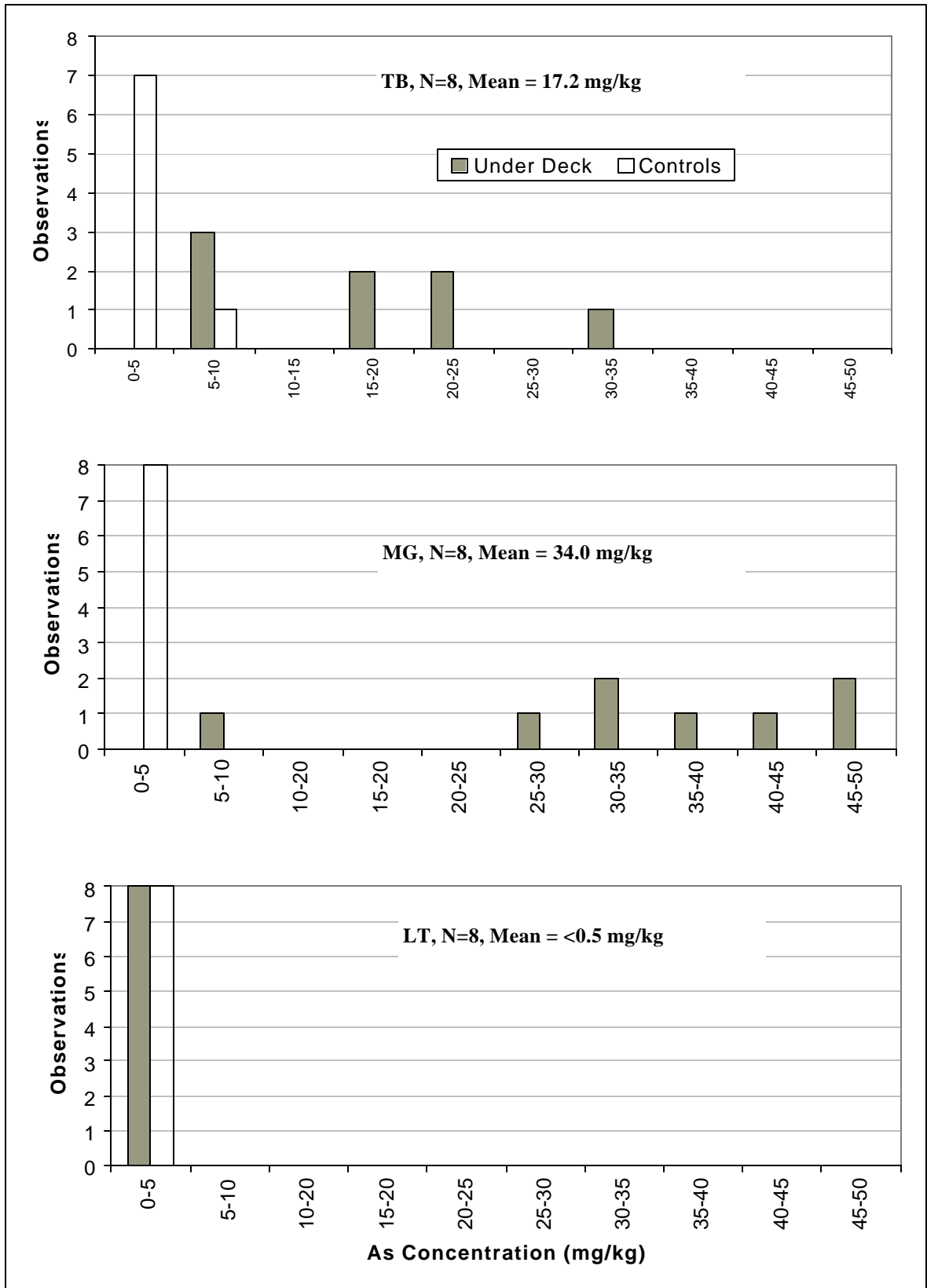


Figure A.20: Arsenic Distribution Below the Tallahassee Decks

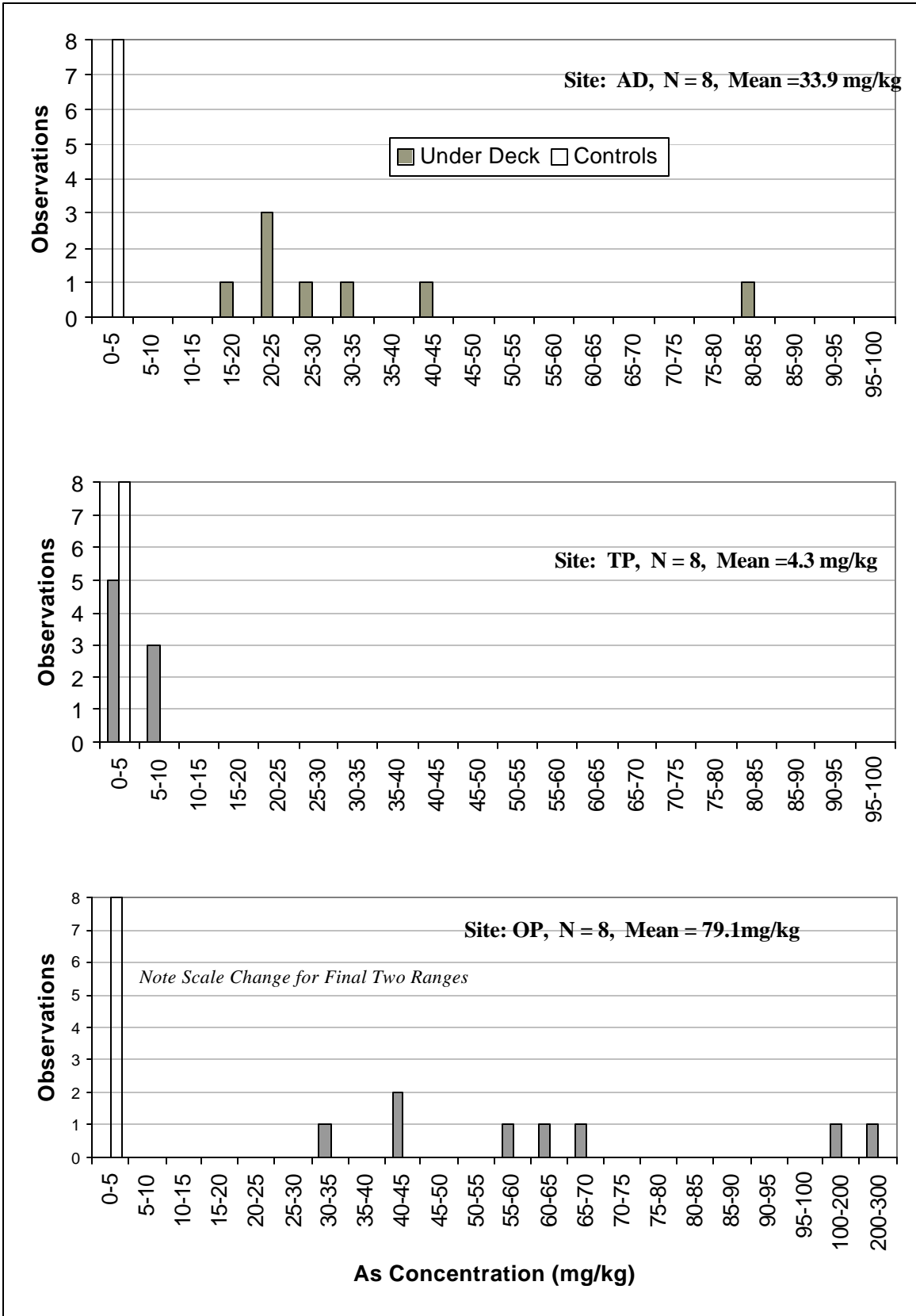


Figure A.21: Arsenic Distribution Below the Miami Decks

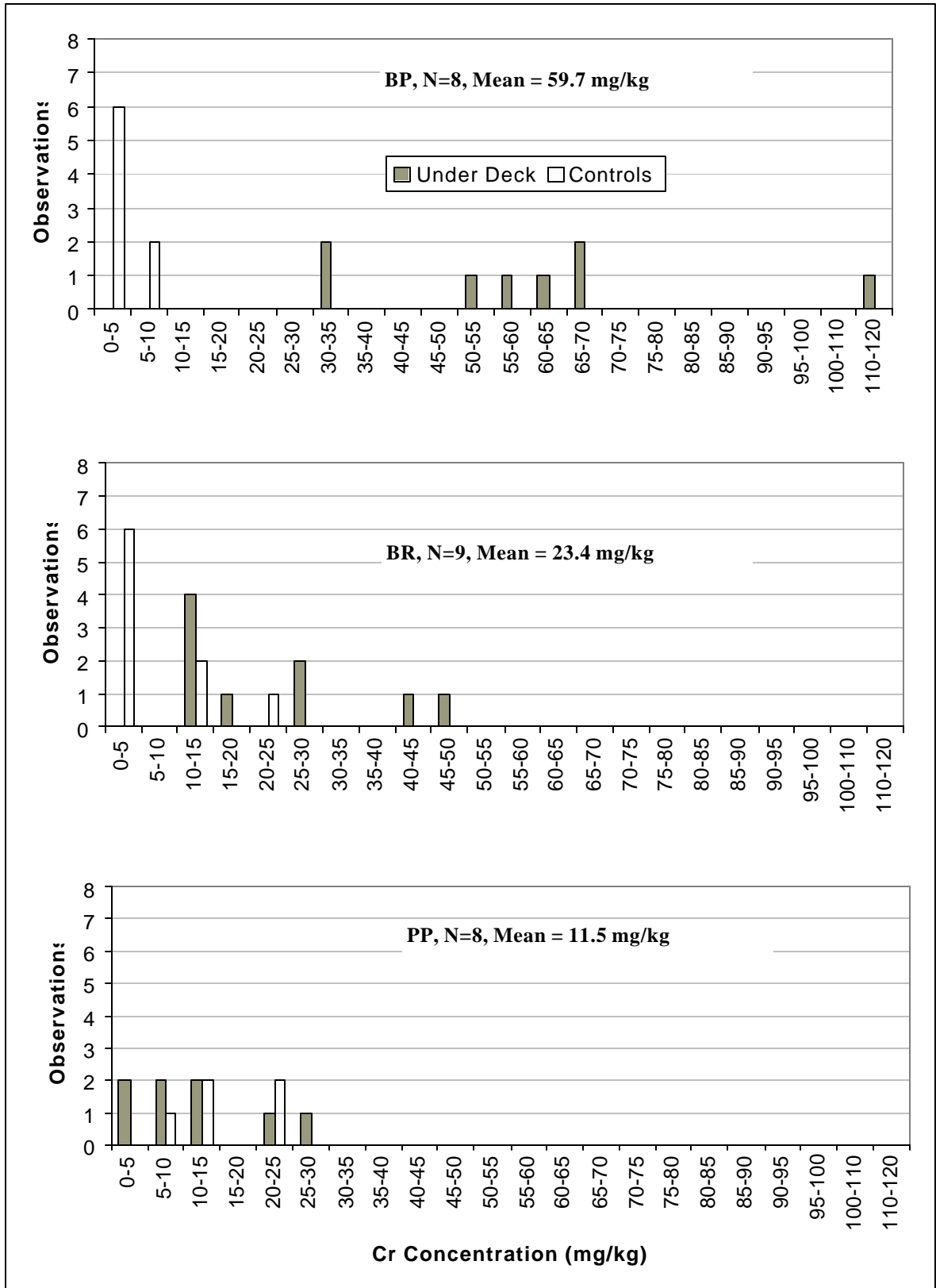


Figure A.22: Chromium Distribution Below the Gainesville Decks

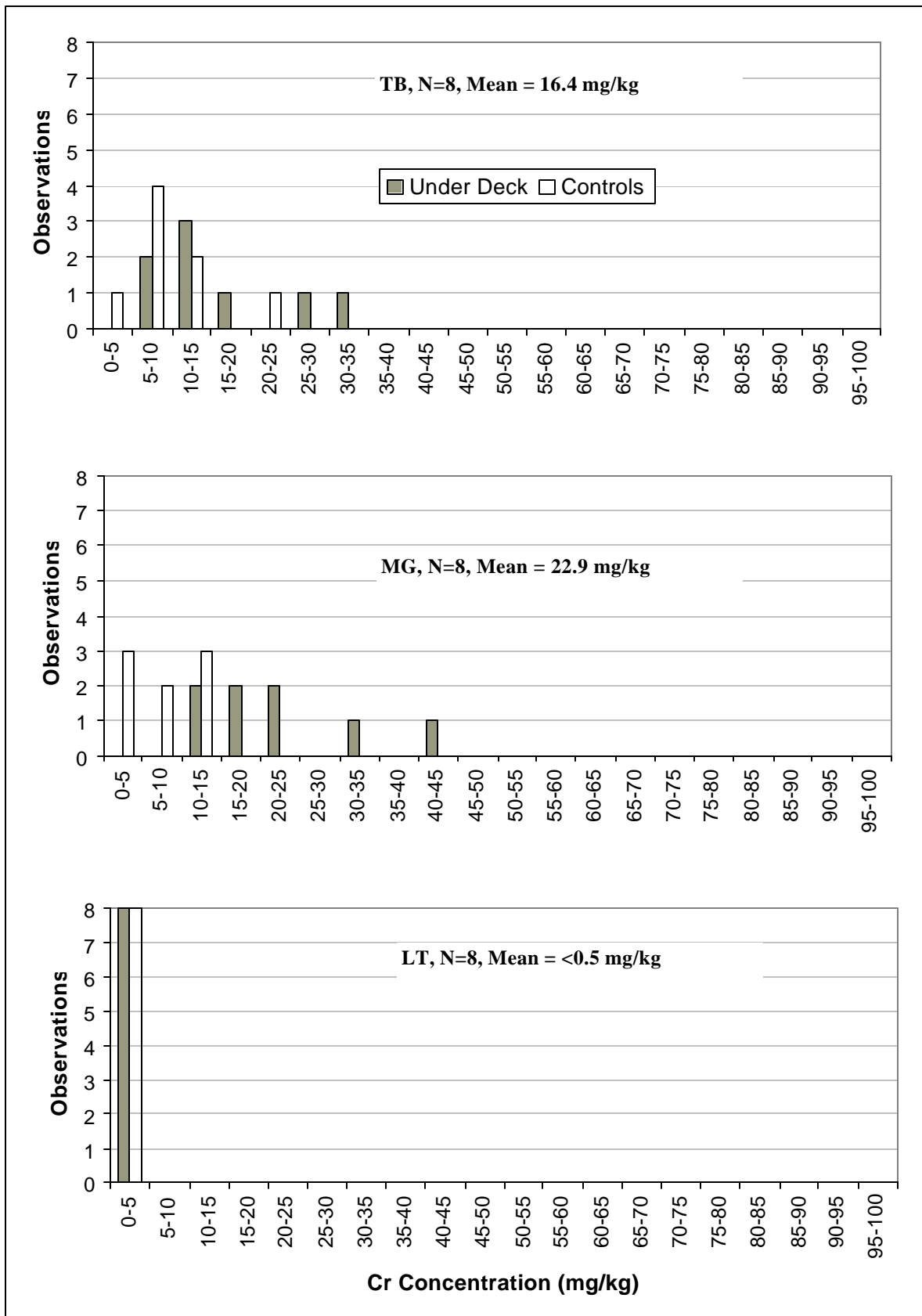


Figure A.23: Chromium Distribution Below the Tallahassee Decks

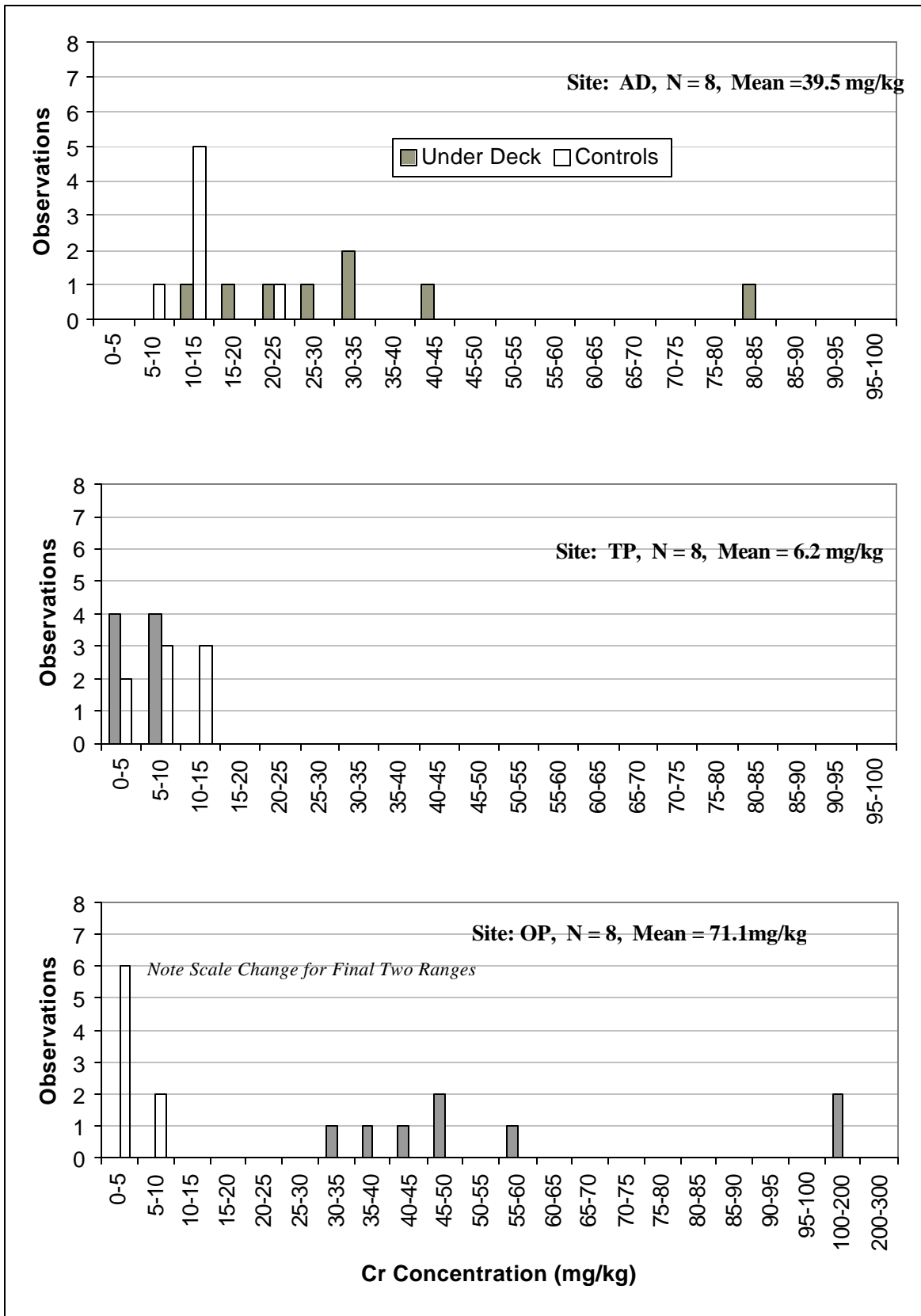


Figure A.24: Chromium Distribution Below the Miami Decks

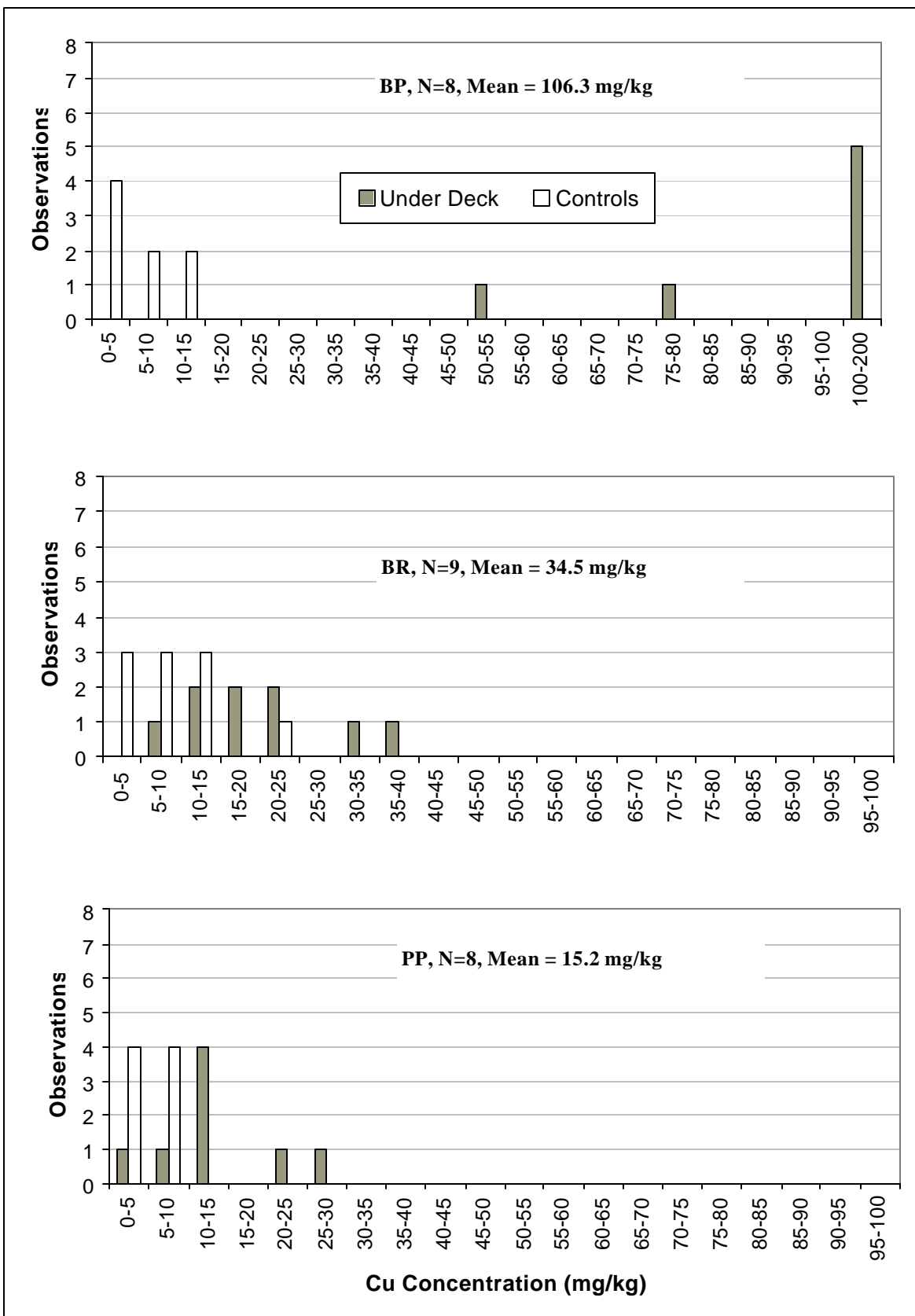


Figure A.25: Copper Distribution Below the Gainesville Decks

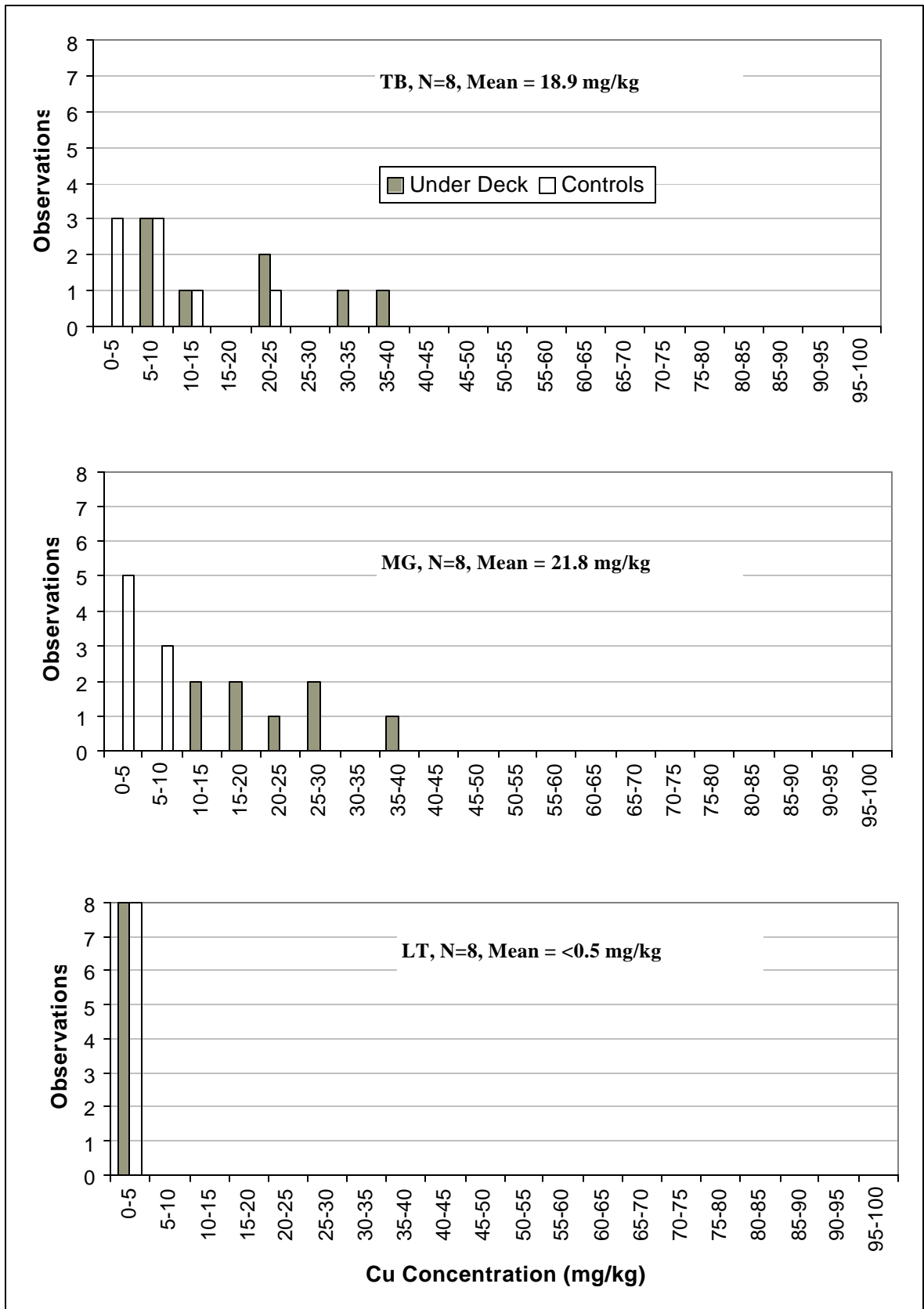


Figure A.26: Copper Distribution Below the Tallahassee Decks

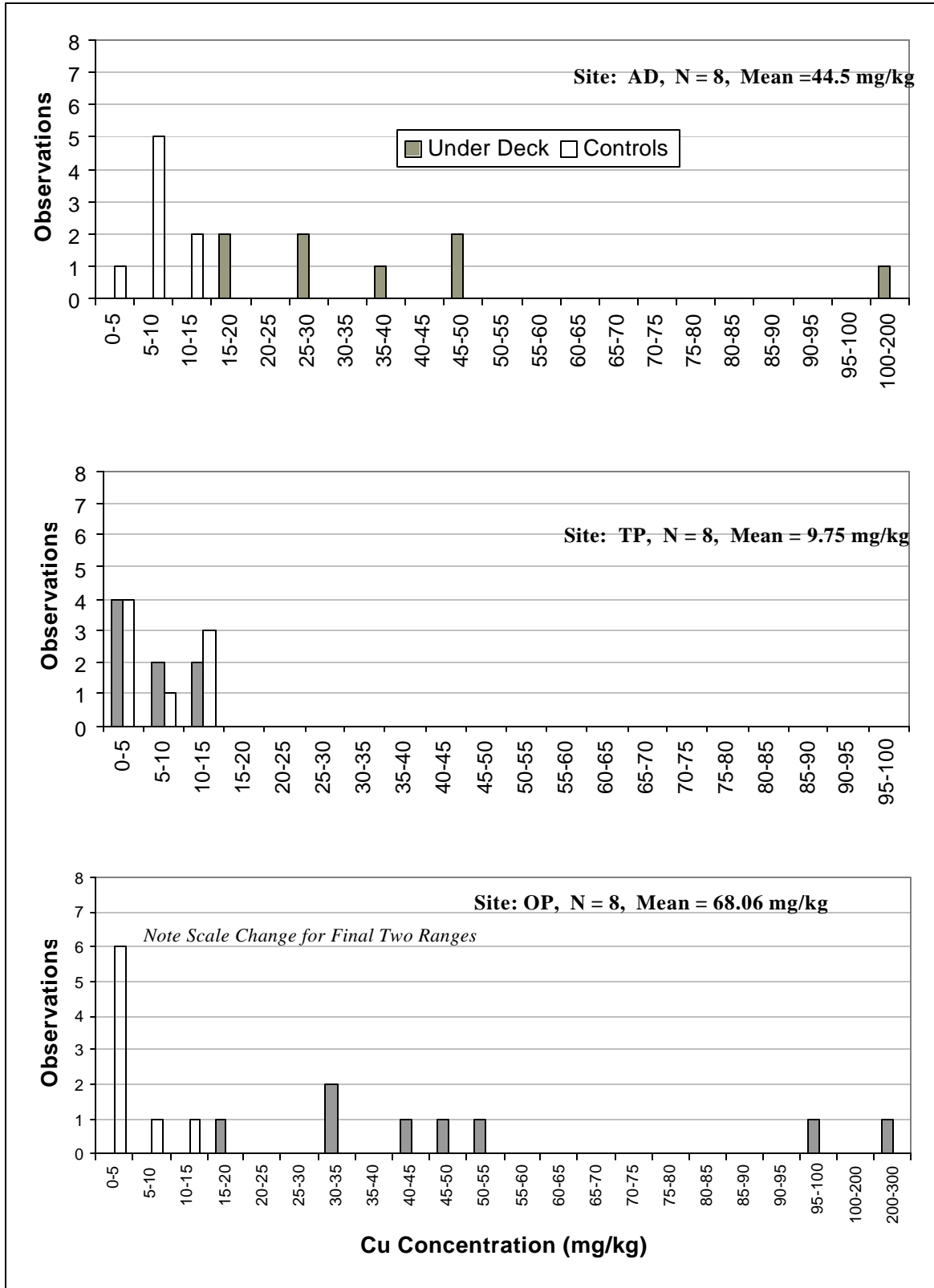


Figure A.27: Copper Distribution Below the Miami Decks



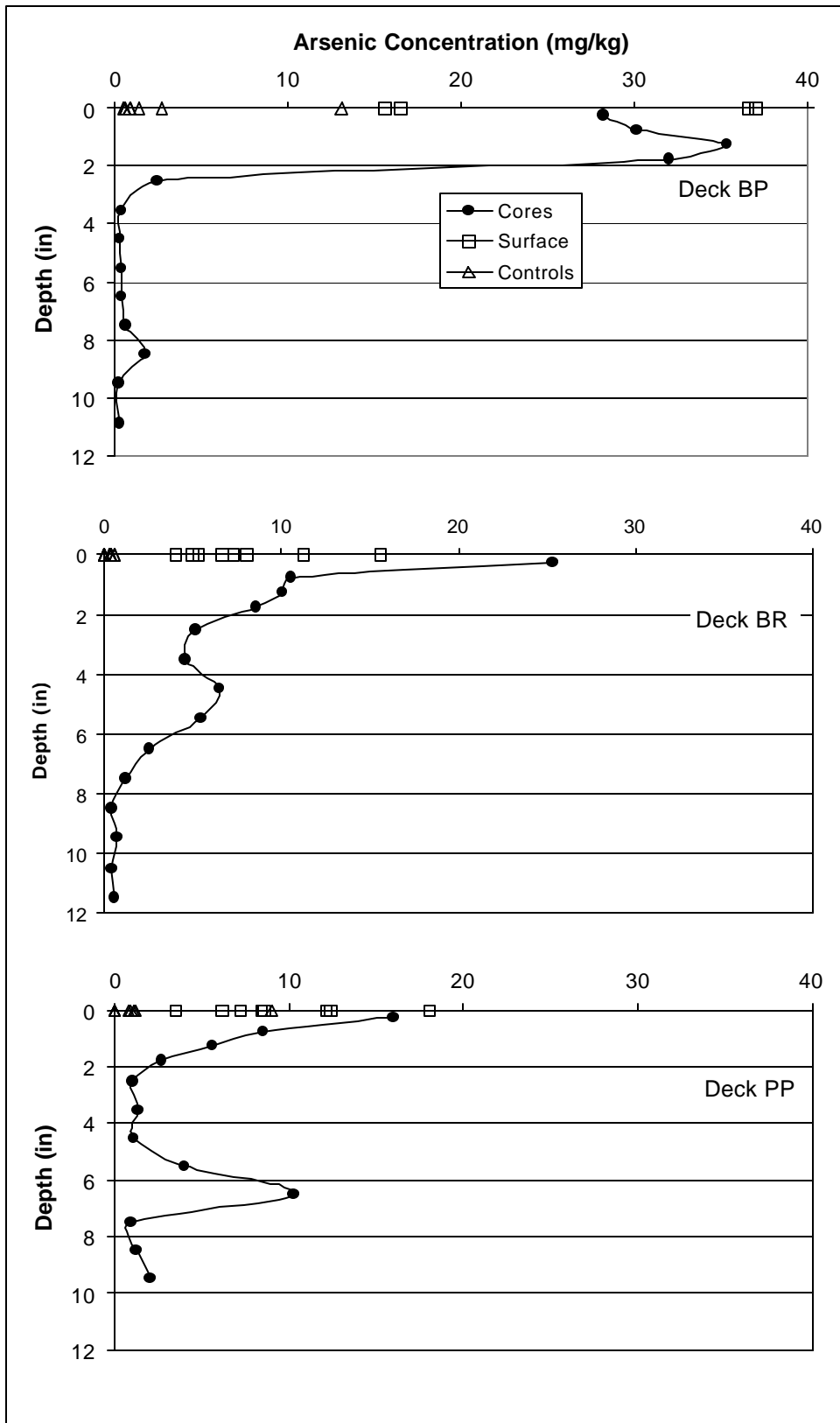


Figure A.28: Arsenic Concentrations as a Function of Depth Below the Gainesville Decks

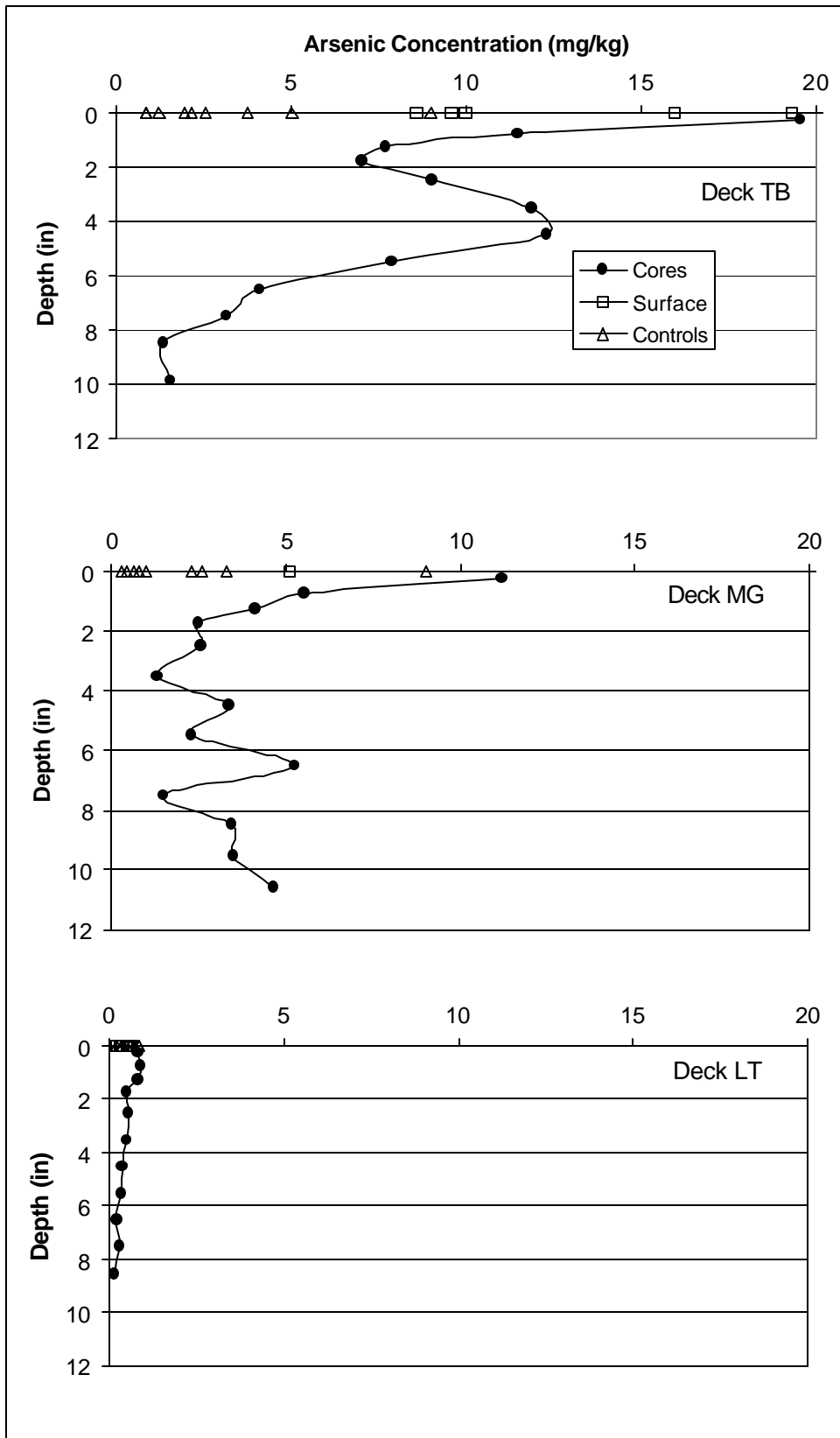


Figure A.29: Arsenic Concentrations as a Function of Depth Below the Tallahassee Decks

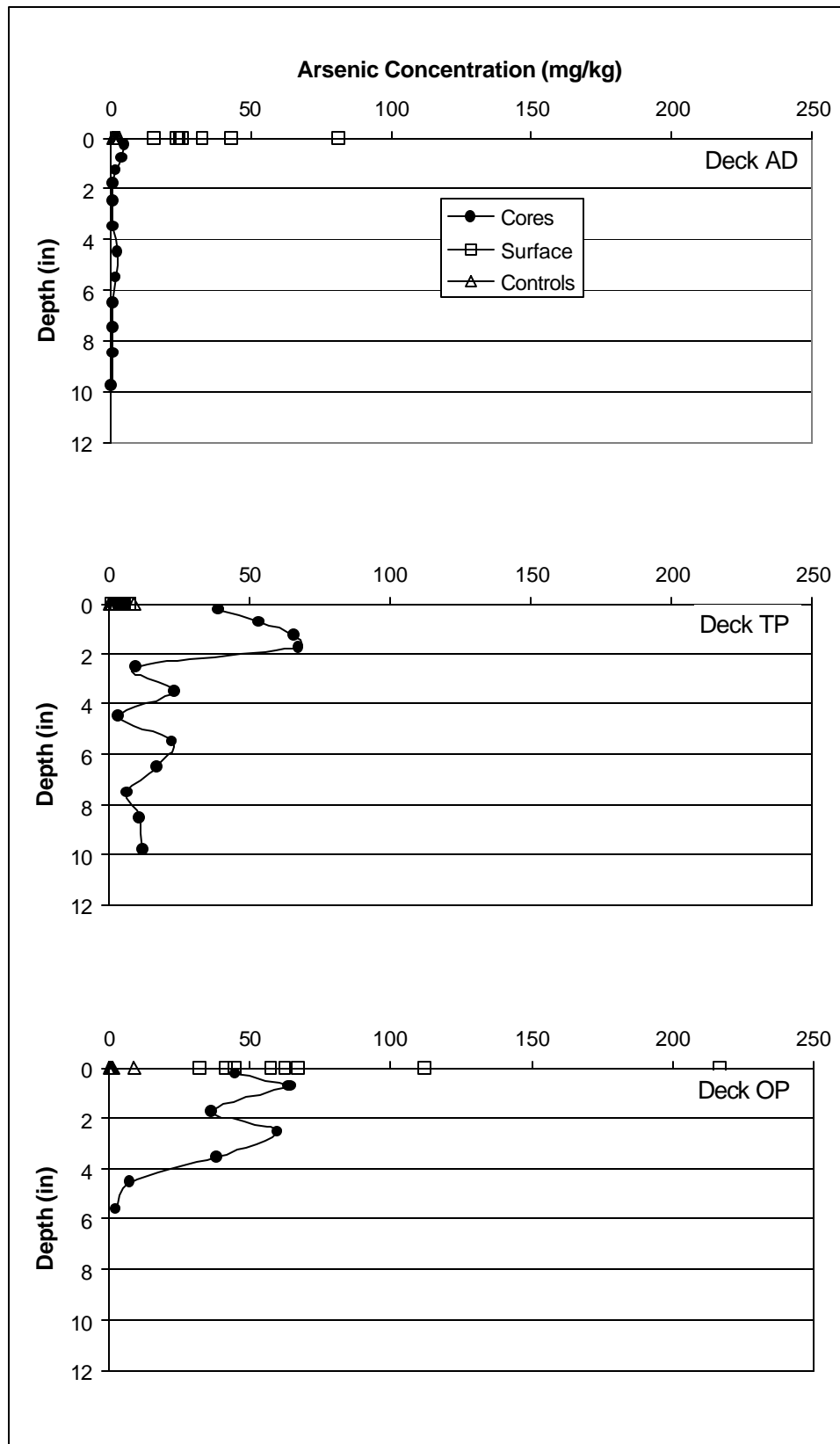


Figure A.30: Arsenic Concentrations as a Function of Depth Below the Miami Decks

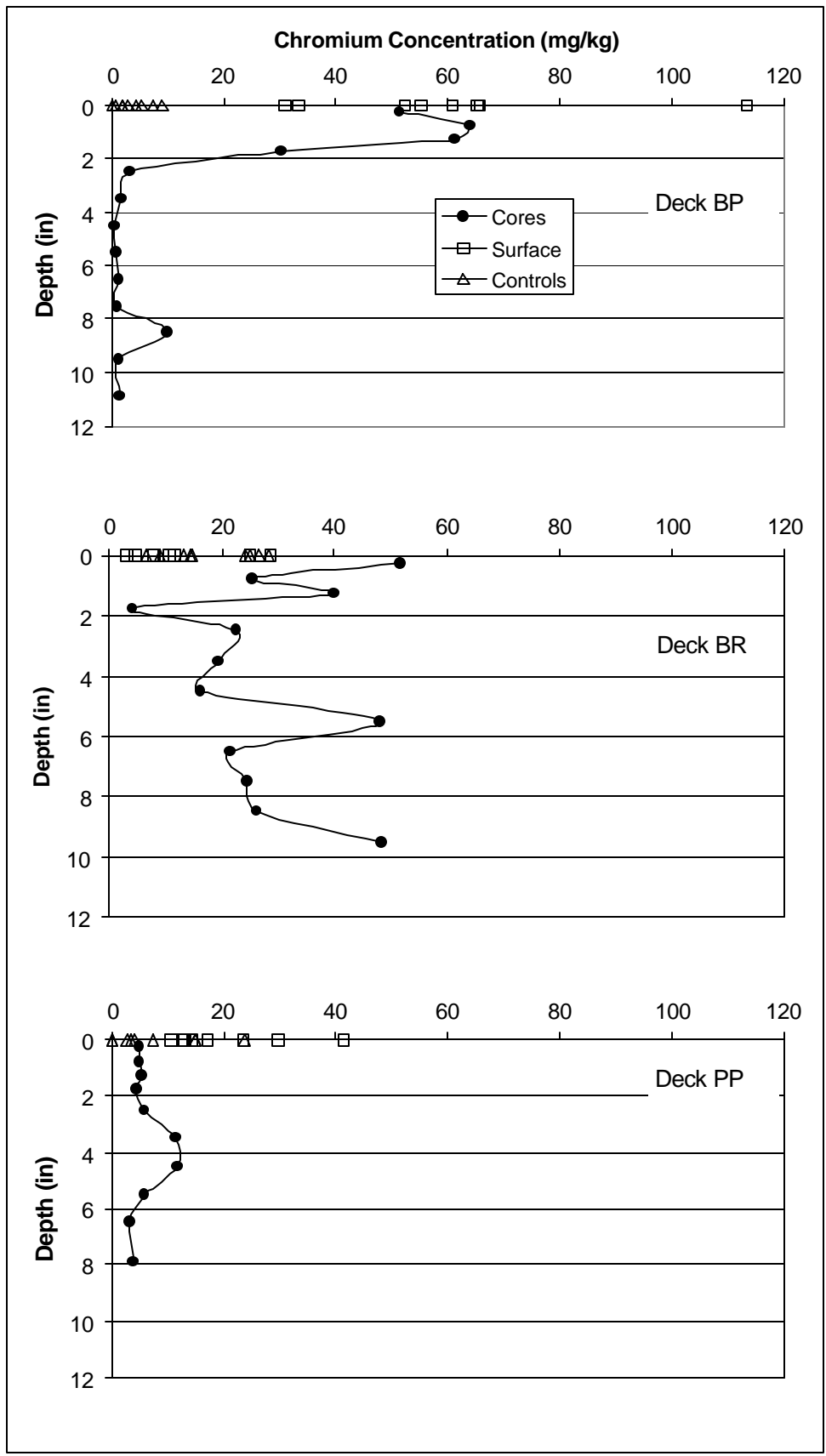


Figure A.31: Chromium Concentrations as a Function of Depth Below the Gainesville Decks

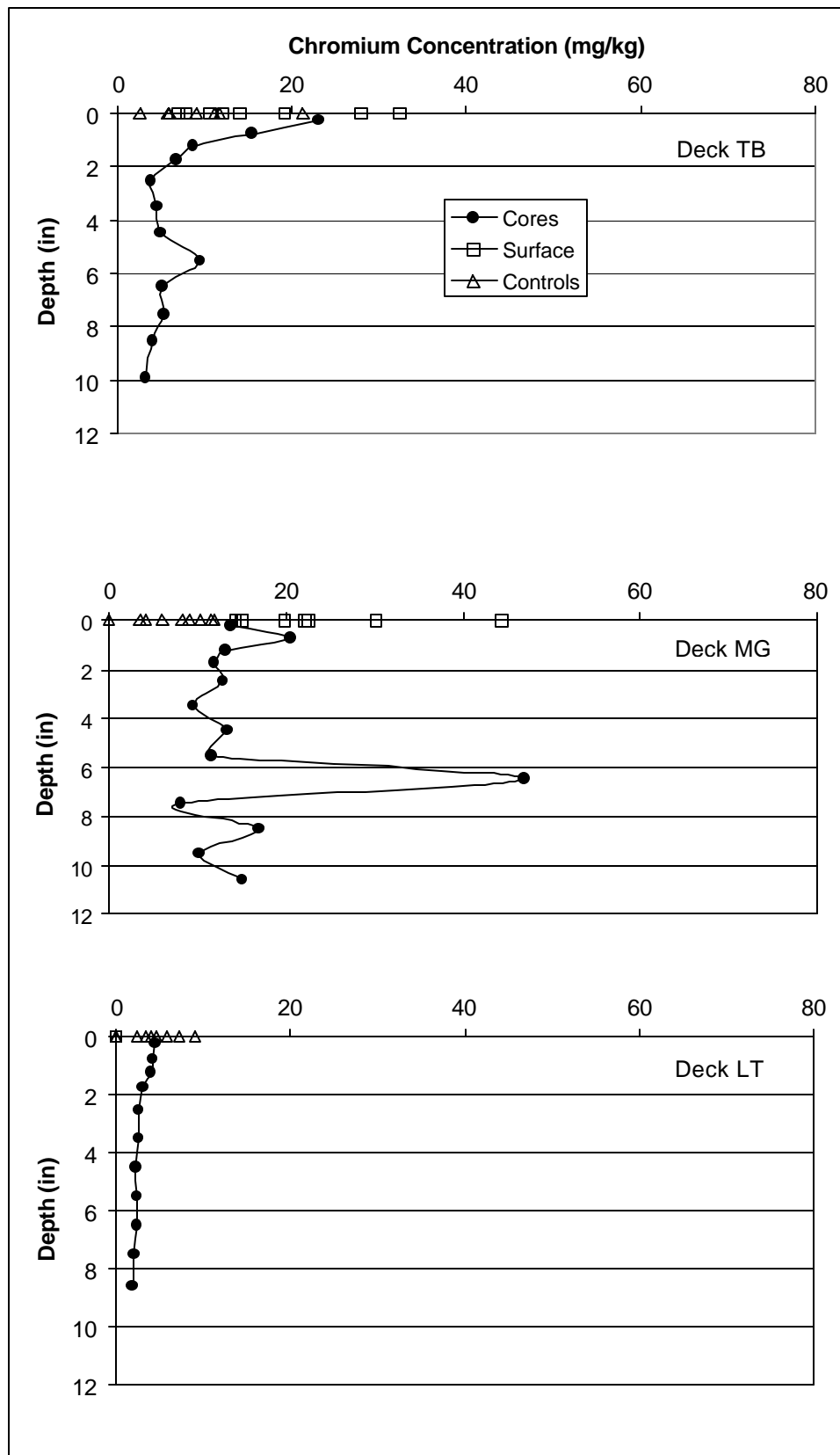


Figure A.32: Chromium Concentrations as a Function of Depth Below the Tallahassee Decks

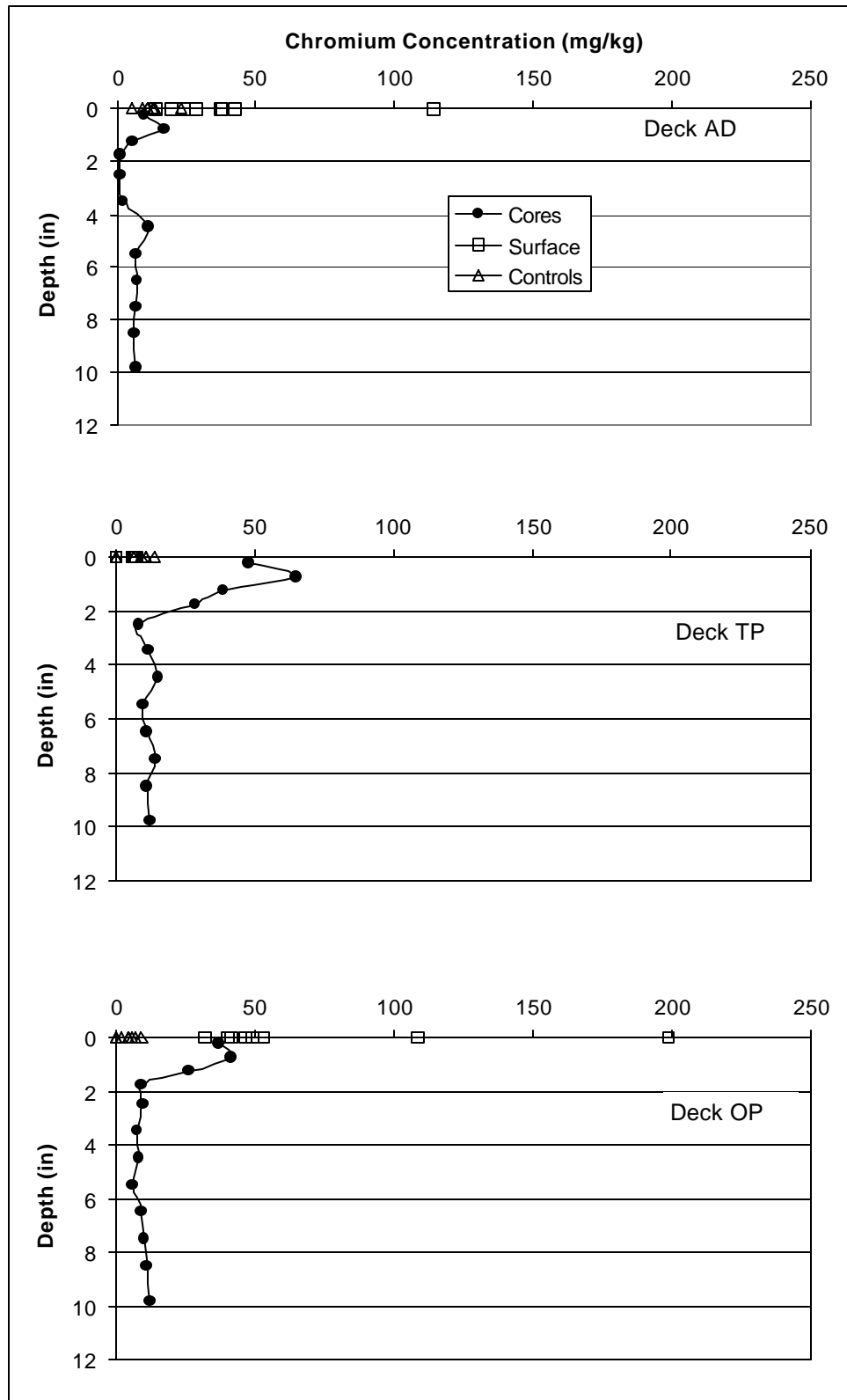


Figure A.33: Chromium Concentrations as a Function of Depth Below the Miami Decks

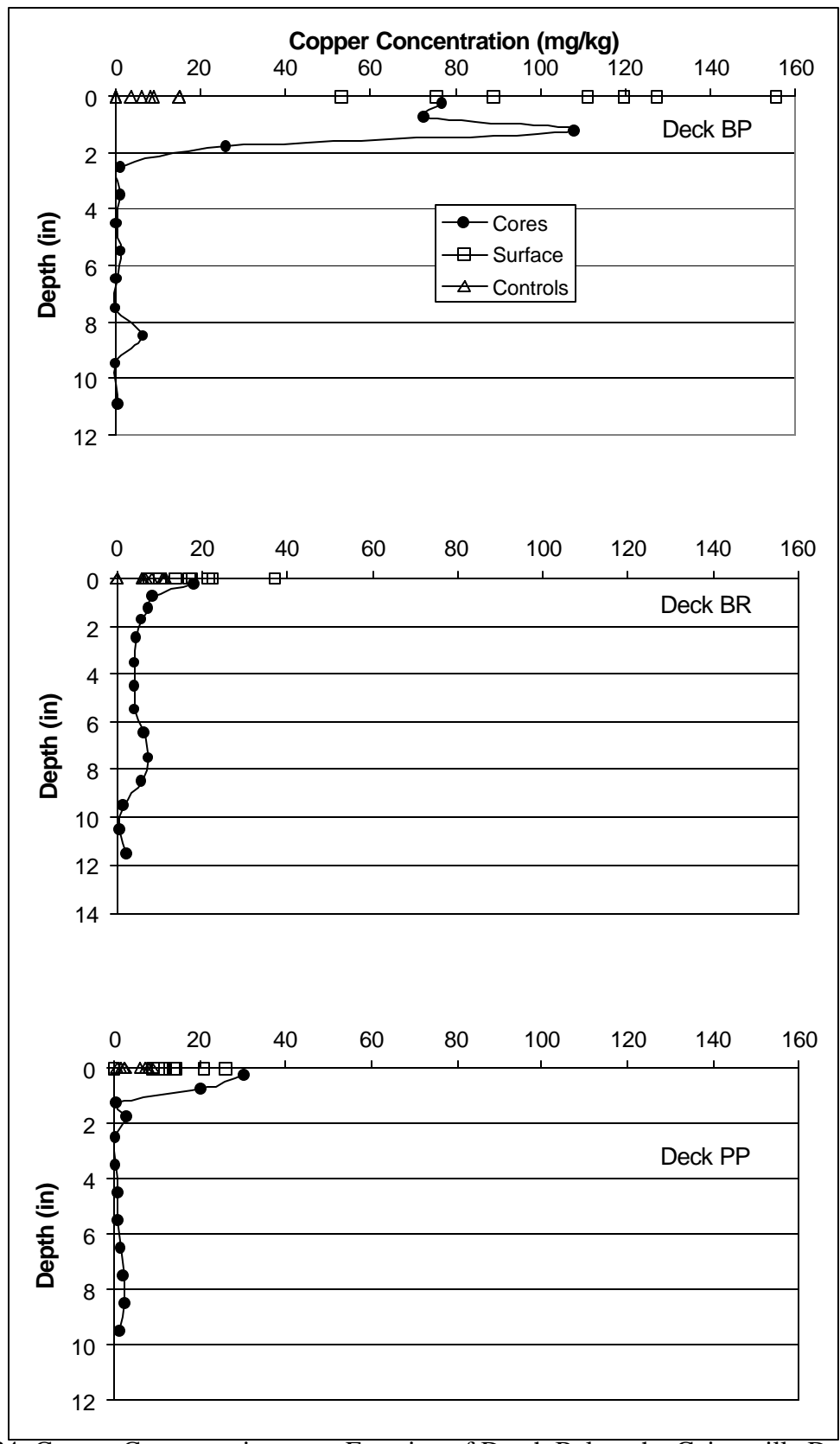


Figure A.34: Copper Concentrations as a Function of Depth Below the Gainesville Decks

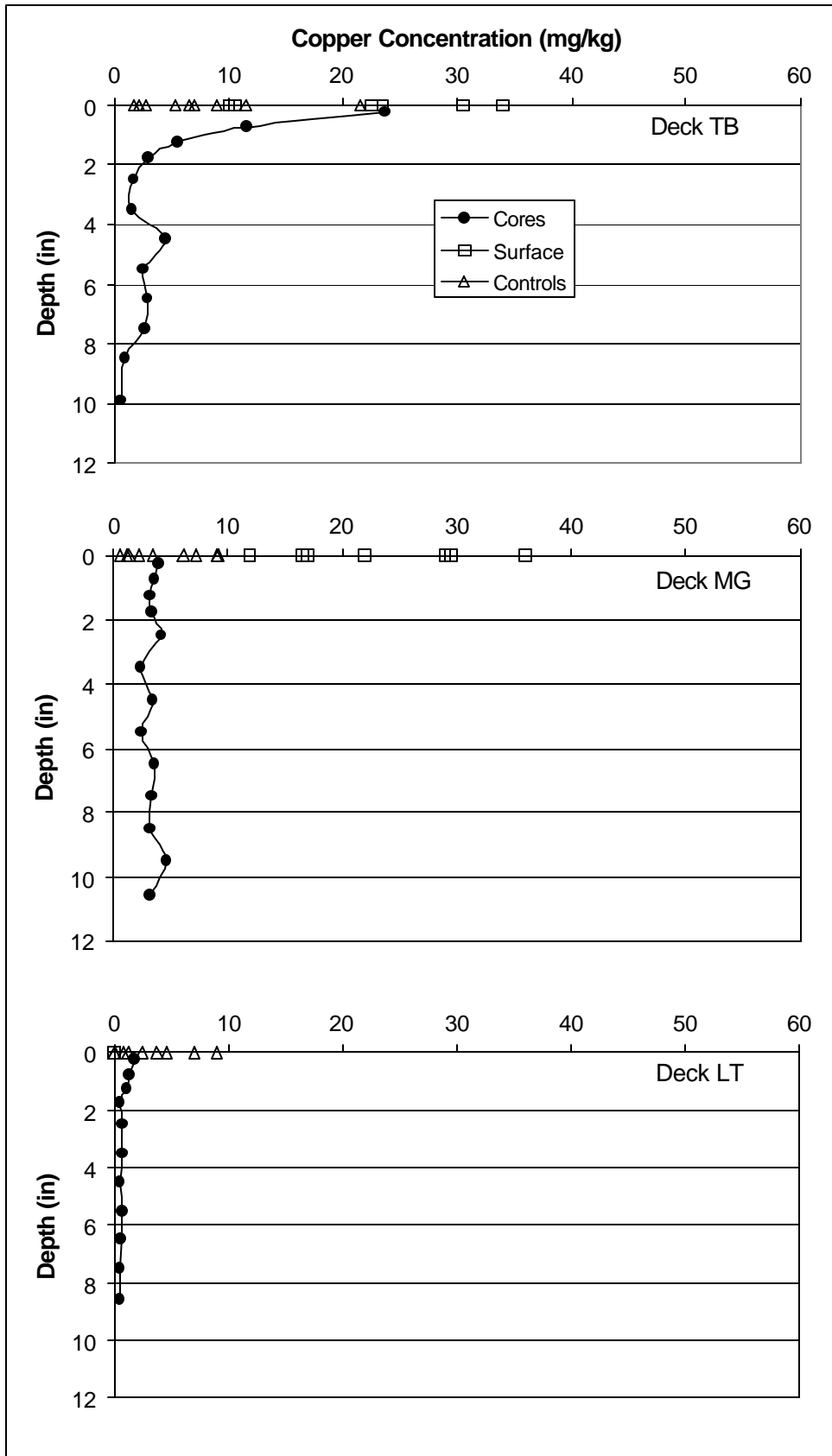


Figure A.35: Copper Concentrations as a Function of Depth Below the Tallahassee Decks



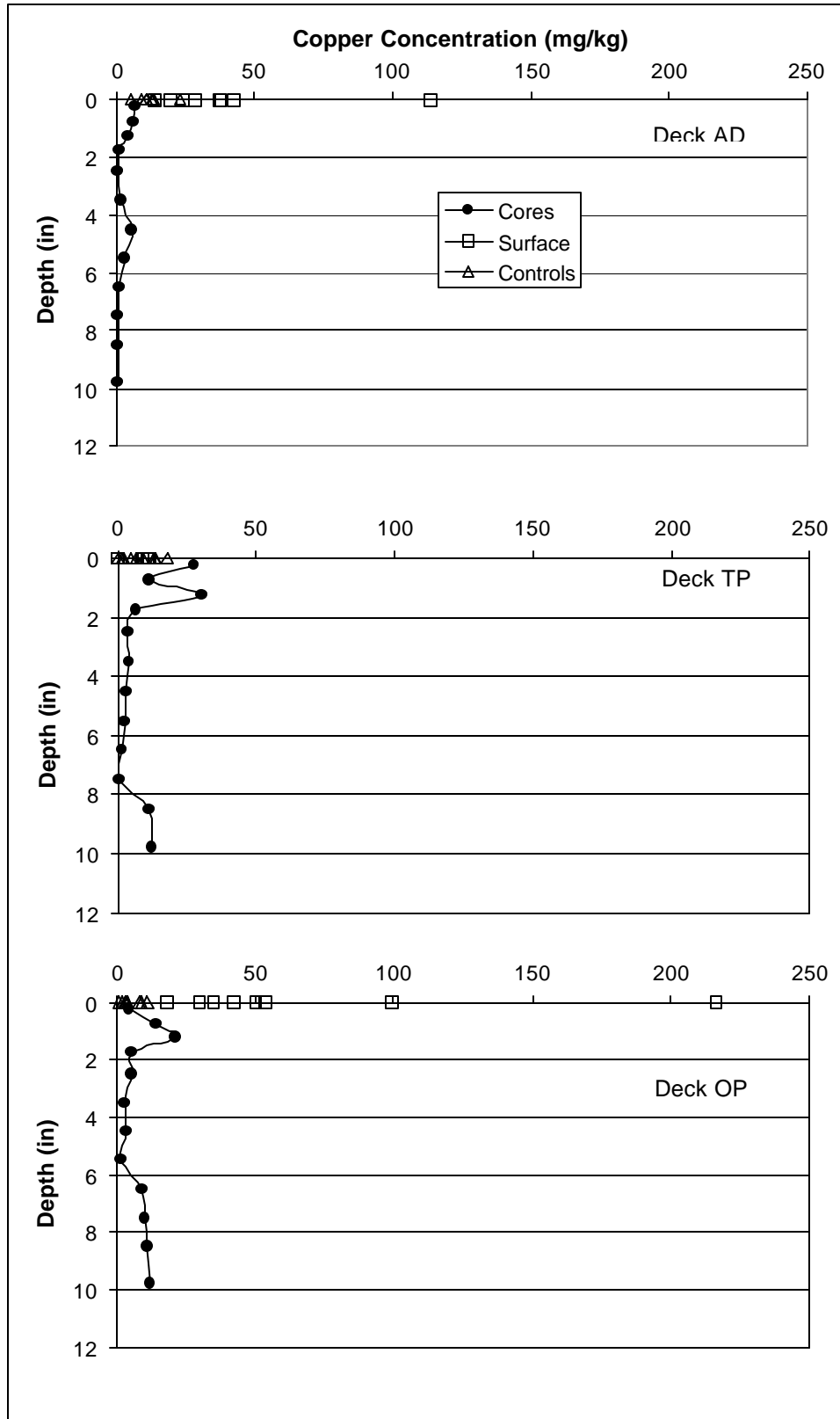


Figure A.36: Copper Concentrations as a Function of Depth Below the Miami Decks

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## **APPENDIX B**

# **BACK-UP INFORMATION FOR CCA-TREATED WOOD INVENTORY FOR FLORIDA**

<b>Major Market</b>	<b>1999 (10<sup>6</sup> ft<sup>3</sup>)</b>	<b>2000 (10<sup>6</sup> ft<sup>3</sup>)</b>	<b>2001 (10<sup>6</sup> ft<sup>3</sup>)</b>	<b>2002 (10<sup>6</sup> ft<sup>3</sup>)</b>	<b>2003 (10<sup>6</sup> ft<sup>3</sup>)</b>	<b>2004 (10<sup>6</sup> ft<sup>3</sup>)</b>
<b>Residential</b>						
Floor Framing	3.4	3.0	2.8	2.7	2.6	2.3
Wall Framing	6.3	5.7	5.4	5.4	5.2	4.8
Roof Framing	1.3	1.2	1.1	1.1	1.0	1.0
Trusses	1.6	1.4	1.3	1.3	1.3	1.2
New Decks	61.8	53.6	51.3	50.0	49.2	45.6
Wood Foundations	12.8	11.0	10.5	10.3	10.2	9.5
Misc. Structures	0.0	0.0	0.0	0.0	0.0	0.0
Int/Ext Fin	0.0	0.0	0.0	0.0	0.0	0.0
Subtotal	87.2	75.8	72.5	70.8	69.6	64.4
<b>Non-Residential</b>						
Floor Framing	0.5	0.5	0.5	0.5	0.4	0.4
Wall Framing	0.3	0.3	0.4	0.4	0.4	0.3
Roof Framing	0.6	0.6	0.6	0.6	0.6	0.5
Trusses	1.4	1.4	1.5	1.5	1.4	1.4
Glulam	0.5	0.5	0.5	0.5	0.5	0.5
Misc Structures	0.0	0.0	0.0	0.0	0.0	0.0
Int/Ext Finish	0.0	0.0	0.0	0.0	0.0	0.0
Subtotal	3.3	3.3	3.3	3.5	3.3	3.1
<b>Rural Construction</b>						
Posts	5.7	5.8	5.8	5.9	5.8	5.4
Headers	0.0	0.0	0.0	0.0	0.0	0.0
Girts & Purlins	0.0	0.0	0.0	0.0	0.0	0.0
Trusses	0.0	0.0	0.0	0.0	0.0	0.0
Misc. Framing	0.5	0.5	0.5	0.5	0.5	0.4
Subtotal	6.2	6.3	6.2	6.3	6.2	5.8
<b>Non-Building Construction</b>						
Marine	86.8	87.6	90.5	94.6	90.1	84.5
Highway	46.4	46.8	48.1	50.0	47.8	44.8
Subtotal	133.2	134.4	138.6	144.6	137.8	129.3
<b>All Construction Markets</b>						
Subtotal	229.9	219.7	220.7	225.2	216.9	202.6
<b>Industrial</b>						
Material Handling	17.1	17.6	18.0	18.5	18.9	19.1
Furniture	0.4	0.4	0.4	0.4	0.4	0.4
Subtotal	17.5	18.0	18.4	18.9	19.2	19.5

Table B.1: Projected Southern Pine Demand in Different Major Markets  
(From SFPA, Steven Bean, personal communication)

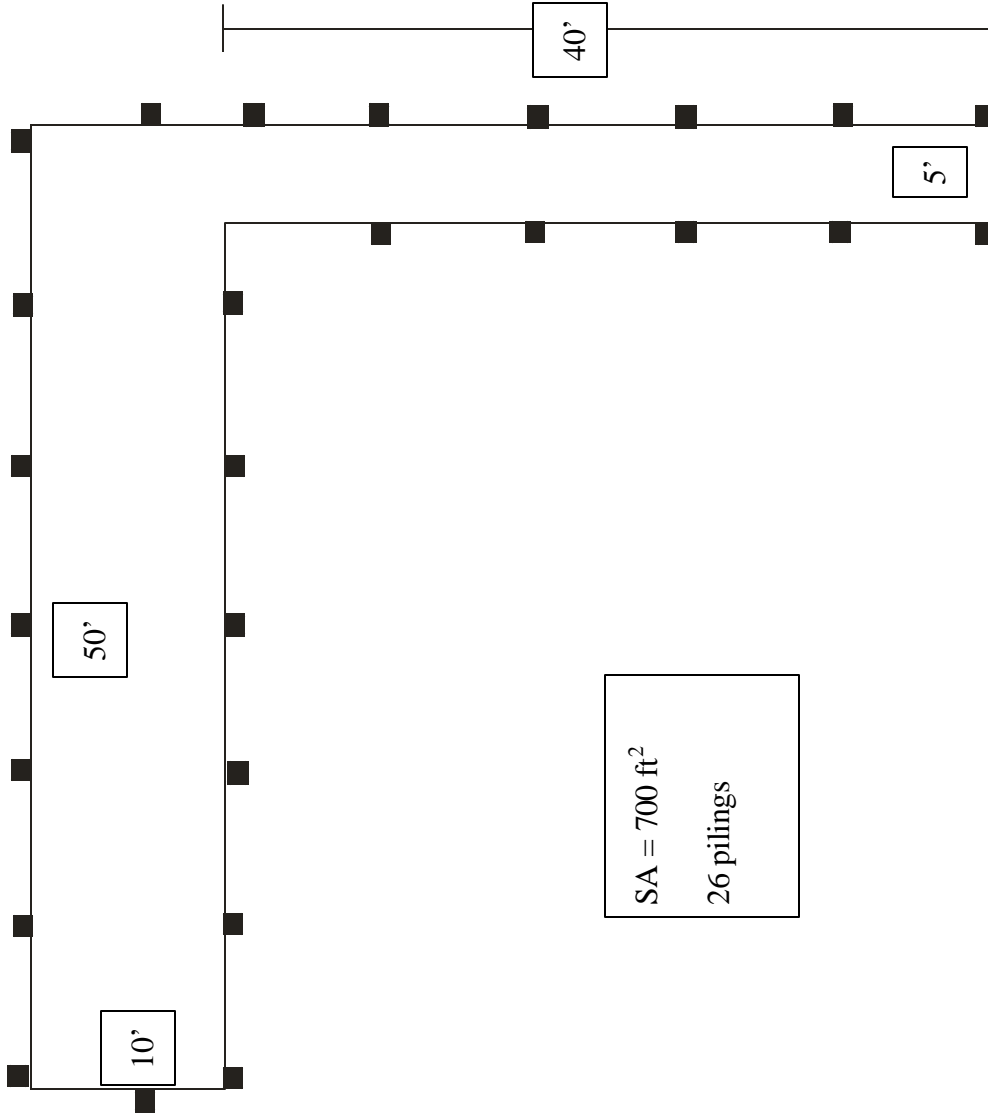
<b>Major Market</b>	<b>1999 (10<sup>6</sup> ft<sup>3</sup>)</b>	<b>2000 (10<sup>6</sup> ft<sup>3</sup>)</b>	<b>2001 (10<sup>6</sup> ft<sup>3</sup>)</b>	<b>2002 (10<sup>6</sup> ft<sup>3</sup>)</b>	<b>2003 (10<sup>6</sup> ft<sup>3</sup>)</b>	<b>2004 (10<sup>6</sup> ft<sup>3</sup>)</b>
<b>Repair &amp; Remodeling</b>						
Room Additions	2.6	2.6	2.6	2.6	2.5	2.6
Paneling	0.0	0.0	0.0	0.0	0.0	0.0
Attached Garages	0.4	0.4	0.4	0.4	0.4	0.4
Finish Basements	0.4	0.4	0.4	0.4	0.4	0.4
Decks	120.8	122.0	123.1	122.9	116.6	122.8
Remodel Other Rooms	0.0	0.0	0.0	0.0	0.0	0.0
Misc Home Projects	0.1	0.1	0.1	0.1	0.1	0.1
Remodel Kitchen/Bath	0.4	0.4	0.4	0.4	0.4	0.4
Finish Attic	0.0	0.0	0.0	0.0	0.0	0.0
Shelving	0.0	0.0	0.0	0.0	0.0	0.0
Subtotal	124.7	125.9	127.0	126.8	120.3	126.7
<b>Addition/Alterations apart from Structures</b>						
Fences	40.6	39.5	39.0	38.2	35.8	37.7
Sheds	1.2	1.2	1.2	1.2	1.1	1.2
Landscaping	70.5	71.8	72.5	71.6	68.0	71.6
Detached Garage	0.5	0.5	0.5	0.5	0.5	0.5
Misc Home Projects	0.1	0.1	0.1	0.1	0.1	0.1
Subtotal	112.7	113.1	113.3	111.6	105.5	111.0
<b>Major Replacements</b>						
Re-roof	0.1	0.1	0.1	0.1	0.1	0.1
Re-side	0.0	0.0	0.0	0.0	0.0	0.0
Replace Windows/Doors	0.0	0.0	0.0	0.0	0.0	0.0
Subtotal	0.1	0.1	0.1	0.1	0.1	0.1
<b>Maintenance/Repairs</b>						
Roof Repair	0.0	0.0	0.0	0.0	0.0	0.0
Misc Home Projects	0.9	0.9	0.9	0.9	0.8	0.9
Subtotal	0.9	0.9	0.9	0.9	0.8	0.9
<b>Total R/R Markets</b>						
Subtotal	238.4	240.0	241.3	239.3	226.7	238.7
<b>Export</b>						
Subtotal	9.0	9.4	9.8	10.2	10.6	11.0
<b>Grand Total</b>						
	494.7	487.0	490.1	493.6	473.5	471.8

Table B.1 (con'd): Projected Southern Pine Demand in Different Major Markets  
(From SFPA, Steven Bean, personal communication)

Year	Utility Poles			
	Method 1 (10 <sup>6</sup> ft <sup>3</sup> )		Method 2 (10 <sup>6</sup> ft <sup>3</sup> )	
	Production	Disposed	Production	Disposed
1960	0.00	0.00	0.00	0.00
1961	0.01	0.00	0.01	0.00
1962	0.01	0.00	0.01	0.00
1963	0.01	0.00	0.01	0.00
1964	0.01	0.00	0.01	0.00
1965	0.01	0.00	0.01	0.00
1966	0.03	0.00	0.03	0.00
1967	0.04	0.00	0.03	0.00
1968	0.05	0.00	0.04	0.00
1969	0.15	0.00	0.12	0.00
1970	0.13	0.00	0.11	0.00
1971	0.09	0.00	0.07	0.00
1972	0.10	0.00	0.08	0.00
1973	0.10	0.00	0.09	0.00
1974	0.11	0.00	0.09	0.00
1975	0.08	0.00	0.07	0.00
1976	0.07	0.00	0.06	0.00
1977	0.21	0.01	0.18	0.00
1978	0.37	0.01	0.31	0.01
1979	0.45	0.01	0.37	0.01
1980	0.53	0.01	0.44	0.01
1981	0.52	0.01	0.43	0.01
1982	0.80	0.02	0.66	0.02
1983	1.06	0.03	0.88	0.02
1984	0.83	0.02	0.68	0.02
1985	0.96	0.02	0.79	0.02
1986	1.11	0.03	0.92	0.02
1987	0.97	0.02	0.80	0.02
1988	0.96	0.02	0.79	0.02
1989	0.85	0.02	0.70	0.02
1990	0.79	0.02	0.65	0.02
1991	0.95	0.02	0.78	0.02
1992	1.10	0.03	0.91	0.02
1993	1.25	0.03	1.03	0.03
1994	2.08	0.05	1.72	0.04
1995	2.41	0.06	1.99	0.05
1996	1.58	0.04	1.30	0.03
1997	1.45	0.04	1.20	0.03
1998	1.45	0.04	1.20	0.03
1999	1.26	0.03	1.04	0.03
2000	1.24	0.03	1.03	0.03
SUM	26.19	0.66	21.63	0.54

Table B.2: Production and Disposal Estimated for CCA-Treated Utility Poles in Florida

# Alachua County – Typical Dock Construction



Alachua County – Typical Dock Construction (con'd)

**Pilings** (nominal dimensions 4 x 8 → 3.5 x 7.25)  
 $(26 \text{ piles}) \times \left( \frac{3.5 \text{ ft}}{12} \times \frac{7.25 \text{ ft}}{12} \right) \times 20 \text{ ft} = 92 \text{ ft}^3$

RET Level:  
 $(0.8 \text{ lb/ft}^3) (92 \text{ ft}^3) = \underline{73 \text{ lb CCA}}$

**Decking**  
 $\text{SA} \times \text{thickness} = 700 \text{ ft}^2 \times \left( \frac{1\frac{1}{2} \text{ ft}}{12} \right) = 87.5 \text{ ft}^3$

RET Level:  
 $(0.25 \text{ lb/ft}^3) (87.5 \text{ ft}^3) = \underline{22 \text{ lb CCA}}$

**Joists** (nominal dimensions 2 x 6 → 1.5 x 5.5)  
 $50 + 10 + 45 + 40 + 5 + 50 + 50 = 250 \text{ ft}$

$$\left( \frac{1.5 \text{ ft}}{12} \times \frac{5.5 \text{ ft}}{12} \right) (250 \text{ ft}) = 14 \text{ ft}^3$$

RET Level:  
 $(0.25 \text{ lb/ft}^3) (14 \text{ ft}^3) = \underline{4 \text{ lb CCA}}$

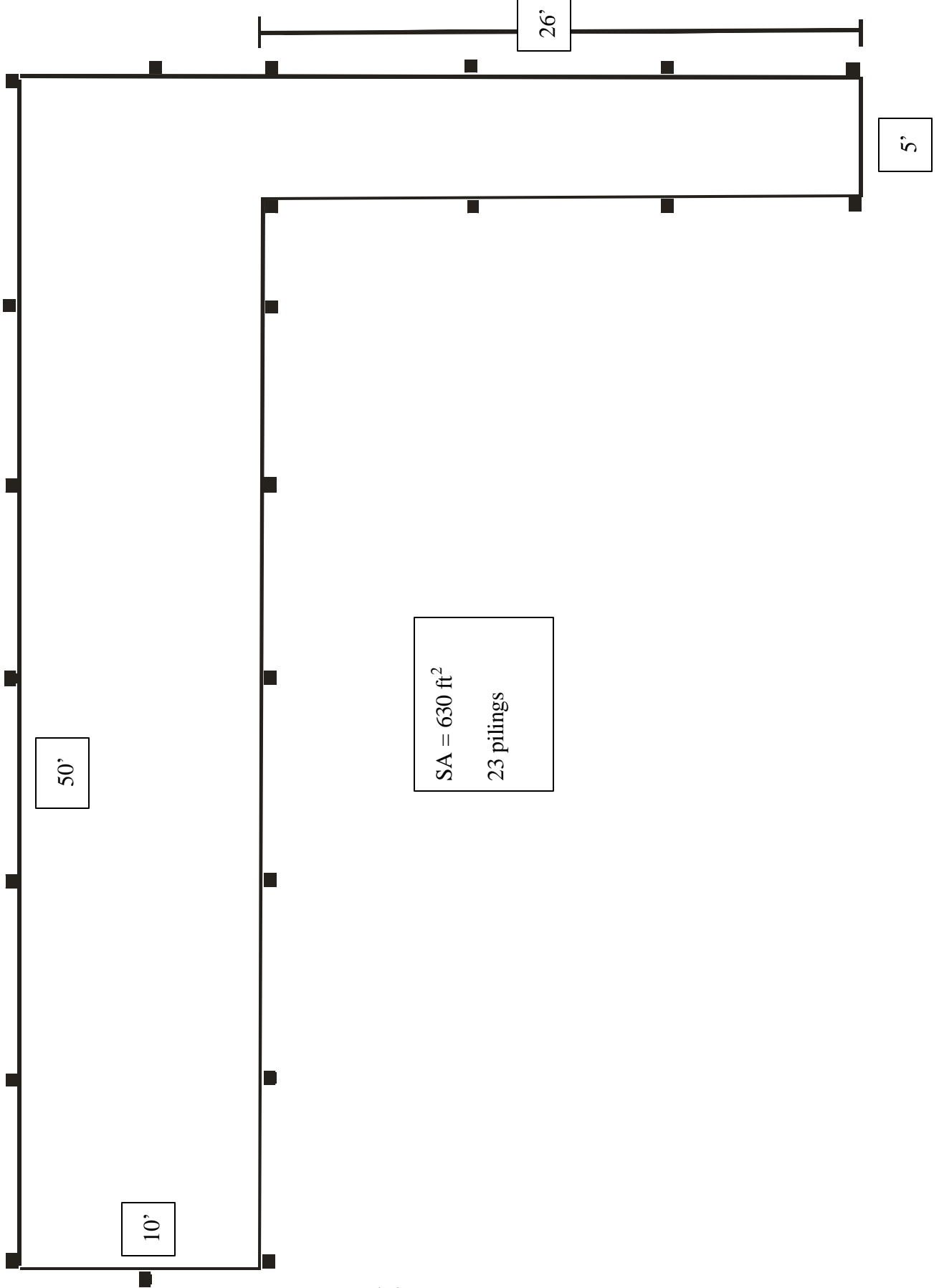
Total CCA per dock:  
 $73 + 22 + 4 = \underline{99 \text{ lb CCA}}$

# docks in Alachua County:  $486 * 0.87 = 423$   
 $\setminus 423 \times 99 \text{ lb CCA} = 41,877 \text{ lb CCA}$

per capita:  $\frac{41,877}{198,000} = \boxed{0.211 \text{ lb CCA/ person}}$



**Leon County – Typical Dock Construction**



**Leon County – Typical Dock Construction (con'd)**

**Pilings** (Nominal dimensions 4 x 8 → 3.5 x 7.25)  
 (23 piles) x (  $\frac{3.5}{12}$  ft x  $\frac{7.25}{12}$  ft) x 20 ft = 81 ft<sup>3</sup>

RET Level:  
 (0.8 lb/ft<sup>3</sup>) (81 ft<sup>3</sup>) = 65 lb CCA

**Decking**

SA x thickness = 630 ft<sup>2</sup> x  $\frac{1\frac{1}{2}}{12}$  ft  
 = 79 ft<sup>3</sup>

RET Level:  
 (0.25 lb/ft<sup>3</sup>) (79 ft<sup>3</sup>) = 20 lb CCA

**Joists** (Nominal dimensions 2 x 6 → 1.5 x 5.5)  
 50 + 10 + 45 + 26 + 5 + 36 + 50 = 222 ft  
 (  $\frac{1.5}{12}$  ft) x (  $\frac{5.5}{12}$  ft) (222 ft) = 13 ft<sup>3</sup>

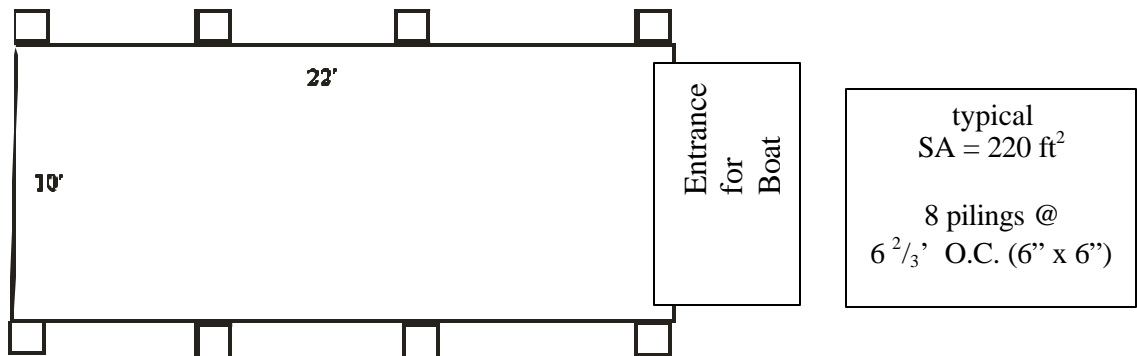
RET Level:  
 (0.25 lb/ft<sup>3</sup>) (13 ft<sup>3</sup>) = 3 lb CCA

Total CCA per dock = 65 + 20 + 3 = 88 lb CCA

# CCA-treated docks in Leon County: 450 \* 0.95 = 428

\ 428 x 88 lb = 37,664 lbs CCA from docks

**Boat Shed Details, Taken from some typical drawings from permits**



**Leon County – Typical Dock Construction (con'd)**

**Pilings** (Nominal dimensions 6 x 6 → 5.5 x 5.5)

$$(8 \text{ piles}) \times \left( \frac{5.5}{12} \times \frac{5.5}{12} \text{ ft} \right) \times 30 \text{ ft} = 50 \text{ ft}^3$$

RET Level:

$$(0.8 \text{ lb/ft}^3) (50 \text{ ft}^3) = \underline{40 \text{ lb CCA}}$$

**Beams** (Nominal dimensions 4 x 10 → 4.5 x 9.25)

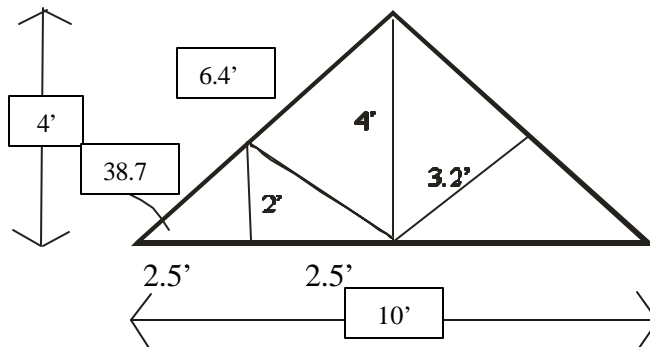
4 beams @ 4" x 10"

$$(4 \text{ beams}) \times \left( \frac{3.5}{12} \times \frac{9.25}{12} \right) \times 22 \text{ ft} = 20 \text{ ft}^3$$

RET Level:

$$(0.4 \text{ lb/ft}^3) (20 \text{ ft}^3) = \underline{8 \text{ lb CCA}}$$

**Trusses**



ft<sup>3</sup> per truss: (Nominal dimensions 2 x 4 → 1.5 x 3.5)

$$6.4 + 6.4 + 10 + 3.2 + 3.2 + 4 = 33.2 \text{ ft}$$

$$(33.2 \text{ ft}) \times \left( \frac{1.5}{12} \times \frac{3.5}{12} \right) = 1.21 \text{ ft}^3/\text{truss.}$$

$$(4 \text{ trusses}) \times (1.21 \text{ ft}^3/\text{truss}) = 4.8 \text{ ft}^3$$

RET Level:

$$(0.4 \text{ lb/ft}^3) \times (4.8 \text{ ft}^3) = \underline{2 \text{ lb CCA}}$$

$$\text{Total CCA per boathouse} = 40 + 8 + 2 = \underline{50 \text{ lbs CCA}}$$

$$\# \text{ CCA-treated boatsheds in Leon County: } 149 \times 0.95 = 142$$

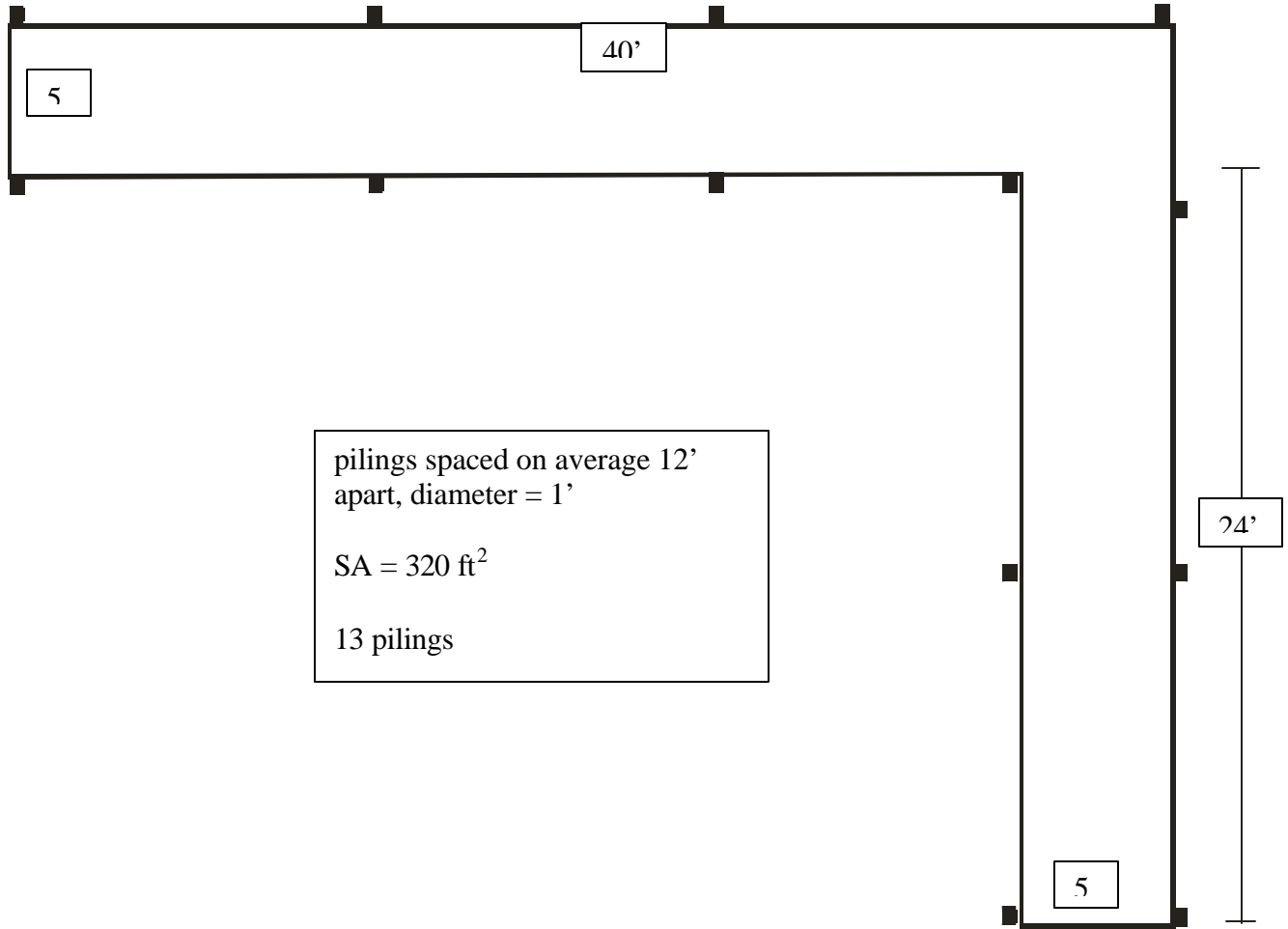
$$\text{Total CCA from boatsheds} = 50 \text{ lbs/shed} \times 142 \text{ sheds} = 7,100 \text{ lb CCA}$$

Total CCA in Leon:

$$\text{Total docks} + \text{Total boatsheds} = 37,664 \text{ lb} + 7,100 \text{ lb} = \underline{44,764 \text{ lbs CCA}}$$

$$\text{per capita: } \frac{44,764}{216,000} = \underline{0.207 \text{ lb CCA/person}}$$

# Miami-Dade County – Typical Dock Construction



## Miami-Dade County – Typical Dock Construction (con'd)

### *Pilings*

$$(13 \text{ piles}) \times \left(\pi \frac{(1^2)}{4} \text{ ft}\right) \times 20\text{ft} = 204 \text{ ft}^3$$

RET Level:

$$(2.5 \text{ lb/ft}^3) (204 \text{ ft}^3) = \underline{511 \text{ lbs CCA}}$$

### *Decking*

$$\text{SA} \times \text{thickness} = 320 \text{ ft}^2 \times \frac{1 \frac{1}{2}}{12} \text{ ft} = 40 \text{ ft}^3$$

RET Level:

$$0.6 \text{ lb/ft}^3 \times 40 \text{ ft}^3 = \underline{24 \text{ lb CCA}}$$

### *Joists* (Nominal dimensions 2 x 6 → 1.5 x 5.5)

$$40 + 5 + 35 + 24 + 5 + 29 = 138 \text{ ft}$$
$$\left(1 \frac{5}{12} \text{ ft} \times 5 \frac{5}{12} \text{ ft}\right) (138 \text{ ft}) = 8 \text{ ft}^3$$

RET Level:

$$(0.6 \text{ lb/ft}^3) (8 \text{ ft}^3) = \underline{5 \text{ lb CCA}}$$

Total CCA typical dock:

$$511 + 24 + 5 = \underline{540 \text{ lbs CCA}}$$

# CCA-treated docks in Dade:  $6000 \times 0.65 = 3,900$

$$3,900 \times 540 \text{ lb} = 2,106,000 \text{ lb CCA}$$

CCA per capita:

$$\frac{2,106,000}{2,180,000} = \boxed{0.970 \text{ lb CCA/person}}$$

County	Class <sup>a</sup>	Population	ft <sup>3</sup> of CCA treated wood per county	tons CCA per county	tons As per county
Alachua	3	198484	82051	21	5
Baker	3	21181	8756	2	0
Bay	1	147958	66703	72	16
Bradford	3	24872	10282	3	1
Brevard	1	470365	212053	228	50
Broward	1	1535468	692228	745	164
Calhoun	2	12436	4874	1	0
Charlotte	1	136992	61760	66	15
Citrus	1	116111	52346	56	12
Clay	2	141353	55401	15	3
Collier	1	207029	93334	100	22
Columbia	3	53738	22215	6	1
Dade	1	2175634	980832	1055	232
Desoto	3	24636	10184	3	1
Dixie	1	12919	5824	6	1
Duval	1	738483	332927	358	79
Escambia	1	282432	127328	137	30
Flagler	1	49110	22140	24	5
Franklin	1	9978	4498	5	1
Gadsden	3	44077	18221	5	1
Gilchrist	3	14056	5811	1	0
Glades	2	8693	3407	1	0
Gulf	1	13562	6114	7	1
Hamilton	2	12785	5011	1	0
Hardee	3	21017	8688	2	0
Hendry	3	29463	12180	3	1
Hernando	1	128482	57923	62	14
Highlands	2	74795	29315	8	2
Hillsborough	1	940484	423994	456	100
Holmes	3	18761	7756	2	0
Indian River	1	100253	45197	49	11
Jackson	3	44549	18416	5	1
Jefferson	3	13090	5411	1	0
Lafayette	3	6477	2678	1	0
Lake	2	209812	82233	22	5
Lee	1	400542	180575	194	43
Leon	2	215926	84629	22	5
Levy	1	32386	14600	16	3
Liberty	2	6703	2627	1	0

Table B.3: Estimated Volume of CCA-Treated Wood, CCA Chemical, and Arsenic Per County Associated with Marine and Freshwater Docks

County	Class	Population	ft <sup>3</sup> of CCA treated wood per county	tons CCA per county	tons As per county
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Madison	3	17919	7407	2	0
Manatee	1	243531	109790	118	26
Marion	3	245975	101683	26	6
Martin	1	118117	53250	57	13
Monroe	1	79941	36039	39	9
Nassau	1	56811	25612	28	6
Okaloosa	1	170049	76662	82	18
Okeechobee	2	32386	12693	3	1
Orange	2	817206	320293	85	19
Osceola	2	150596	59024	16	3
Palm Beach	1	1049420	473105	509	112
Pasco	1	330704	149090	160	35
Pinellas	1	878499	396050	426	94
Polk	2	457347	179251	47	10
Putnam	2	70215	27520	7	2
Santa Rosa	1	120952	54528	59	13
Sarasota	1	306546	138199	149	33
Seminole	2	357390	140074	37	8
St. Johns	1	119685	53957	58	13
St. Lucie	1	181850	81983	88	19
Sumter	3	42754	17674	5	1
Suwannee	2	32972	12923	3	1
Taylor	1	19049	8588	9	2
Union	3	12720	5258	1	0
Volusia	1	425601	191692	206	45
Wakulla	1	19179	8646	9	2
Walton	1	38124	17187	18	4
Washington	3	20614	8522	2	0
<b>SUM</b>			<b>6627222</b>	<b>6012</b>	<b>1323</b>

<sup>a</sup> Dade = Class 1 (primarily coastal), Leon = Class 2 (large lakes),  
Alachua = Class 3 (no major water sources)

Table B.3 (con'd): Estimated Volume of CCA-Treated Wood, CCA Chemical, and Arsenic Per County Associated with Marine and Freshwater Docks

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## **APPENDIX C**

### **ADDITIONAL GRAPHS AND FIGURES FOR CCA-TREATED WOOD LEACHING**

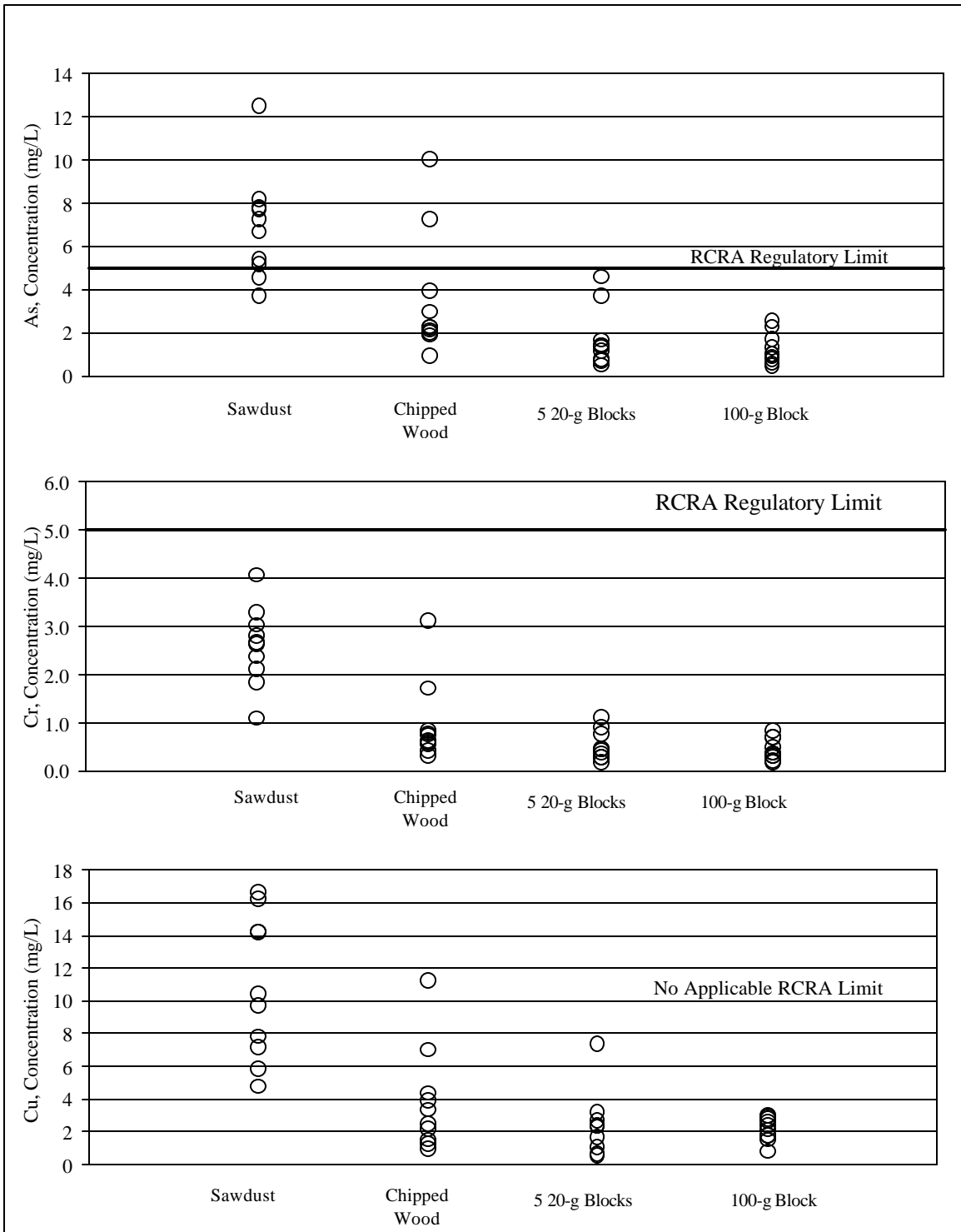


Figure C.1: Particle Size Effect on Arsenic (Above), Copper (Middle), and Chromium (Lower) Leachability from CCA-Treated Wood Using the TCLP

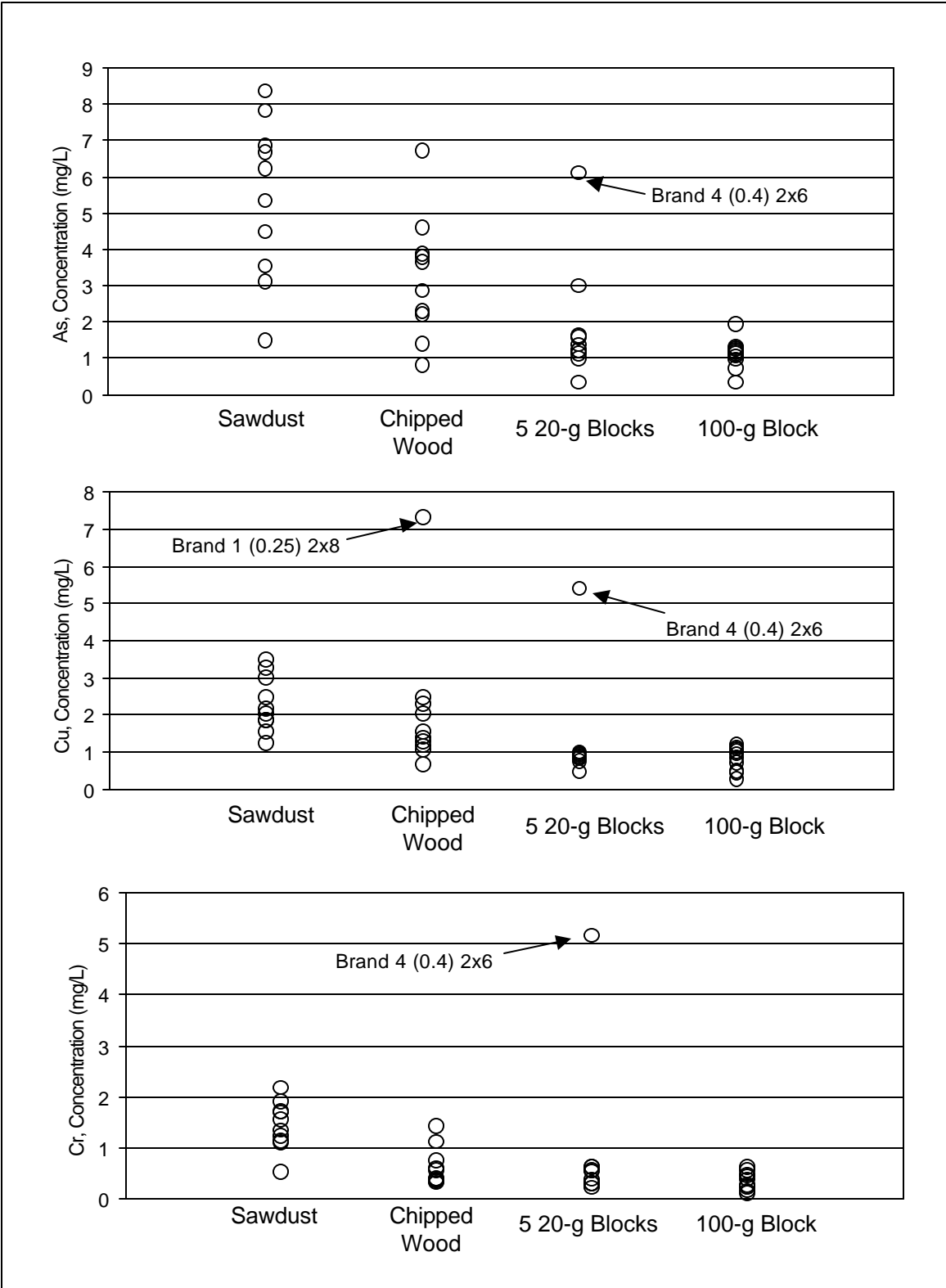


Figure C.2: Particle Size Effect on As (Above), Copper (Middle), and Chromium (Lower) Leachability from CCA-Treated Wood Using the SPLP

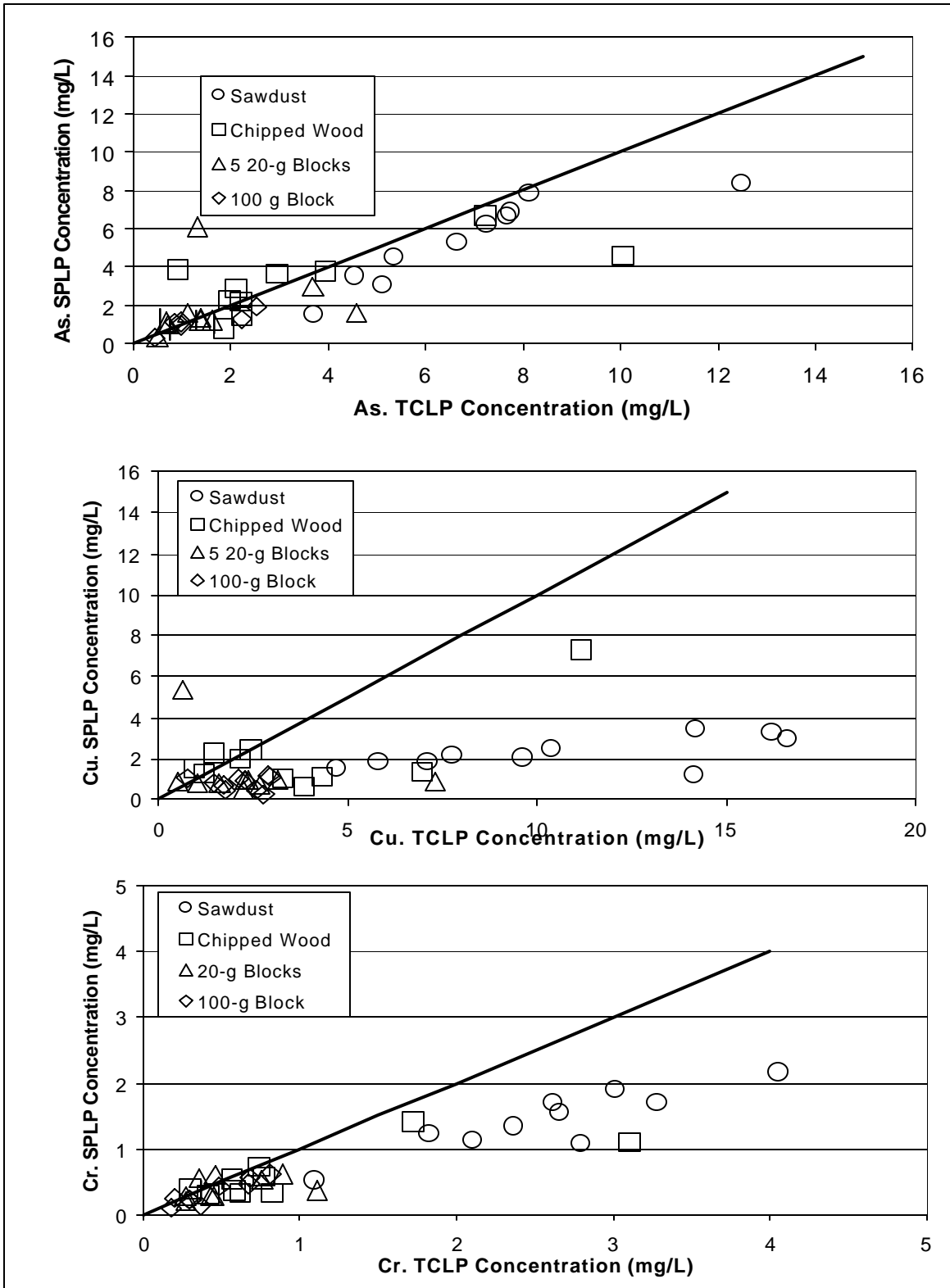


Figure C.3: Comparison of Arsenic (upper), Copper (Middle), and Chromium (Lower) Leachability Using SPLP and TCLP Extraction Fluids

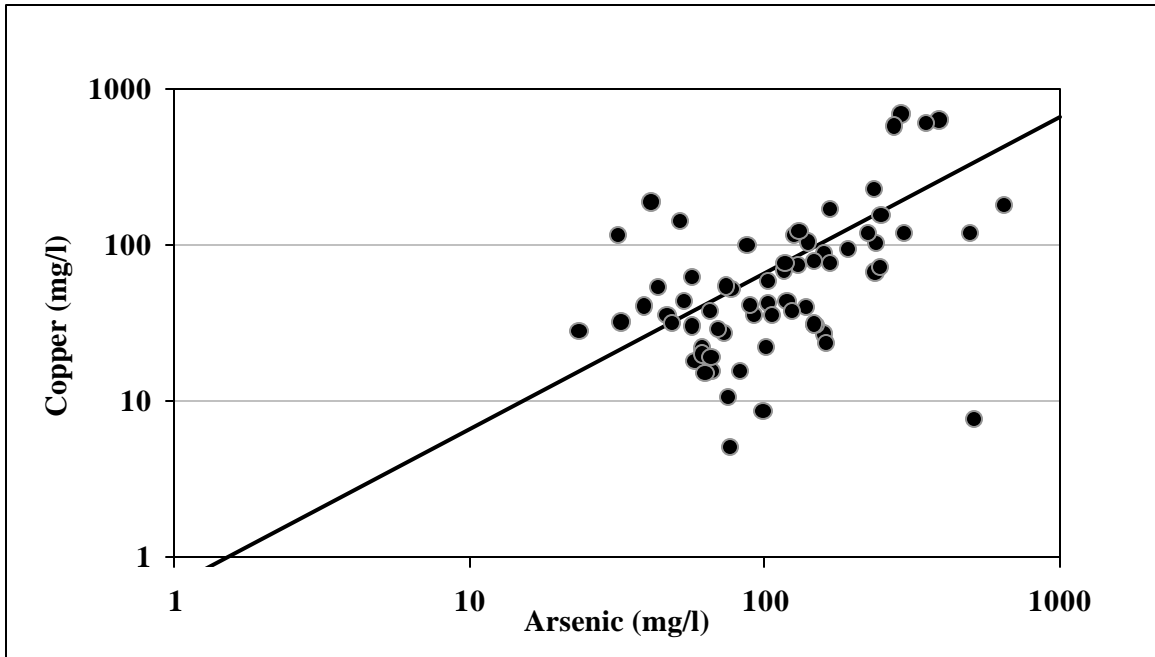


Figure C.4: Comparison of Copper and Arsenic in Leachates

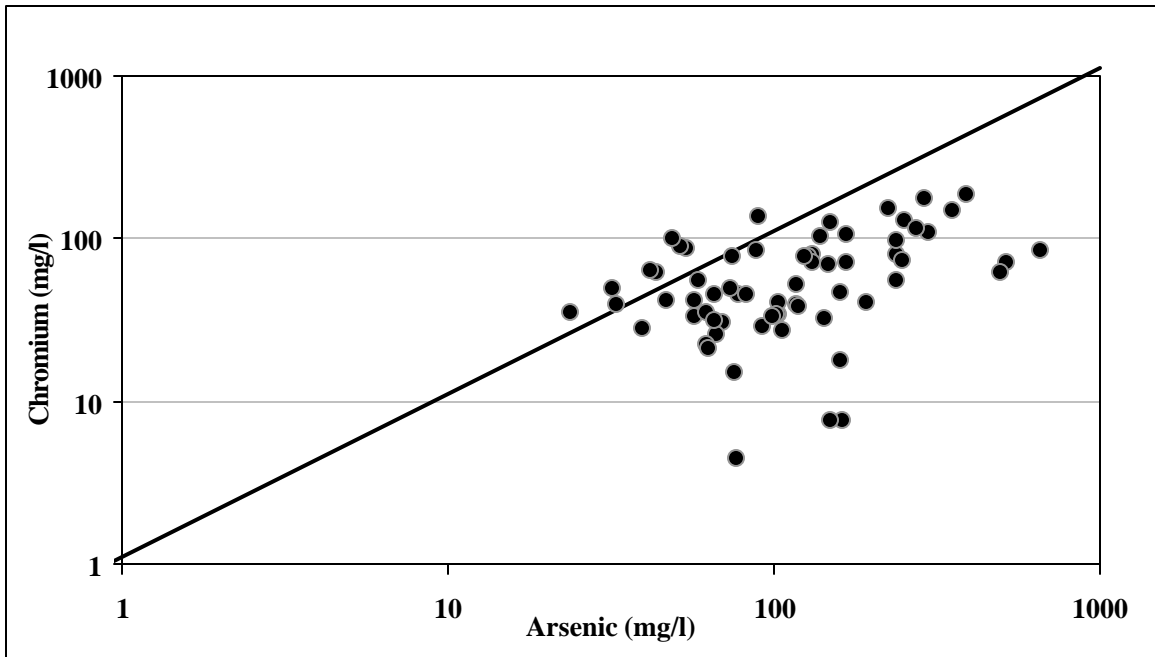


Figure C.5: Comparison of Chromium and Arsenic in Leachates

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## **APPENDIX D**

### **LIST OF TECHNICAL ADVISORY GROUP MEMBERS AND MEETING ATTENDEES**

Name/Title	Organization	Address	Telephone	email
Kevin Archer, Ph.D. Product Development Manager	Chemical Specialties Inc.	One Woodlawn Green Suite 250 200 East Woodlawn Road Charlotte, NC 28217	(704)522-0825 (800)421-8661 Fax: (704)527-8232	kevina@chemspec.com <a href="http://www.chemspec.com">http://www.chemspec.com</a> <a href="http://www.treatedwood.com">http://www.treatedwood.com</a>
Phil Badger	General Bioenergy, Inc.	P.O. Box 26 Florence, Alabama 35631-0026	(256)740-5634 Fax: (256)740-5530	pbadger@ bioenergyupdate.com
Lee Casey, Chief Environmental Compliance Division	Metro-Dade County Dept. of Solid Wste. Mgt.	8675 NW 53 Street Suite 201 Miami, FL 33166	(305)594-1670 Fax:(305)594-1581	le1@co.miami-dade.fl.us
Kenneth E. Cogan Plant Manager Alternate: Bob Gruber, Vice President Regulatory Affairs	Hickson Corporation	1579 Koppers Road Conley, GA 30027  1955 Lake Park Dr., Suite 250 Smyrna, GA 30080	(404)363-6300 Fax: (404)363-8585  (770)801-6600 Fax: (770)801-8170	ken_cogan@hicksoncorp. com  bob_gruber@hicksoncorp.com
David Dee, Attorney  Alternate: Pete Rosendahl, VP Environmental Relations	Landers & Parsons  Florida Crystals Incorporated	310 West College Avenue P.O. Box 271 Tallahassee, FL 32302 316 Royal Poinciana Plaza Palm Beach, FL 33480	(850)681-0311 Fax: 850-224-5595  (561)655-6303 Fax:(561)659-9846	ddee@landersandparsons.com
Keith D. Drescher, Environmental Specialist Alternate: Russel S. Ketchem, Corporate Recycling Coordinator	Florida Power & Light	2455 Port West Blvd., Bldg. A West Palm Beach, FL 33407	(561)845-4968 (561)845-3366 Fax: (561)845-3308 (561)845-4976 Fax: (561)845-4889	keith_drescher@ email.fpl.com  Russell_S_Ketchem@FPL.Com
Jeffrey Fehrs, P.E. Consultant	Jeffrey Fehrs, Consultant	20 Hideaway Lane Williston, VT 05495	(802)865-3480 Fax: (802)872-8255	jfehhrs@together.net
Jim Gabbert	Meyer & Gabbert Excavating Contractors Recycling	8001 Fruitville Road Sarasota, FL 34241	(941)377-5370 (941)486-1352 Fax: (941)378-0844	jgabbert@co.sarasota.fl.us

Table D.1: Technical Advisory Group Members for Year 3



Name/Title	Organization	Address	Telephone	email
Bill Gay, Wood Preserving Vice President Alternate: Jim Hickman	Langdale Forest Products Co.	P.O. Box 1088 Valdosta, GA 31603-1088	(912)333-2513 Fax: (912)3332533 (912)333-2501	<a href="mailto:wgay@surfsouth.com">wgay@surfsouth.com</a> <a href="mailto:jhickman@surfsouth.com">jhickman@surfsouth.com</a>
Danny Kreiser Manager	East Coast Recycling	4880 Glades Cut-off Road Ft. Pierce, FL 34981	(561)461-5833 (561)595-0009	
William Krumbholz, Environmental Manager Alternate: Jeff Gould, Professional Geologist II, Waste Cleanup	Dept. of Env. Protection Solid Waste Division	2295 Victoria Ave., Suite 364 Ft. Myers, FL 33901  P.O. Box 2549 Ft. Myers, FL 33902-2549	(941)332-6975 Fax:(941)332-6969	<a href="mailto:Bill.Krumbholz@dep.state.fl.us">Bill.Krumbholz@dep.state.fl.us</a>  Jeffrey.Gould@dep.state.fl.us
Dave Mason Engineer 2 Alternate: Richard Tedder, Professional Engineer 3	Dept. of Environmental Protection	2600 Blair Stone Road MS# 4565 Tallahassee, FL 32399-2400	(850)921-9237 Fax: (850)414-0414	David.Mason@dep.state.fl.us
Jim Nix, Head Operator	Kodiak, Inc.	PO Box 99 Hwy. 278 East at Airport Road Allendale, SC 29810	(803)584-9137 Fax: (803)584-2208	NixJ@Kodiakwood.com
George Parris, Ph.D Director of Environmental & Regulatory Affairs	American Wood Preservers Institute	2750 Prosperity Avenue, Suite 550 Fairfax, VA 22031-4312	(703)204-0500 Fax: (703)204-4610	internet site: <a href="http://www.awpi.org">http://www.awpi.org</a>
Michael E. Provenza Environmental Health and Safety Manager Alternate: Gary Hurst, General Manager	Robbins Manufacturing	13001 N. Nebraska Ave. Tampa, FL 33612  P.O. Box 17939 Tampa, FL 33682	(813) 971-3030 Fax: (813)972-3980	
John Schert Executive Director	Florida Center for Solid and Hazardous Waste Management	University of Florida 2207 NW 13 Street, Suite D Gainesville, FL 32609	(352)392-6264 Fax: (352)846-0183	fcshwm@eng.ufl.edu
Chih-Shin Shieh, Ph.D Principal Researcher/Director	Florida Institute of Technology, Research Center for Waste Utilization,DMES	150 W. University Blvd. Melbourne, FL 32901	(407) 768-8000 x7240 Fax: (407)674-7212	cshieh@fit.edu

Table D.1 (con'd): Technical Advisory Group Members for Year 3

Name/Title	Organization	Address	Telephone	email
Helena Solo-Gabriele, Ph.D, P.E Assistant Professor (Graduate Students:Kelvin Gary, Naila Hosein, Bernine Khan, Monika Kormienko)	University of Miami, Dept. of Civil, Arch. & Environ. Engrg.	P.O. Box 248294 Coral Gables, FL 33124- 0630	(305)284-3489 or (305)284- 3391 Fax: (305)284-3492	hmsolo @miami.edu
August (Gus) Staats Manager of Environmental Services	Osrose Wood Preserving Division	P.O. Drawer 0 Griffin, Georgia 30224-0249	(770)228-8434 Fax: (770)229-5225	
Donald R. Surrency, Manager of Plant and Sales Alternate: Jim Healey, Plant Manager	Koppers Industries, Inc.	P.O. Box 1067 Gainesville, FL 32609  200 NW 23 Ave. Gainesville, FL 32605	(352)376-5144 1-800-342-6860 Fax: (352)371-4657	don_surrency@koppers.com  jim_healey@koppers.com
Ram Tewari, Ph.D., P.E., Project Manager	Broward County Commission Solid Waste Operations Division	201 S. Andrews Avenue Fort Lauderdale, FL 33301	(954)765-4202 x254 (954)680-0087 x224 Fax:(954)765-4237	rtewari@co.broward.fl.us
Timothy Townsend, Ph.D Assistant Professor (Graduate Students: Kristin Stook, Jin-Kun Song, Thabet Tolaymat)	University of Florida Dept.of Environ. Engrg.Sci., Solid & Haz.Wst Prgrm	333 New Engineering Bldg. Gainesville, FL 32611-6450	(352)392-0846 Fax: (352)392-3076	ttown@eng.ufl.edu
George Varn, Jr. Project Manager Alternate:G. Micheal Hollingsworth, Comptroller	Varn Wood Products	P.O. Box 128 Hoboken, GA 31542	(912)458-2187 Fax: (912)458-2190	justpine@aol.com

Table D.1 (con'd): Technical Advisory Group Members for Year 3

**Attendees of the Technical Advisory Group Meeting Held December 9, 1999  
at the University of Miami, College of Engineering, Coral Gables, Florida**

Kevin Archer, Chemical Specialties Inc., Charlotte, NC  
Sean Bennie, University of Miami, Coral Gables, FL  
Mark Bingham, Dade Recycling, Miami, FL  
Scott Conklin, Universal Forest Products, Grand Rapids, MI  
Diana Davis, Florida Power and Light, Juno Beach, FL  
David Dee, Landers & Parsons, Tallahassee, FL  
Louis DiVita, Delta Recycling Corp., Pompano Beach, FL  
Rick Donaldson, Great Southern Wood Preserving, Bushnell, FL  
Keith Drescher, Florida Power and Light, West Palm Beach, FL  
Tom Evans, Coastal Lumber, Weldon, NC  
Kelvin Gary, University of Miami, Coral Gables, FL  
Bill Gay, Langdale Forest Products, Valdosta, GA  
Alex Gomez, Dade Recycling, Miami, FL  
Jeff Gould, Florida Dept. of Environmental Protection, Ft. Myers, FL  
Bob Gruber, Hickson Corp., Smyrna, GA  
Jimmy Harris, Great Southern Wood Preserving, Bushnell, FL  
Jim Healey, Koppers Industries Inc., Gainesville, FL  
Jim Hickman, Langdale Forest Products, Valdosta, GA  
Naila Hosein, University of Miami, Coral Gables, FL  
Gary Hurst, Robbins Manufacturing, Tampa, FL  
Mitch Joiner, Osmose Wood Preserving, Griffin, GA  
Russel Ketchem, Florida Power and Light, West Palm Beach, FL  
Bernine Khan, University of Miami, Coral Gables, FL  
Frank Klasnick, Osmose Wood Preserving, Griffin, GA  
Monika Kormienko, University of Miami, Coral Gables, FL  
Danny Kreiser, East Coast Recycling, Ft. Pierce, FL  
William Krumbholz, Florida Department of Environmental Protection, Ft. Myers, FL  
Jim Langdale, Langdale Forest Products, Valdosta, GA  
Marc Laurent, Miami-Dade County Solid Waste, Miami, FL  
Dave Mason, FL Dept. of Environ. Protection, Tallahassee, FL  
Jerry McMullan, Florida Power and Light, West Palm Beach, FL  
Russ Morgan, Occidental Chemical, Castle Hayne, NC  
Don Pardue, Wood Treaters, Jacksonville, FL  
George Parris, American Wood Preservers Inst., Fairfax, VA  
Scott Ramming, American Wood Preservers Inst., Fairfax, VA  
Jay Robbins, Robbins Manufacturing, Tampa, FL  
Tom Roberts, Delta Recycling Corp., Pompano Beach, FL  
Steven Roundtree, Southeastern Lumber Manufacturers Assoc., Forest Park, GA  
John Schert, Univ. Florida Florida Center for Solid and Haz. Waste Mgt., Gainesville, FL  
Jim Seufert, Universal Forest Products, Grand Rapids, MI  
Helena Solo-Gabriele, University of Miami, Coral Gables, FL  
Gus Staats, Osmose Wood Preserving Division, Griffin, GA  
Kristin Stook, University of Florida, Gainesville, FL  
Thabet Tolaymat, University of Florida, Gainesville, FL  
Tim Townsend, University of Florida, Gainesville, FL  
George Varn Jr., Varn Wood Products, Hoboken, GA  
Shakir Wissa, Southern Soft Wood Inc., Orlando, FL  
Edward Zillioux, Florida Power and Light, Juno Beach, FL

**Attendees of the Technical Advisory Group Meeting Held March 17, 2000  
at the University of Florida, Reitz Union, Gainesville, Florida**

Kevin Archer, Chemical Specialties Inc., Charlotte, NC  
Allison Barnes, University of Florida, Gainesville, FL  
David Bullock, Wood Protection Products, Charlotte, NC  
Diana Davis, Florida Power and Light, Juno Beach, FL  
David Dee, Landers & Parsons, Tallahassee, FL  
Dottie Delfino, Univ. FL Florida Center for Solid and Haz. Waste Mgt., Gainesville, FL  
Rick Donaldson, Great Southern Wood Preserving, Bushnell, FL  
Keith Drescher, Florida Power and Light, West Palm Beach, FL  
Kelvin Gary, University of Miami, Coral Gables, FL  
Alex Green, University of Florida - Dept. of Mechanical Engineering, Gainesville, FL  
Bob Gruber, Hickson Corp., Smyrna, GA  
Tim Hannon, Pride of Florida, Starke, FL  
Jim Healey, Koppers Industries, Gainesville, FL  
Scott Hiaasen, Palm Beach Post, West Palm Beach, FL  
Jim Hickman, Langdale Forest Products, Valdosta, GA  
Naila Hosein, University of Miami, Coral Gables, FL  
Jake Huffman, University of Florida - School of Forest Resources, Gainesville, FL  
Gary Hurst, Robbins Manufacturing, Tampa, FL  
Russel Ketchem, Florida Power and Light, West Palm Beach, FL  
Kim Kochran, University of Florida, Gainesville, FL  
Monika Kormienko, University of Miami, Coral Gables, FL  
William Krumbholz, Ft. Myers, FL  
Lena Ma, University of Florida - Soil and Water Science, Gainesville, FL  
Dave Mason, FL Dept. of Environ. Protection, Tallahassee, FL  
Ron Matus, Gainesville Sun, Gainesville, FL  
Jerry McMullan, Florida Power and Light, West Palm Beach, FL  
John Mousa, Alachua County Environ. Protection, Gainesville, FL  
Kevin O'Donnell, Florida Power and Light, West Palm Beach, FL  
Don Pardue, Wood Treaters, Jacksonville, FL  
Michael Provenza, Robbins Manufacturing, Tampa, FL  
Scott Ramminger, American Wood Preservers Inst., Fairfax, VA  
Dan Rawson, Florida Power and Light, West Palm Beach, FL  
Bill Robbins, Robbins Manufacturing, Tampa, FL  
Jay Robbins, Robbins Manufacturing, Tampa, FL  
Rhonda Rogers, Univ. FL Florida Center for Solid and Haz. Waste Mgt., Gainesville, FL  
Steve Rountree, Southeastern Lumber, Forest Park, GA  
Roger Sanders, Florida Power and Light, West Melbourne, FL  
John Schert, Univ. Florida Florida Center for Solid and Haz. Waste Mgt., Gainesville, FL  
Robert A. Schmidt, University of Florida - School of Forest Resources, Gainesville, FL  
Jim Seufert, Universal Forest Products, Grand Rapids, MI  
Helena Solo-Gabriele, University of Miami, Coral Gables, FL  
Jin Kun Song, University of Florida, Gainesville, FL  
Gus Staats, Osmose Wood Preserving Division, Griffin, GA  
Kristin Stook, University of Florida, Gainesville, FL  
Don Surrency, Koppers Industries, Gainesville, FL  
Thabet Tolaymat, University of Florida, Gainesville, FL  
Tim Townsend, University of Florida, Gainesville, FL  
Yongchul Yang, University of Florida, Gainesville, FL  
Edward Zillioux, Florida Power and Light, Juno Beach, FL

**Attendees of the Technical Advisory Group Meeting Held July 28, 2000  
at the Florida Dept. of Environmental Protection Bldg located in Tallahassee, Florida**

Kevin Archer, Product Development Manager, Chemical Specialties Inc, Charlotte, NC  
David Bullock, Wood Protection Products, Charlotte, NC  
Jennifer Caldwell-Kurka, Florida Department of Environmental Protection, Tallahassee, FL  
Jenna Carlson, University of Florida, Gainesville, FL  
Lee Childers, Suwannee Lumber Mfg., Cross City, FL  
Jan Rae Clark, Florida Department of Environmental Protection, Tallahassee, FL  
Raoul Clarke, Florida Department of Environmental Protection, Tallahassee, FL  
Steve Cox, Co XRF, Atlanta, GA  
Keith Drescher, Environmental Specialist, Florida Power and Light, West Palm Beach , FL  
David Dee, Landers and Parsons, Tallahassee, FL  
Richard Gentry, Florida Home Builders Association, Tallahassee, FL  
Jack Glenn, Florida Home Builders Assoc., Tallahassee, FL  
Peter Goren, Florida Department of Environmental Protection, Tallahassee, FL  
Phil Gornick, Florida Forestry Assn, Tallahassee, FL  
Bob Gruber, Hickson Corp., Smyrna, GA  
David Hahn, University of Florida, Gainesville, FL  
Julie Hauserman, St. Petersburg Times, Tallahassee ,FL  
Jim Healey, Koppers Industries, Inc., Gainesville, FL  
Ron Henricks, Florida Department of Environmental Protection, Tallahassee, FL  
Jim Hickman, Langdale Forest Products Co, Valdosta, GA  
William Hinkley, Florida Department of Environmental Protection, Tallahassee, FL  
Naila Hosein, University of Miami, Coral Gables, FL  
Gary Hurst, Robbins Manufacturing, Tampa, FL  
Robbin Jackson, Elementis, Corpus Christi, TX  
Francine Joyal, Florida Department of Environmental Protection, Tallahassee, FL  
Mike Kaiser, Burns and McDowell, Jacksonville, FL  
Russell Ketchem, Florida Power and Light, West Palm Beach, FL  
Bernine Khan, University of Miami, Coral Gables, FL  
Curt Leonard, Florida Forestry Assn, Tallahassee, FL  
Lena Ma, University of Florida, Gainesville, FL  
Tom Marr, Osmose Inc., Griffin GA  
Dave Mason, Southern Forest Products Association, Kenner, LA  
Dave Mason, Florida Department of Environmental Protection, Tallahassee, FL  
Daniel Moore, Dept. of Agriculture and Consumer Services, Tallahassee, FL  
Karen S. Moore, Florida Department of Environmental Protection, Tallahassee, FL  
Russ Morgan, Scientist, Occidental Chemical, Castle Hayne, NC  
Gus Olmos, Alachua County, Gainesville, FL  
John Paling, John Paling and Co, Gainesville FL  
Keith Parmer, Dept. of Agriculture and Consumer Services, Tallahassee, FL  
George Parris, Ph.D., American Wood Preservers Institute, Fairfax, VA  
Mike Petrovich, Hopping Green Sams & Smith, P.A., Tallahassee, FL  
Scott Ramming, American Wood Preservers' Institute, Fairfax, VA  
Tom Roberts, Delta Recycling, Ft. Lauderdale, FL  
John Schert, Florida Center for Solid and Hazardous Waste Management, Gainesville, FL  
Jay Sego, Coastal Lumber Co., Havana, FL  
Jim Seufert, Universal Forest Products, Grand Rapids, MI  
Helena Solo-Gabriele, University of Miami, Coral Gables, FL

**Attendees of the Technical Advisory Group Meeting Held July 28, 2000  
at the Florida Dept. of Environmental Protection Bldg located in Tallahassee, Florida**

**(continued)**

August Staats, Osmose Wood Preserving Division, Griffin, Georgia  
Kristin Stook, University of Florida, Gainesville, FL  
Donald Surrency, Koppers Industries, Inc., Gainesville, FL  
Richard Tedder, Florida Department of Environmental Protection, Tallahassee, FL  
Laurie Tenace, Florida Department of Environmental Protection, Tallahassee, FL  
Thabet Tolaymat, University of Florida, Gainesville, FL  
Timothy Townsend, University of Florida, Gainesville, FL  
Tuck Tucker, Gulf Power, Pensacola, FL  
George Varn, Jr., Varn Wood Products, Hoboken, GA

**Attendees Via Teleconference**

Bonaventure Akinlosutu U.S. Environmental Protection Agency, Washington D.C.  
Winston Dang, U.S. Environmental Protection Agency, Washington D.C.  
Najm Shamim, U.S. Environmental Protection Agency, Washington D.C.