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**CCA-Treated Wood in Commercial  
Landscaping Mulch and Effects of Colorants  
on Metal Leaching Rates**

**(FINAL)**

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## **LIST OF ABBREVIATIONS AND ACRONYMS**

As	Arsenic
BDL	Below Detection Limit
CCA	Chromated Copper Arsenate
C&D	Construction and Demolition
Cr	Chromium
Cu	Copper
DEP	Department of Environmental Protection
DI	De-ionized
EPA	Environmental Protection Agency
FCSHWM	Florida Center for Solid and Hazardous Waste Management
FDEP	Florida Department of Environmental Protection
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectroscopy
QAQC	Quality Assurance and Quality Control
RDF	Refuse Derived Fuel
SCTL	Soil Cleanup Target Level
SPLP	Synthetic Precipitation Leaching Procedure
UF	University of Florida
UM	University of Miami
USEPA	U.S. Environmental Protection Agency
Vol.	Volume
XRF	X-ray Fluorescence Spectroscopy

## UNITS OF MEASURE

%	Parts per hundred
ug	Microgram
ug/L	Micrograms per liter
ul	Microliter
um	Micron (1 millionth of a meter)
°C	Degrees Celsius
Eh	Measure of electron activity
ft <sup>3</sup>	Cubic feet
g	Grams
L	Liter
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/L	Milligrams per liter
ml	Milliliter
mm	Millimeter
ng	Nanogram
M	Molar concentration units
mM	Millimolar
N	Normality (equivalents per liter)
pcf	Pounds of chemical per cubic foot of wood. Chemical typically refers to CCA on an oxide basis.
pH	Measure of the hydrogen ion activity
ppb	Parts per billion
ppm	Parts per million

## ABSTRACT

Preliminary evidence prior to the current study indicated that some mulch produced from recycled dimensional wood may be contaminated with CCA (chromated copper arsenate) treated wood, thereby increasing metal concentrations within mulch. Also mulch made from recycled dimensional wood is also typically dyed with an iron-oxide colorant. These colorants can potentially bind with the arsenic in CCA and provide some protection against leaching. The objectives of the current study were thus twofold. The first objective focused on evaluating the extent to which commercially-available mulch was contaminated within the State of Florida. Samples were evaluated both visually and chemically. Visual analysis focused on documenting whether or not the samples were colored, whether or not they were made from recycled C&D wood, and documenting the wood-chip size distribution. Chemical analysis included measurements of total recoverable metals and leachable metals as per the standardized Synthetic Precipitation Leaching Procedure (SPLP). The second objective of this study was to evaluate the impact of iron-oxide colorants on leaching rates from CCA contaminated mulch. Mulch samples for testing were made from recycled C&D wood and the samples were paired, with one colored and the other non-colored. Leaching was measured using the SPLP test and from observation boxes that were placed outdoors and subjected to natural rainfall conditions.

Of the 84 wood mulch samples collected from Florida, 44 were colored and 40 were non-colored. Among the colored samples that contained evidence of C&D wood ( $n = 13$ ), about  $\frac{3}{4}$  of the samples contained enough arsenic to exceed regulatory guidelines for leaching and land application of recycled materials. In general, these samples were characterized by CCA-treated wood fractions of 1 to 5% with the remainder of the mulch being untreated. Also, “open bin<sup>a</sup>” samples ( $n = 4$ ) and samples characterized by small chip sizes were also found to be suspect for contamination. The maximum metals concentrations for the mulch samples evaluated were 230 mg/kg for As, 240 mg/kg for Cu, and 510 mg/kg for Cr. The maximum SPLP concentrations were 190 ug/L, 130 ug/L, and 120 ug/L, for As, Cu, and Cr, respectively. The commercially-available mulch sample characterized by the maximum fraction of CCA-treated wood (15%) was colored, contained plywood, and was obtained from an “open bin.”

Experiments focusing on evaluating the impacts of iron oxide colorants were conducted using a similar proportion of CCA-treated wood (5% treated and 95% untreated) as that found in the colored samples made from C&D wood. The average arsenic concentration for the non-colored sample within the SPLP leachate was 920 ug/L and for the observation box the average arsenic leachate concentration was 580 ug/L. For the colored sample the arsenic concentration for the SPLP leachate was 380 ug/L and the average arsenic concentration observed from the observation box was 390 ug/L. Overall, the iron-oxide colorant was found to decrease arsenic leaching by 30% during the 6-month study period for all sets of samples evaluated under natural rainfall conditions.

In summary, results of this study indicate that CCA-treated wood has contaminated consumer mulch. The likely source of the contamination is from recycled dimensional wood. The larger proportion of “hits” is consistent with the locations of highly urban areas in Florida where C&D recycling facilities are found. The increased demand for mulch in these areas along with limitations in landfill space promotes recycling of dimensional wood. Efforts should focus on improving sorting practices at these facilities to assure that mulch is essentially free of CCA ( $< 0.5\%$ ). The use of iron-oxide colorants may help reduce leaching of arsenic from contaminated mulch at least during the short term ( $< 6$  months).

<sup>a</sup> Samples that were not pre-bagged upon purchase and were intended for purchase in bulk.

**CHAPTER I**  
**BACKGROUND, MOTIVATION, AND OBJECTIVES**

# CHAPTER I

## BACKGROUND, MOTIVATION, AND OBJECTIVES

This chapter focuses on describing the background and motivation for this study (Section I.1) and the project objectives (Section I.2).

### I.1 BACKGROUND AND MOTIVATION

The primary disposal pathway for CCA-treated wood in Florida is through construction and demolition (C&D) facilities. Once within these facilities the treated wood is ultimately disposed through one of three methods: in C&D landfills which are generally unlined in Florida, burned as fuel, or recycled for the production of mulch. Among these three practices the recycling of CCA-treated wood into mulch is the most troubling because of: 1) the direct contact by Florida residents with the ground-up material which could be potentially inhaled, and 2) the larger in surface area of the wood which would promote leaching of CCA chemicals.

The potential for C&D wood to contain CCA-treated wood has been well documented. Samples collected from 12 facilities in Florida during 1996 contained 6% CCA-treated wood on average. Wood waste was again characterized during 1999 at 3 C&D facilities, two of which practiced visual sorting of CCA-treated wood. During the 1999 study C&D wood was characterized by 9 to 30% CCA-treated wood. During 2001, an extensive wood waste characterization study conducted at one facility located in Florida found that 22% of the incoming wood waste stream was CCA-treated (Solo-Gabriele and Townsend 1999; Tolaymat et al. 2000; Blassino et al. 2002; Solo-Gabriele et al. 2001; Solo-Gabriele et al. 2004). These results indicate that there is a high likelihood that recycled C&D wood contains considerable amounts of CCA, so care must be taken concerning how C&D wood is recycled.

A major market for recycled C&D wood includes residential and commercial landscaping. Typically, C&D wood used for mulch is dyed to mask the typical grayish color associated with recycled C&D wood. In particular, the use of the red-colored mulch and to a lesser extent gold-, and black- colored mulch, has become very popular in Florida. The red mulch has become so popular that even wood made from pure vegetative wood, from non-C&D sources, is now available in distinctive dye-enhanced colors.

A preliminary study was conducted to evaluate the leaching characteristics of mulch material in Florida (Townsend et al. 2000; Townsend et al. 2003). The samples evaluated included mulch samples from 20 C&D facilities, 3 yard waste facilities, 3 colored-mulch samples from retail stores, and 3 vegetative-mulch samples from retail stores. Results indicated that of the 20 C&D mulch samples, 18 exceeded Florida's Groundwater Clean-up Target Level (GWCTL) for arsenic and 5 exceeded for chromium. Two of the three colored mulches purchased from retail establishments exceeded the GWCTL for arsenic. One of the yard waste samples exceeded the arsenic GWCTL and one exceeded the chromium GWCTL. None of the vegetative mulch samples (e.g. cypress mulch / pine bark mulch) exceeded the GWCTL's. The results from this preliminary study were troubling given that it documented that contaminated mulch was sold at retail establishments to unsuspecting consumers.

A considerable amount of media attention was given to the observation that mulch purchased at retail establishments may be contaminated with CCA. Given this coverage, home owners, gardeners, child care centers, and schools have contacted members of the research team asking for additional guidance concerning how to recognize mulch that may be contaminated. Samples from these concerned citizens were mailed by these citizens to members of the research team and analyzed on a case-by-case basis using a few different methods including chemical stains and some leaching tests. It was found that some of these mulches from concerned citizens did contain CCA-treated wood whereas others did not.

The tests on mulch from retail establishments and homeowners prior to the existing study were limited and somewhat disjointed. The more “organized” evaluation included only 3 samples of commercial red mulch and only evaluated the leaching characteristics of these samples. The remaining samples obtained from concerned citizens were evaluated using various methods depending upon the researcher contacted and communications with the citizen. In this earlier work, if there was an attempt to determine the quantity of CCA-treated wood in the mulch mix, it was based upon the use of chemical stains which is useful for establishing the presence of CCA but imprecise for establishing the fraction of CCA within the wood mix. Furthermore, the stains did not work well when the mulch was colored. These preliminary studies were sufficient, nevertheless, to indicate that there was a problem associated with contaminated mulch, but it was not sufficient to establish the extent of this problem.

## **I.2 OBJECTIVES**

The overall goals of this study were to assess the extent to which mulch purchased by the Florida consumer was contaminated with CCA and to evaluate the adequacy of visual methods in establishing whether or not a mulch sample contains CCA-treated wood. Furthermore, there was an interest in establishing whether or not the red colorants used to dye wood mulch are effective at reducing the leaching rates of metals from CCA-contaminated mulch. As a result of this interest, experiments were conducted to evaluate the effect of colorants on leachable arsenic concentrations.

Specifically, during this project, mulches were purchased from retail establishments located throughout Florida and were gathered from mulch currently in use, such as that found in playgrounds. Analysis of these samples included quantifying recoverable metals in the original mulch samples, the fraction of CCA-treated wood within these mulches, and the amount of leachable As, Cr, and Cu. All of the mulch samples were visually inspected prior to analysis. Visual inspection focused on evaluating the size of the mulch pieces, whether or not the mulch was colored or contained remnants of engineered wood, such as plywood or particleboard. If CCA contamination correlates with visual characteristics, then such visual characteristics could help consumers identify suspect mulch at the point of purchase or use.

In order to evaluate the impact of colorants on leaching rates, observation boxes were filled with mulch, some of which were colored with an iron oxide colorant and some of which were not colored. These observation boxes were placed outdoors for a period of 6 months and leachate samples were periodically collected and analyzed for arsenic. These measurements were used to establish possible differences in leaching rates.

The organization of this report is consistent with the objectives of this study and includes a chapter that focuses on evaluating the extent to which consumer mulches in Florida were contaminated with CCA (Chapter II). Experiments designed to evaluate the impacts of iron oxide colorants on leaching rates of arsenic are described in Chapter III. The report closes with a summary, conclusions, and a set of acknowledgments (Chapter IV).

## **CHAPTER II**

# **EXTENT OF CCA CONTAMINATION WITHIN COMMERCIAL MULCHES FOUND IN FLORIDA**

## CHAPTER II, EXTENT OF CCA CONTAMINATION WITHIN COMMERCIAL MULCHES FOUND IN FLORIDA

This chapter is separated into 4 sections. The first section (Section II.1) focuses on methods. The last 3 sections summarize the results. The results are compiled for: visual inspection and size distribution (Section II.2), leachable metals from mulches using the SPLP (Section II.3), and “recoverable” metals from mulch and the fraction of CCA-treated wood in mulch samples (Section II.4).

### II.1 METHODS

A grand total of 92 samples (including 3 controls) were evaluated in this study. Among these 92 samples, 85 wood mulch samples (not including the controls) were collected (Section II.1.a). Of the 85 wood mulch samples, 84 were collected in Florida and 1 came from Arizona. The non-wood mulch samples evaluated in the count of 92 included a rubber mulch sample, a sample of RDF, a sample of RDF fine soil, and a wood-soil mix.

Upon collection, samples were split into 4 sub-samples (Figure II.1). Two sub-samples were subjected to physical analysis. One of these was utilized for visual inspection for evidence that it came from C&D wood. The other was utilized to measure the wood-chip size distribution of the sample. The last two sub-samples were ultimately subjected to chemical analysis. One of these was first ashed and then analyzed for total recoverable metals. The other was subjected to the synthetic precipitation leaching procedure (SPLP). A description of the methods used for physical processing of the samples (visual inspection and size distribution) is provided in section II.1.b. Section II.1.c describes the methods employed for chemical processing and analyses.

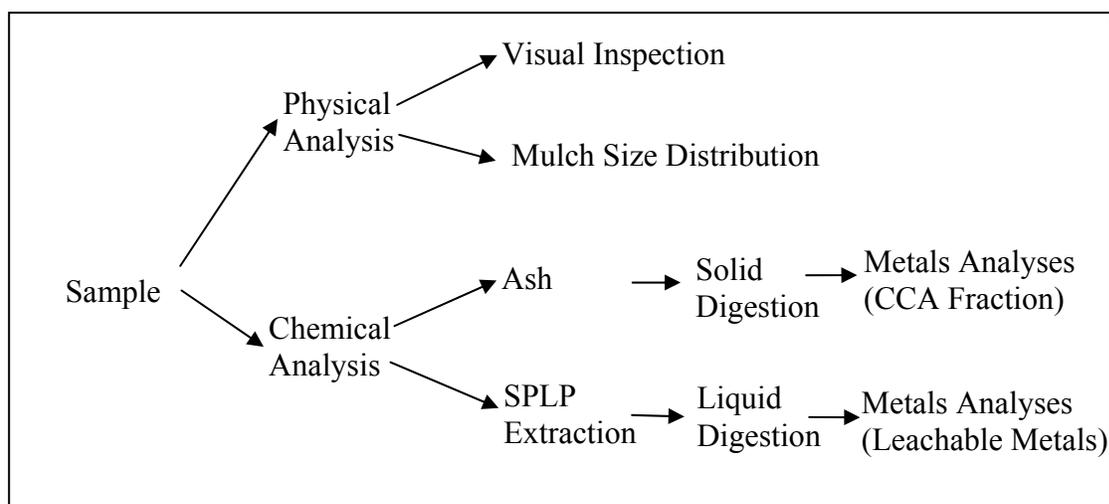


Figure II.1: Schematic for Sample Processing and Analysis

#### II.1.a Sample Collection

Most of the 85 wood mulch samples were collected from large retail stores, small nursery establishments, and mulch manufacturing facilities. Upon sample collection, the date, location, price, and brand-name of the sample were recorded. Upon receipt at the laboratory a sample number was assigned and the sample was placed in a plastic container. Gloves were used to

transfer the samples to the containers and new gloves were used each time contact was made with a different mulch sample. The majority of the samples were pre-bagged from the manufacturer, although some unbagged or “open-bin” samples were collected at some nursery establishments.

Samples were collected in two batches. The total number of wood mulch samples collected in the first batch was 29. The majority of the first batch of samples was collected at retail establishments from Miami-Dade and Broward Counties between September and December 2002 (Table II.1). Some new samples from the first batch were also collected from stores located in Sebastian and Brandon, FL and some “in-use” samples were collected from playgrounds, schools, and a residence located in South Florida. One mulch sample was retrieved from a sample archive. This sample came from Arizona and was originally provided to the University on December 7, 2000. This mulch sample was marketed in Arizona specifically for use on playgrounds. The first batch of 29 samples was supplemented with a set of three controls and three additional non-mulch samples. The non-mulch samples included one sample of Refuse Derived Fuel (RDF) (sample #16) and one sample of soil made by an RDF processing plant (sample #21). These two samples were collected March 8, 2001 and were archived at the University of Miami laboratory until analyzed for this project. The third non-mulch sample consisted of a wood/soil mix purchased at a local nursery (Sample #28). Note that no sample was assigned an identification number of 27.

The second batch of samples was collected exclusively from retail stores, nurseries, and mulch manufacturing facilities from cities outside of Miami-Dade and Broward Counties (Table II.2). A total number of 56 wood mulch samples were collected in this second sampling effort. One additional sample consisting of mulch made from rubber tires (sample #63) was also collected as part of the second batch. This rubber-mulch sample was subjected to visual analysis and to SPLP only. Sample #63 was not ashed. The cities visited during the second sampling effort included Orlando, Jacksonville, Tallahassee, Pensacola, Gainesville, Tampa, Fort Myers, St. Petersburg, Marathon, Key Largo, and Lake Worth. Stores were identified through the on-line yellow pages. The majority of these samples were collected between August and September 2003. All these samples were pre-bagged by the manufacturer with the exception of sample 81 which was an “open bin” mulch. Note that no samples were assigned identification numbers of 37 through 40.

Controls (samples 29, 30, and 31) corresponded to well characterized wood/mulch samples that have been archived at the University of Miami (Solo-Gabriele et al. 2003; Solo-Gabriele et al. 1999). Details concerning the collection and analysis of these control samples are included in the references. In brief, the control samples were prepared from untreated wood (sample #31) and from treated wood rated at 0.25 pcf by the manufacturer (sample #30). The manufacturer rating is based upon the amount of chemical retained in the outer 0.6 inches of the wood and represents the minimum amount of treatment within this outer layer. Also samples were collected and analyzed from the entire cross-section of the wood. Retention corresponding to the entire cross-section was needed for mass balance computations. A summary of the measured retention level data for these samples is provided in Table II.3 and Table II.4. Multiple measurements for the treated wood sample indicate that the actual retention level was 0.34 pcf for the outer 0.6 inches and 0.22 pcf for the entire cross-section. For samples collected from the entire cross-section of the treated wood, the corresponding average chromium, copper, and arsenic concentrations were 1,800 mg/kg, 1,140 mg/kg, and 1,300 mg/kg, on average. The untreated wood control was characterized by chromium, copper, and arsenic concentrations of 1.2 mg/kg, 0.7 mg/kg, and 1.0 mg/kg. A third control (sample 29) was prepared by mixing the untreated and treated wood controls to provide a ratio of 5% treated wood and 95% untreated wood, by weight. This proportion was chosen because it was

representative of the proportion of CCA-treated wood within contaminated mulches evaluated in this study.

Sample #	Date	City, State	Artificially Colored	Price	Source
1	10/13/2002	Miami, FL	YES, Red	\$2.49	Large Retail Store, Pre-Bagged
2	10/13/2002	Miami, FL	YES, Red	\$2.47	Large Retail Store, Pre-Bagged
3	10/16/2002	Miami, FL	YES, Red	\$2.98	Nursery, Pre-Bagged
4	10/16/2002	Miami, FL	YES, Red	\$3.50	Nursery, Open Bin
5	10/16/2002	Miami, FL	YES, Red	\$2.25	Nursery, Pre-Bagged
6	10/16/2002	Miami, FL	YES, Red	\$2.00	Nursery, Pre-Bagged
7	10/24/2002	Miami, FL	YES, Red	\$1.80	Nursery, Pre-Bagged
8	10/24/2002	Miami, FL	YES, Gold	\$1.80	Nursery, Open Bin
9	10/24/2002	Miami, FL	YES, Gold	\$1.80	Nursery, Pre-Bagged
10	10/24/2002	Miami, FL	YES, Red	\$3.00	Nursery, Open Bin
11	12/7/2000	Scottsdale, AZ	NO	NA	Playground
12	9/24/2002	Broward County <sup>a</sup> , FL	YES, Red	NA	Playground
13	9/24/2002	Broward County <sup>a</sup> , FL	YES, Red	NA	Playground
14	11/12/2002	Miami, FL	YES, Red	NA	Playground
15	11/12/2002	Miami, FL	YES, Red	NA	Playground
16	3/8/2001	Florida <sup>a</sup>	NO	NA	RDF Fuel (Processed Waste)
17	11/19/2002	Miami, FL	NO	\$3.98	Nursery, Pre-Bagged
18	11/19/2002	Miami, FL	NO	\$2.15	Nursery, Pre-Bagged
19	11/19/2002	Miami, FL	NO	\$11.95	Nursery, Pre-Bagged
20	11/19/2002	Miami, FL	NO	\$3.95	Nursery, Pre-Bagged
21	3/8/2001	Florida <sup>a</sup>	NO	NA	Fine Soil from RDF Processing Plant
22	11/19/2002	Miami, FL	NO	\$3.95	Nursery, Pre-Bagged
23	11/13/2002	Miami, FL	NO	\$1.49	Large Retail Store, Pre-Bagged
24	12/16/2002	Cross City, FL (Miami)	YES, Red	NA	Provided by School in Miami-Dade County, Pre-Bagged
25	11/23/2002	Miami, FL	NO	\$1.75	Nursery, Pre-Bagged
26	2/15/2003	Key Largo, FL	NO	NA	Home Residence
28	11/19/2002	Miami, FL	NO	\$3.50	Wood/Soil Mix from Nursery, Open Bin
29	1998	Miami, FL	NO	NA	Control. CCA Mix. 95% untreated, 5% CCA-treated. Mixture prepared by mixing samples 30 and 31.
30	1998	Miami, FL	NO	NA	Control. Mulch made from 0.25 pcf CCA-treated wood. Whole wood purchased from Lumber Yard
31	1998	Miami, FL	NO	NA	Control. Mulch made from untreated wood. Whole wood purchased from Lumber Yard
32	12/10/2002	Miami, FL	YES, Gold	NA	Playground
33	12/23/2002	Sebastian, FL	Yes, Red	\$2.67	Large Retail Store, Pre-Bagged
34	12/28/2002	Brandon, FL	No	\$2.19	Large Retail Store, Pre-Bagged
35	12/29/2002	Brandon, FL	No	\$3.48	Large Retail Store, Pre-Bagged
36	12/30/2002	Brandon, FL	No	\$2.99	Large Retail Store, Pre-Bagged

<sup>a</sup>City not provided to Maintain Specific Sampling Locations Confidential

Table II.1: Samples Collected During First Sampling Round

Sample	Date	City, State	Artificially Colored	Price	Source
41	8/6/2003	Orlando	Yes, Red	\$2.70	Mulch establishment, Pre-Bagged
42	8/6/2003	Orlando	Yes, Red	\$2.25	Mulch establishment, Pre-Bagged
43	8/6/2003	Orlando	No	\$1.99	Mulch establishment, Pre-Bagged
44	8/6/2003	Orlando	Yes, Red	\$2.49	Large Retail Store, Pre-Bagged
45	8/6/2003	Orlando	No	\$1.49	Large Retail Store, Pre-Bagged
46	8/7/2003	Jacksonville	No	\$2.39	Mulch establishment, Pre-Bagged
47	8/7/2003	Jacksonville	No	\$1.85	Mulch establishment, Pre-Bagged
48	8/7/2003	Jacksonville	Yes, Red	\$2.25	Mulch establishment, Pre-Bagged
49	8/7/2003	Jacksonville	No	\$1.85	Mulch establishment, Pre-Bagged
50	8/7/2003	Jacksonville	Yes, Red	\$2.25	Mulch establishment, Pre-Bagged
51	8/7/2003	Jacksonville	No	\$2.50	Mulch establishment, Pre-Bagged
52	8/7/2003	Jacksonville	Yes, Red	\$3.29	Large Retail Store, Pre-Bagged
53	8/7/2003	Jacksonville	No	\$2.00	Large Retail Store, Pre-Bagged
54	8/7/2003	Jacksonville	Yes, Black	\$3.29	Large Retail Store, Pre-Bagged
55	8/7/2003	Jacksonville	Yes, Black	\$2.99	Large Retail Store, Pre-Bagged
56	8/7/2003	Tallahassee	Yes, Red	\$3.97	Large Retail Store, Pre-Bagged
57	8/7/2003	Tallahassee	Yes, Red	\$2.49	Large Retail Store, Pre-Bagged
58	8/7/2003	Tallahassee	No	\$1.49	Large Retail Store, Pre-Bagged
59	8/7/2003	Tallahassee	Yes, Gold	\$2.49	Large Retail Store, Pre-Bagged
60	8/7/2003	Tallahassee	Yes, Red	\$2.49	Large Retail Store, Pre-Bagged
61	8/7/2003	Tallahassee	Yes, Gold	\$2.49	Large Retail Store, Pre-Bagged
62	8/7/2003	Tallahassee	No	\$1.99	Large Retail Store, Pre-Bagged
63	8/7/2003	Tallahassee	Yes, Red	\$8.97	Large Retail Store, Pre-Bagged, Rubber
64	8/7/2003	Pensacola	Yes, Gold	\$2.49	Large Retail Store, Pre-Bagged
65	8/7/2003	Pensacola	Yes, Red	\$2.00	Large Retail Store, Pre-Bagged
66	8/7/2003	Pensacola	No	\$2.97	Large Retail Store, Pre-Bagged
67	8/7/2003	Pensacola	Yes, Red	\$2.49	Large Retail Store, Pre-Bagged
68	8/7/2003	Pensacola	No	\$1.47	Large Retail Store, Pre-Bagged
69	8/8/2003	Gainesville	Yes, Red	\$2.49	Large Retail Store, Pre-Bagged
70	8/8/2003	Gainesville	No	\$1.49	Large Retail Store, Pre-Bagged
71	8/7/2003	Tallahassee	Yes, Red	\$1.49	Large Retail Store, Pre-Bagged
72	8/8/2003	Tampa	Yes, Red	\$2.49	Nursery, Pre-Bagged
73	8/8/2003	Tampa	No	\$1.49	Large Retail Store, Pre-Bagged
74	8/8/2003	Tampa	No	\$2.49	Large Retail Store, Pre-Bagged
75	8/8/2003	Tampa	No	\$2.95	Large Retail Store, Pre-Bagged
76	8/8/2003	Tampa	Yes, Red	\$2.39	Nursery, Pre-Bagged
77	8/9/2003	Fort Myers	No	\$2.59	Mulch establishment, Pre-Bagged
78	8/9/2003	Fort Myers	No	\$1.99	Mulch establishment, Pre-Bagged
79	8/9/2003	Fort Myers	No	\$1.65	Mulch establishment, Pre-Bagged
80	8/9/2003	Fort Myers	No	\$2.29	Mulch establishment, Pre-Bagged
81	8/9/2003	Fort Myers	Yes, Red	Free	Mulch establishment, Open Bin
82	8/9/2003	Fort Myers	No	\$5.50	Mulch establishment, Pre-Bagged

Table II.2: Samples Collected During Second Sampling Round

Sample	Date	City, State	Artificially Colored	Price	Source
83	8/9/2003	Fort Myers	No	\$1.69	Mulch establishment, Pre-Bagged
84	8/9/2003	Fort Myers	Yes, Red	\$2.49	Mulch establishment, Pre-Bagged
85	8/9/2003	Fort Myers	No	\$2.59	Mulch establishment, Pre-Bagged
86	8/8/2003	St. Petersburg	Yes, Red	\$2.49	Large Retail Store, Pre-Bagged
87	9/19/2003	Marathon	No	\$1.59	Large Retail Store, Pre-Bagged
88	9/19/2003	Marathon	No	\$2.49	Large Retail Store, Pre-Bagged
89	9/19/2003	Marathon	Yes, Red	\$2.49	Large Retail Store, Pre-Bagged
90	9/19/2003	Marathon	No	\$2.95	Large Retail Store, Pre-Bagged
91	9/19/2003	Key Largo	Yes, Red tint	\$1.59	Large Retail Store, Pre-Bagged
92	9/19/2003	Key Largo	Yes, Red	\$2.59	Large Retail Store, Pre-Bagged
93	9/18/2003	Lake Worth	No	\$1.25	Mulch establishment, Pre-Bagged
94	9/18/2003	Lake Worth	Yes, Red	\$1.85	Mulch establishment, Pre-Bagged
95	9/18/2003	Lake Worth	No	\$1.80	Mulch establishment, Pre-Bagged
96	9/18/2003	Lake Worth	No	\$3.75	Mulch establishment, Pre-Bagged
97	9/18/2003	Lake Worth	No	\$2.00	Mulch establishment, Pre-Bagged

Table II.2 (con'd): Samples Collected During Second Sampling Round

Sample ID	XRF (Outer 6/10")						
	Wood Treatment Plant #1 Analysis (pcf as CCA)	Wood Treatment Plant #2 Analysis, pcf					Average of Analysis by Plant #1 and #2 (pcf as CCA)
		#1	#2	#3	#4	Average	
Untreated Sample 31	0.006	0.05	0.0	0.05	0.0	0.025	0.016
0.25 pcf Sample 30	0.352	0.32	0.32	0.33	0.32	0.322	0.337

Table II.3: Measured Retention Level of the Outer 6/10" of the Untreated and 0.25 pcf Control Samples Used in this Study

Sample	ICP-AES (Entire Cross-Section)										XRF (Outer 6/10")
	Cr (mg/kg)	Ave Cr (mg/kg)	pcf as CrO <sub>3</sub>	Cu (mg/kg)	Ave Cu (mg/kg)	pcf as CuO	As (mg/kg)	Ave As (mg/kg)	pcf as As <sub>2</sub> O <sub>5</sub>	pcf as CCA	
Untreated Sample 31	1.2	1.2	0.000	0.7	0.7	0.000	1.0	1.0	0.000	0.000	0.016
	1.2			0.6			BDL				
0.25 pcf Sample 30	1,893	1800	0.111	1,157	1137	0.046	1,379	1305	0.064	0.220	0.337
	1,708			1,117			1,232				
	407			225			267				

<sup>a</sup>BDL = Below Detection Limit

Table II.4: Metals Concentrations of the Entire Cross-Section of Wood Control Samples Used in this Study

## II.1.b Physical Processing of Samples

Physical processing of the samples included visual inspection and the analysis of wood-chip size distributions.

### *Visual Inspection*

The primary purpose of visual inspection of the mulch was to identify if the mulch was: a) colored and, b) to look for evidence that it was made from recycled C&D wood. Non-colored mulch would have natural variations in color. When the change in color on a piece of mulch was abrupt or in the case where the color was extremely uniform, then the mulch was identified as artificially colored. Abrupt changes in color occurred when the colorant did not penetrate the crevices of the wood showing distinct areas of the natural wood color in contrast with other areas where the colorant penetrated the mulch. An extremely uniform color is an indication that excessive amounts of colorant were used giving the mulch a “heavily painted” appearance. When in doubt pieces of the mulch were broken open to determine if the color of the outside of the mulch sample was different than the inside, again indicating that the mulch was colored. Evidence that the wood was made from recycled C&D wood was provided by the presence of painted wood, other objects that are associated with recycled wood (e.g. nails, rope, and plastic), and engineered wood (e.g. plywood, particle-board, oriented strand board, and possible excess of smooth surfaces on the wood). Smooth surfaces on the wood chips were documented since engineered wood is characterized by sawn boards which are characterized by a greater proportion of smooth or straight edges.

In addition to evaluating the color and evidence that the mulch originated from C&D recycling operations, the presence of pine bark within the mulch samples was also documented since pine bark is readily recognized by its darker color and layered appearance. The process for visually identifying wood samples followed the steps below.

1. Mix mulch in bin to get a representative sample.
2. Weigh 100 g of sample.
3. Carefully spread sample on large sheet of paper.
4. Label sheet with sample number.
5. Sift through sample for 20 minutes looking for plywood, particleboard, oriented strand-board, smooth (once cut wood), painted wood, and other objects.
6. Weigh amount found in each category and record.
7. Record sample color and uniformity. Note if mulch was artificially colored.
8. Take picture of sample.
9. Repeat for each sample changing paper and gloves every time.

### *Wood-Chip Size Distribution*

Wood-chip size-distribution was evaluated because representatives from the mulch industry suggested that mulch with more fines may contain a higher fraction of C&D wood. Size-distribution analysis was based upon the use of standard sieves (Das 1985). The sieve sizes utilized were characterized by the following opening sizes: 1.5 in., 0.75 in., 0.375 in., 0.187 in. (#4), 0.079 in. (#10), 0.033 in. (#20), and 0.017 in. (#40). The sieve with the largest opening was placed at the top of the stack and the bottom pan which contained no openings was placed at the bottom to catch

any mulch particulates that passed the finest sieve. The sieves were pre-weighed prior to sample addition. The methods used were as follows.

1. Place about 300 grams of mulch into the pre-weighed dish.
2. Weigh the sample and record.
3. Place the sample in the top sieve of the stack of sieves.
4. Place the stack of sieves containing the sample on the shaker and allow the stack to shake for 10 minutes.
5. Remove the stack from the shaker and record the weight of sample retained on each sieve.

Data collected from each of the sieves were then utilized to compute the chip-size distribution, which was based upon the percent mass retained on each sieve (equation II.1), on the cumulative percentage of the mass retained (equation II.2), and the fraction that was finer than a set sieve size (equation II.3).

$$\text{Percent Mass on Sieve} = \left( \frac{\text{Mass on Sieve}}{\text{Sum of Weight on all Sieves}} \right) \times 100\% \quad (\text{eqn. II.1})$$

$$\text{Cumulative Percent Retained} = \sum \text{Percent Mass on Sieve} \quad (\text{eqn. II.2})$$

$$\text{Percent Finer} = 100 - \text{Cumulative Percent Retained} \quad (\text{eqn. II.3})$$

Sizes corresponding to a set fraction of the material passing a sieve were then used to characterize the average size of the chip and the uniformity of the distribution of chip sizes. The average size of the chip is based upon the “d<sub>50</sub>” value which is the size at which 50% of the chips are finer (equation II.4). The computation of d<sub>50</sub> is based upon an interpolation scheme which requires the identification of sieve sizes that “straddle” the 50% finer value. The smaller sieve opening size, SS, and a larger sieve size, LS, along with the percent finer associated with each of these sieves were used in the interpolation.

$$d_{50} = \left[ \left( \frac{50 - \text{percent finer of SS}}{(\text{percent finer of SS}) - (\text{percent finer of LS})} \right) \times (SS - LS) \right] + LS \quad (\text{eqn. II.4})$$

The uniformity of the distribution was based upon the ratio of the d<sub>60</sub> to d<sub>10</sub> (a.k.a. uniformity coefficient, UC), where d<sub>60</sub> corresponds to the size where 60% of the chips were finer and d<sub>10</sub> corresponds to the size where 10% of the chips are finer (equation II.5). A smaller value of UC indicates that the sample is more uniform (characterized by chip sizes that are more similar in size) whereas a larger value of UC indicates that the sample is less uniform with chips that are more variable in size. The computation of d<sub>60</sub> and d<sub>10</sub> is similar to that of d<sub>50</sub> except that the values of 60% and 10% finer are used as the points for the interpolation.

$$UC = \frac{d_{60}}{d_{10}} \quad (\text{eqn. II.5})$$

### II.1.c Chemical Processing of Samples

The chemical processing of samples consisted of two main parts: a) analysis of leachable metals by subjecting unburned samples to the Synthetic Precipitation Leaching Procedure (SPLP) and b) ashing and subsequent analysis of the ash digestates to measure the recoverable metals in the original mulch samples and to estimate the fraction of CCA-treated wood within the mulch. Due to concerns associated with the possible volatilization of metals during the ashing process, a set of mulch samples were spiked with arsenic, chromium, and copper to document possible volatilization during the ashing step. Furthermore, a considerable effort was placed in the analysis of samples for quality assurance and quality control (QAQC). Details of volatilization experiment and the additional QAQC analyses are provided in Appendix G.

#### *SPLP Analysis*

SPLP analysis was performed on unburned mulch samples. The process required the extraction of leachable metals as per the SPLP protocol (US EPA, 1996), a liquid digestion of the leachate, and metals analysis of the digestate.

As part of the SPLP procedure 100 g of mulch were placed within 2 liters of leaching fluid resulting in a 20:1 liquid to solids ratio. This mixture was tumbled at  $30 \pm 2$  rpm for a period of  $18 \pm 2$  hours. The mixture was then filtered using a pressurized filtration apparatus with a 0.7- $\mu$ m borosilicate glass fiber filter (Environmental Express TCLP filter). The filtrates were collected in 1-L plastic bottles, acidified to a pH of less than 2 and stored at 4°C until digestion and analysis. The SPLP leaching fluid, which simulates acidic rainfall, was prepared by adding a strong inorganic acid to de-ionized water until a pH of  $4.20 \pm 0.05$ . The strong acid consisted of a mixture of 60-g of sulfuric acid with 40-g of nitric acid. About 0.4 ml of the sulfuric/nitric acid mixture were needed per 2 L of de-ionized water.

Prior to analysis, the SPLP leachates were digested following US EPA method 3010 (US EPA, 1996). This method is an open vessel digestion procedure that requires the addition of concentrated nitric acid and hydrochloric acid to a representative 100-ml sample. A Thermo Jarrel Ash inductively coupled plasma atomic emission spectrophotometer (ICP-AES, Thermo Jarrel Ash Trace Analyzer) was used to analyze arsenic, copper, and chromium in the digestates according to US EPA Method 6010B. Detection limits for the instrument were 12, 4, and 5  $\mu$ g/L for arsenic, copper and chromium, respectively. Two sets of duplicates were analyzed. The first set corresponded to duplicates on the same SPLP extract and the second set corresponded to “complete” duplicates which were performed on two separate aliquots of the mulch which were subjected to the SPLP within different vessels. In brief, duplicates either on the same SPLP extract or “complete” duplicates were within 18% for arsenic, copper, and chromium, with the exception of the “complete” duplicates for chromium which showed greater variability. The variability observed for chromium on the “complete” duplicates was likely due to the difficulty in obtaining truly homogeneous samples with respect to this analyte. Analyses of blank samples were consistently below the detection limit and spike analysis results were good with recoveries between 93 and 115%. More details concerning QAQC analyses are provided in Appendix G.

## *Ashing*

Ashing was a necessary step in the analytical method used to determine the recoverable metals and the fraction of CCA contained within the mulch samples. The method followed a modification of the protocol established by Tolaymat et al. 2000. The modification consisted of lowering the temperature of the drying oven from 105°C to 65°C. The temperature was lowered due to the spontaneous ignition of one of the mulch samples during drying at the higher temperature. The lower temperature was used to avoid sample ignition. The steps utilized during the ashing process are outlined below.

1. Record weight of empty aluminum pan.
2. Place mulch sample in the aluminum pan and record combined weight. This weight minus the weight of the pan is the original sample weight.
3. Cover the sample with aluminum foil and place the sample in a drying oven at 65°C. Maintain the sample in the oven until it reaches a constant weight and record. The length of time the sample must remain in the oven is dependent on the moisture content of the sample.
4. Place sample in a muffle furnace at 550°C (Thermolyne F6020C-60-80; Thermolyne F48025). Keep the sample in the furnace until no wood chips are visible and a fine ash is formed. This process usually takes about four days.
5. Transfer sample to a plastic acid-washed container and label.

It is noted that the furnace temperatures were checked against an independent reading using a thermocouple (Omega Engineering Inc., Model XCIB-K-1-2-3; Model HH11) and the temperatures read by the thermocouple and the furnace were within 5 degrees Celsius of each other. Concerns have been raised about potential arsenic volatilization during the ashing step. Experimentation described in greater detail in Appendix G indicates that a majority of the arsenic (75%) is recovered in the ash. Thus, total arsenic values reported in the current study likely represents low values.

## *Analysis of the Ash Samples (Recoverable Metals)*

The ashed samples were processed as per protocol developed by Tolaymat et al. 2000. This protocol requires the ashing of the samples (described earlier), digestion of the ash, followed by analysis of the digestates. Digestion of the ash followed method 3050B (US EPA 1996) which was based on subjecting 1 to 2 grams of ash to sequential additions of nitric acid, hydrogen peroxide, and hydrochloric acid. These samples were refluxed using a hot plate for a period of approximately 8 hours. At the end of digestion the samples were filtered by gravity using Whatman 41 filters. The filtrate was analyzed using an ICP-AES (Thermo Jarrel Ash Trace Analyzer) following US EPA Method 6010B (US EPA, 1996). The detection limit for arsenic, chromium and copper in mg/kg of ash (milligrams of metals per kilogram of ash) was 0.60 mg/kg, 0.25 mg/kg and 0.20 mg/kg, respectively. This translates to 0.02 to 0.07 mg/kg for arsenic in terms of the original unburned mulch sample and 0.01 to 0.03 mg/kg for chromium and copper. The range in the detection limit was due to the variable volatile fractions of each sample. All samples were analyzed in triplicate requiring the analysis of three separate aliquots of ash per sample. In general the coefficient of variation (standard deviation divided by the average) was 14% for copper, 16% for chromium, and 23% for arsenic. Spike recovery was between 82% and 100%. Reproducibility of the metal concentrations from the spike duplicates were within 5%. More details of the QA/QC analyses are provided in Appendix G.

*Fraction of CCA-treated Wood Within the Wood Mulch Samples*

Results from the analysis of the ash samples were used in conjunction with theoretical metals concentrations in CCA-treated wood to estimate the fraction of CCA-treated wood, by weight, within the original mulch samples,  $F_{cca}$ . The equation used for this analysis is show below (equation II.6) where  $C_{M^s}$  corresponds to the concentration of metal “M” (either chromium, copper, or arsenic) in the sample,  $C_{M^u}$  corresponds to the concentration of metal “M” in untreated wood, and  $C_{M^cca}$  corresponds to the concentration of metal “M” in CCA-treated wood. The metal concentrations in the samples,  $C_{M^s}$ , and in untreated wood,  $C_{M^u}$ , were measured during this study. The  $C_{M^cca}$  values are theoretical values corresponding to 0.4 pcf CCA-treated wood (entire cross-section). The values for  $C_{M^cca}$  and  $C_{M^u}$  are provided in Table II.5 below. For reporting purposes, the %CCA ( $F_{CCA} * 100\%$ ) was computed from the average %CCA as determined from the copper and chromium concentrations. The %CCA as determined from the arsenic concentrations was not used due to concerns associated with volatilization of arsenic during the ashing sample processing step. This method of computation is consistent with that recommended by Tolaymat et al. 2000.

$$F_{cca} = \frac{C_{M^s} - C_{M^u}}{C_{M^cca} - C_{M^u}} \quad \text{eqn. II.6}$$

Wood Type	Metal Concentration (mg/kg)		
	Cu	Cr	As
CCA, 0.4 pcf approximately, $C_{M^cca}$	1,791	2,994	2,691
Untreated, $C_{M^u}$	1.3	0.9	1.1

Table II.5: Assumed Concentrations of CCA-Treated Wood and Untreated Wood In Computations Used to Estimate the Fraction of CCA-treated Wood Within the Mulch Samples

## II.2 RESULTS FROM VISUAL INSPECTION AND SIZE DISTRIBUTION ANALYSIS

This section summarizes the results from the visual inspection of the samples (Section II.2.a) and from the size distribution analysis (Section II.2.b).

### II.2.a Results from Visual Inspection

Of the 84 wood mulch samples from Florida evaluated in this study, 52% (n = 44) were artificially colored. Of the 44 colored samples, 37 were red, 5 were gold, and 2 were black (Table II.6). Sixteen of the 84 mulch samples were observed to contain plywood (18%), three were observed to contain particle board (3%), and none were observed to contain oriented strand board. Painted wood was found in six samples (7%), and other objects including nails, rope, string, plastic, rocks, and glass were found in nine samples (11%). A little more than one-half of the samples contained mulch pieces that were considered to have “smooth or straight edges”. Similarly a little more than one-half of the samples contained at least some pine bark. Of the 84 samples, 7 were composed of at least 95% pine bark.

Of the 44 colored wood samples, 13 were observed to contain plywood (30%), 2 were observed to contain particle board (5%), and none were observed to contain oriented strand board (Table II.7). Painted wood was found in six samples (14%) and other objects including nails, rope, string, plastic, rocks, and glass were also found in five samples. The majority of these samples (70%) were considered to contain mulch characterized by smooth or straight edges. A little more than half (59%) contained at least some pine bark and 2 of these samples consisted of at least 95% colored pine bark.

Visual Analysis Category	Fraction of Samples	Number of Samples	Additional Information
Colored	52%	44	Of the colored samples, 37 were red, 5 were gold, and 2 were black
Contain Plywood	18%	16	
Contain Particle Board	3%	3	
Contained Oriented Strand Board	0%	0	
Contained Painted Wood	7%	6	
Contained Other Objects	11%	9	Other objects included, nails, rope, string, plastic, rocks, and glass.
Pine Bark	56%	47	Of the 47 samples that contained pine bark, 7 consisted of at least 95% pine bark

Table II.6: Summary of Results from Visual Inspection of All Wood Mulch Samples from Florida (n = 84)

Visual Analysis Category For Colored Samples Only	Fraction of Samples	Number of Samples	Additional Information
Contain Plywood	30%	13	
Contain Particle Board	5%	2	
Contained Oriented Strand Board	0%	0	
Contained Painted Wood	14%	6	
Contained Other Objects	11%	5	Other objects included, nails, rope, string, plastic, rocks, and glass.
Pine Bark	59%	26	Of the 26 samples that contained pine bark, 2 consisted of at least 95% pine bark

Table II.7: Summary of Results from Visual Inspection of the Florida Wood Mulch Samples that Were Colored (n = 44)

## II.2.b Results from Size Distribution Analysis

The average  $d_{50}$  of the samples was 0.3 in. The majority of the samples (89%) were characterized by  $d_{50}$  values between 0.1 to 0.5 inches (Figure II.2a). The average uniformity coefficient for all of the samples was measured at 5.0. A majority of the samples (85%) were characterized by uniformity coefficients between 3 and 8 (Figure II.2b).

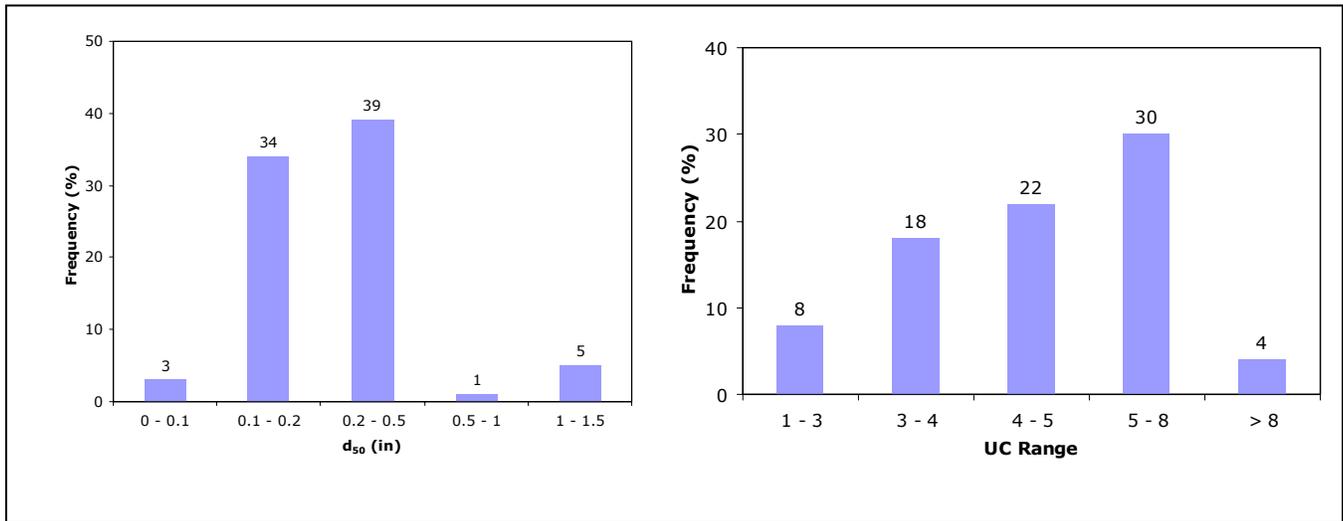


Figure II.2: Histogram Plot of  $d_{50}$  (plot A) and Uniformity Coefficient (plot B) Values for Florida Wood Mulch Samples ( $n = 82$ . Insufficient sample size to process 2 of the 84 Florida wood mulch samples)

## **II.3 LEACHABLE METALS FROM MULCHES USING THE SPLP**

Leachable metals results are described using a series of figures and tables. The first set of figures focus on describing the results for all metals and is organized by sample number (section III.3.a). Comparisons are also provided between metals (section III.3.b). The main focus of subsequent discussion is on leachable arsenic concentrations, and includes an overall summary of the arsenic SPLP results in tabular format (section III.3.c), an emphasis on the geographic distribution of results (section III.3.d), and relationship of the results with the size distribution of the mulch (section III.3.e).

### **II.3.a SPLP As, Cr, and Cu Concentrations By Sample Number**

SPLP results were split into two general categories for plotting purposes: samples collected within South Florida plus the one playground mulch sample collected in Arizona (Figure II.3) and samples collected in the rest of Florida (Figure II.4). Overall for the first group of samples (Figure II.3), the results between the metals were generally consistent. When leachable arsenic concentrations were elevated, generally the leachable chromium and copper values were also elevated. The primary exceptions were observed for samples 19, 22, and 24 for which leachable copper was elevated but chromium and arsenic were measured below detection limits. The source of copper to these samples does not appear to be CCA. Of the 3 playground samples that did not contain plywood, only 1, the one from Arizona, contained elevated levels of leachable Cu, Cr, and As (left side of Figure II.3). Of the 3 playground samples that were colored and contained plywood, all 3 were characterized by elevated leachable levels of all three metals. Of note is that the SPLP arsenic concentrations were on the order of 100 ug/L for all three of these samples. There was one residential mulch sample collected from a home garden (Sample 26). This one sample was also characterized by elevated leachable levels of all three metals, but the concentrations were not as high as those observed for the playground samples. For the first batch, 4 of the 5 store-bought samples that were colored and contained plywood were characterized by leachable arsenic concentrations above the detection limit. Three of the 5 contained leachable arsenic concentrations above 100 ug/L. Only 1 sample of the 13 South Florida wood mulches bought at stores that did not contain plywood were characterized by elevated leachable metals concentrations for all three metals (sample 23). The leachable metals concentrations for this sample were on the order of 10 ug/L.

For the second set of samples representing the “rest of Florida” (Figure II.4), results were less consistent between metals. Many of the samples were characterized by leachable arsenic concentrations below the detection limit, but chromium and copper for these same samples were in many cases considerably above the detection limit. A few samples were characterized by elevated levels of all three metals. These included 4 of the 5 samples that were colored and contained plywood (left side of Figure II.4). Of the 24 wood mulch samples that were colored but did not contain plywood 1 was characterized by concentrations above the detection limits for all three metals. The concentration of leachable arsenic in this set was not as high as in the South Florida set. For the “rest of Florida” samples that were not colored nor contained plywood (n = 30), none were characterized by SPLP concentrations above detection limits for all three metals.

Overall, it appears that leachable arsenic concentrations were highest for the South Florida samples, and most of these samples were characterized by elevated concentrations of leachable chromium and copper as well. For the “rest of Florida” samples, the SPLP arsenic concentrations were generally not as high with the exception of a few colored samples.

### **II.3.b Comparisons Between SPLP Metal Concentrations**

In general, the greater the amount of chromium leached, the greater the amount of arsenic and copper leached (Figures II.5 and II.6). The concentrations of copper and chromium in the SPLP leachates were similar. The concentrations of arsenic were generally higher than the concentrations of chromium and copper. Of note is that the 5% CCA control leached copper and chromium near the upper limits of those observed in the samples. The arsenic concentration of the SPLP leachate was higher in the 5% CCA control than that observed in the remaining samples.

### **II.3.c Summary of Arsenic SPLP Results in Tabular Format**

Of the 84 wood mulch samples collected in Florida, 37 contained no color and no plywood. Within these 37 samples, 5% were characterized by SPLP arsenic concentrations in excess of 12 ug/L and none were characterized by concentrations in excess of 100 ug/L. In contrast, 13 of the 84 samples evaluated were artificially colored and contained plywood. Among these 13 samples the vast majority (85%) was characterized by SPLP arsenic concentrations in excess of 12 ug/L and almost one-half (46%) were characterized by concentrations in excess of 100 ug/L. A total of 31 samples were artificially colored but did not contain plywood. Among these samples roughly one-tenth were characterized by SPLP arsenic concentrations above 12 ug/L and only a very small fraction exceeded 100 ug/L. Only one of the 3 samples that contained plywood but were not colored was characterized by levels of arsenic above detection limits.

Among the 47 samples that contained at least some pine bark, over one tenth were characterized by SPLP arsenic concentrations in excess of 12 ug/L. Among the 7 samples that were composed of at least 95% pine bark, none were characterized by SPLP arsenic concentrations above detection limits.

Of interest is the large proportion of open bin samples that were characterized by elevated SPLP arsenic concentrations. Samples characterized as “open bin” samples were not pre-bagged. These mulch samples were obtained from large piles located near the buildings of the retail stores. Although the number of “open bin” samples evaluated was small (4 samples total), three quarters of the samples were characterized by SPLP arsenic concentrations in excess of 12 ug/L and one-half of the samples were characterized by concentrations in excess of 100 ug/L.

### **II.3.d Geographic Distribution of SPLP Results for Arsenic**

To evaluate possible geographic distributions, SPLP arsenic results for the 84 wood mulch samples were super-imposed on a map of Florida (Figure II.7). Circles on the plot correspond to colored samples and triangles correspond to non-colored samples. Results clearly show that the majority of the “hits” were observed within the South Florida area (Dade and Broward Counties), with a higher proportion of the hits among the colored mulch samples. A few samples with very high SPLP levels were also collected from Ft. Myers and Lake Worth.

### **II.3.e Relationships Between SPLP Arsenic Concentration and Size Distribution Parameters**

There was no direct correlation between the  $d_{50}$  and the arsenic SPLP concentration. However, the samples with the higher arsenic SPLP concentrations were characterized by  $d_{50}$  values

smaller than 0.25 inches (Figure II.8), suggesting that the samples contaminated with arsenic (SPLP arsenic concentrations greater than 16 ug/L) were ground up to smaller sizes, on average. Samples that were finely ground were not necessarily contaminated with arsenic, but only the finely ground samples ( $d_{50}$  less than 0.25 inches) contained highly elevated levels of leachable arsenic. None of the mulch samples characterized by a  $d_{50}$  greater than 0.25 inches contained elevated levels of leachable arsenic. No relationship could be observed between arsenic SPLP concentration and the uniformity coefficient (UC) of the mulch size distribution (Figure II.9).

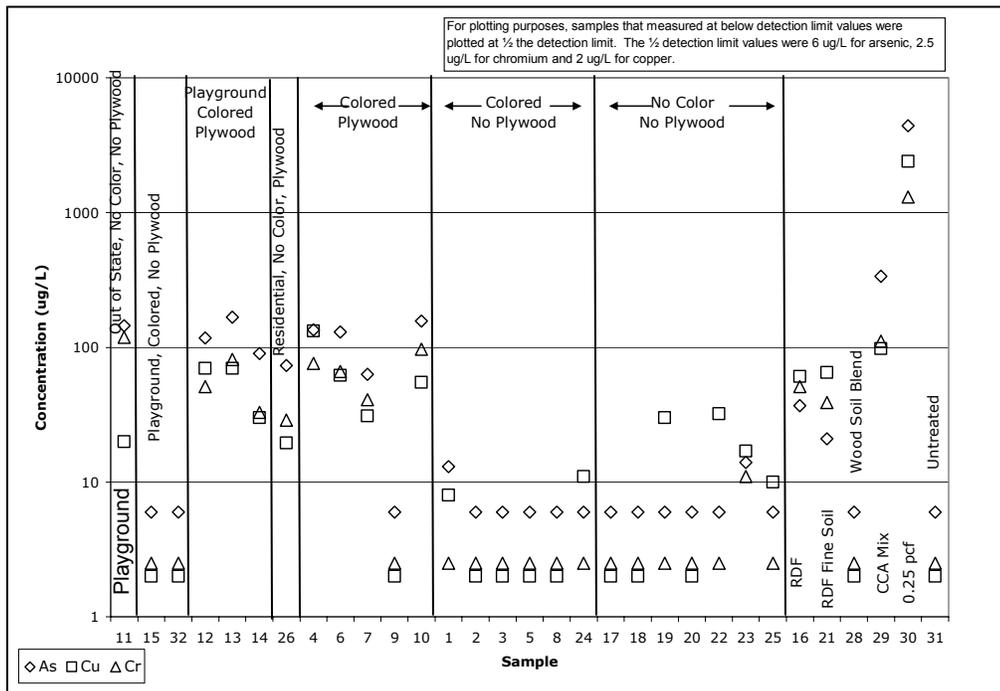


Figure II.3: SPLP Metals Concentrations Versus Sample Number for Samples Collected in South Florida

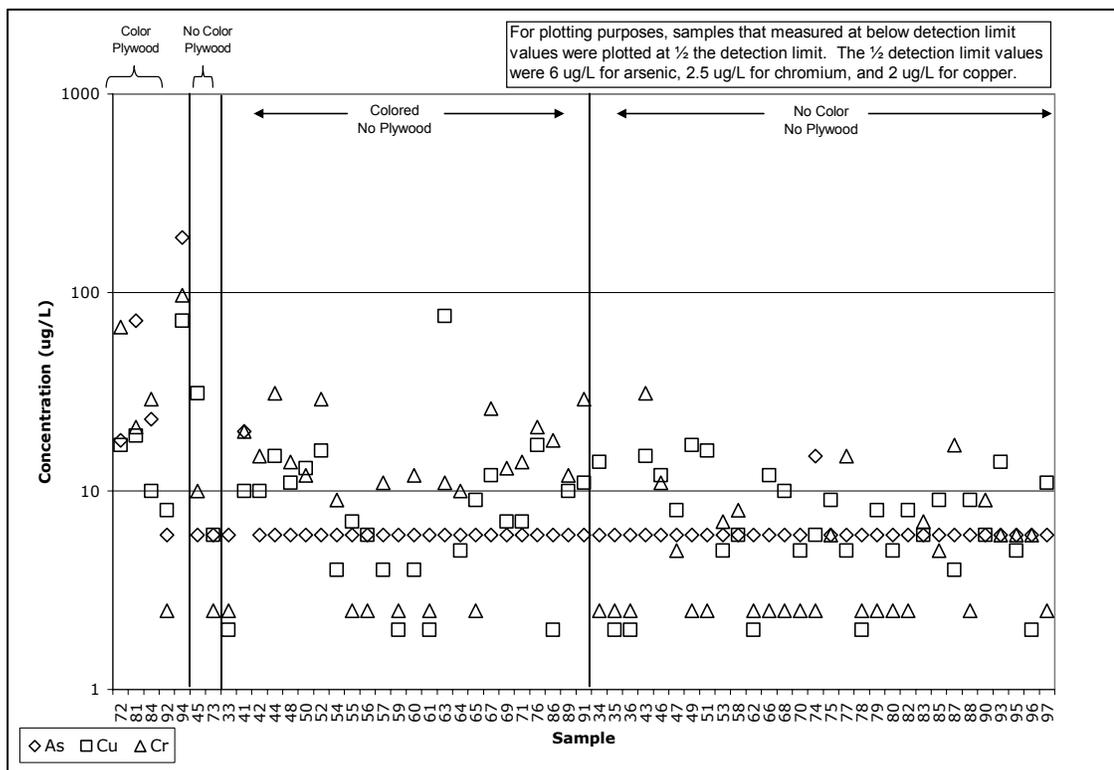


Figure II.4: SPLP Metals Concentrations Versus Sample Number for Samples Collected Outside of South Florida (Note: Sample 63 is the only non-wood mulch sample. This mulch sample was made from rubber tires)

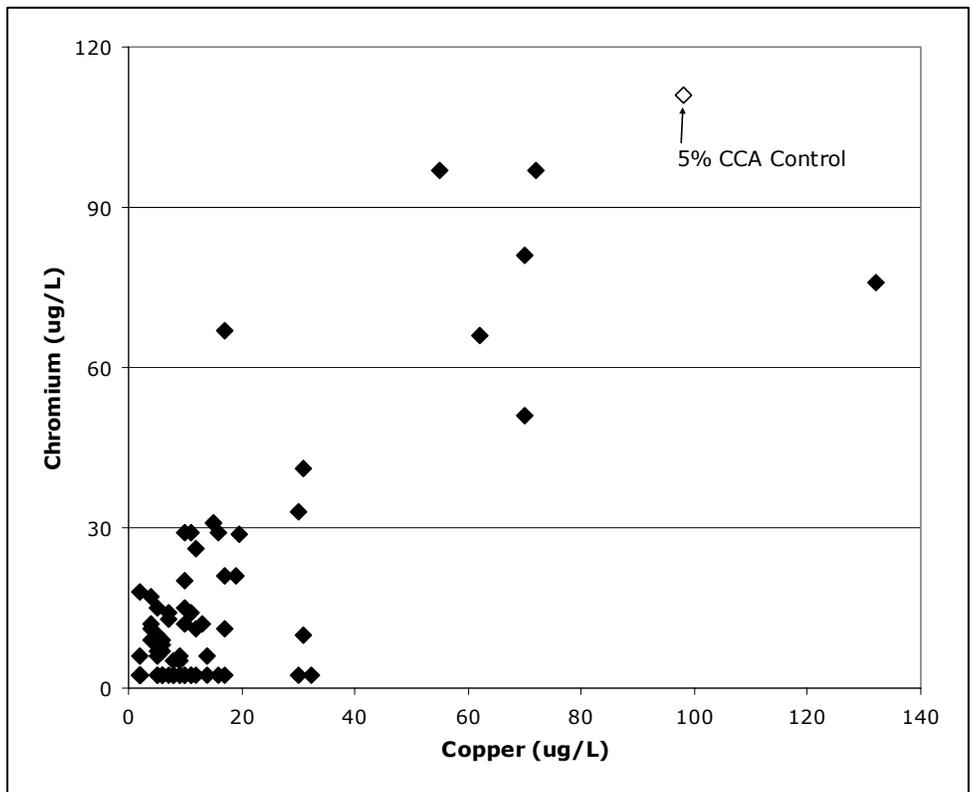


Figure II.5: Leachable Copper Versus Leachable Chromium for Mulch Samples Subjected to the SPLP Test

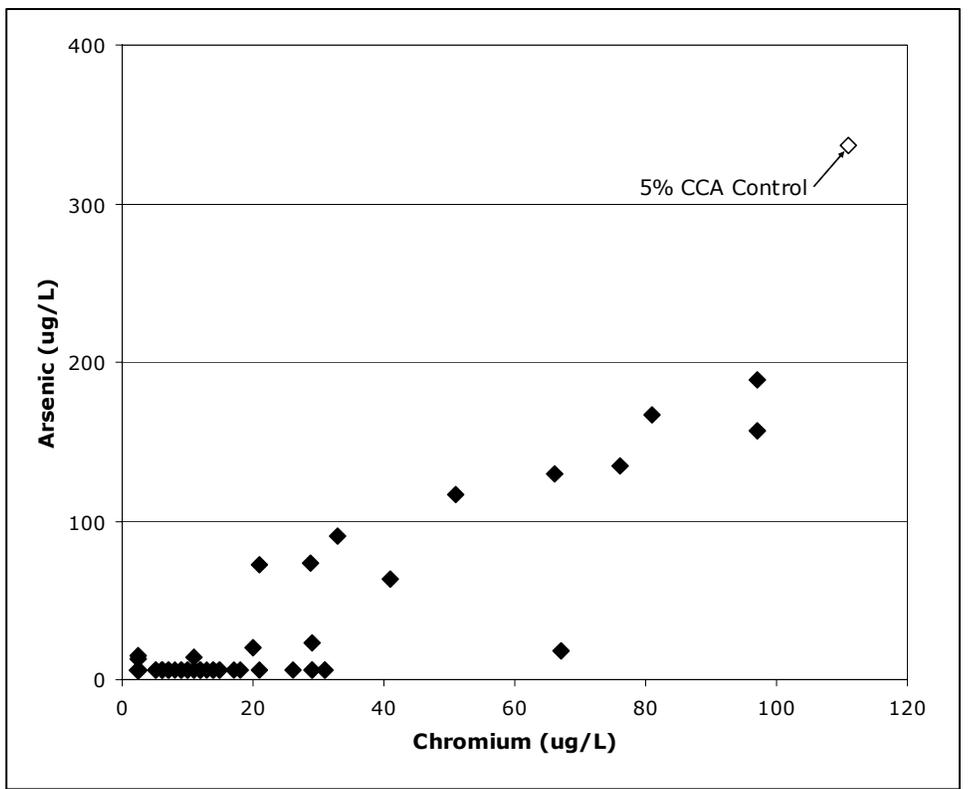


Figure II.6: Leachable Chromium Versus Leachable Arsenic for Mulch Samples Subjected to the SPLP Test

Category		Number of Samples in Category	Fraction of Samples in Category with SPLP Values Greater Than Indicated		
Colored	Plywood		> 12 μg/L Arsenic	> 50 μg/L Arsenic	> 100 μg/L Arsenic
		37	5%	0%	0%
√		31	6%	0%	0%
	√	3	33%	33%	0%
√	√	13	85%	69%	46%
Open Bin		4	75%	75%	50%
Contain Some Pine Bark		47	11%	4%	2%
Contain more than 95% Pine Bark		7	14%	0%	0%

Table II.8: Summary of SPLP Results for Arsenic (Florida Wood Mulch Samples Only, n = 84)

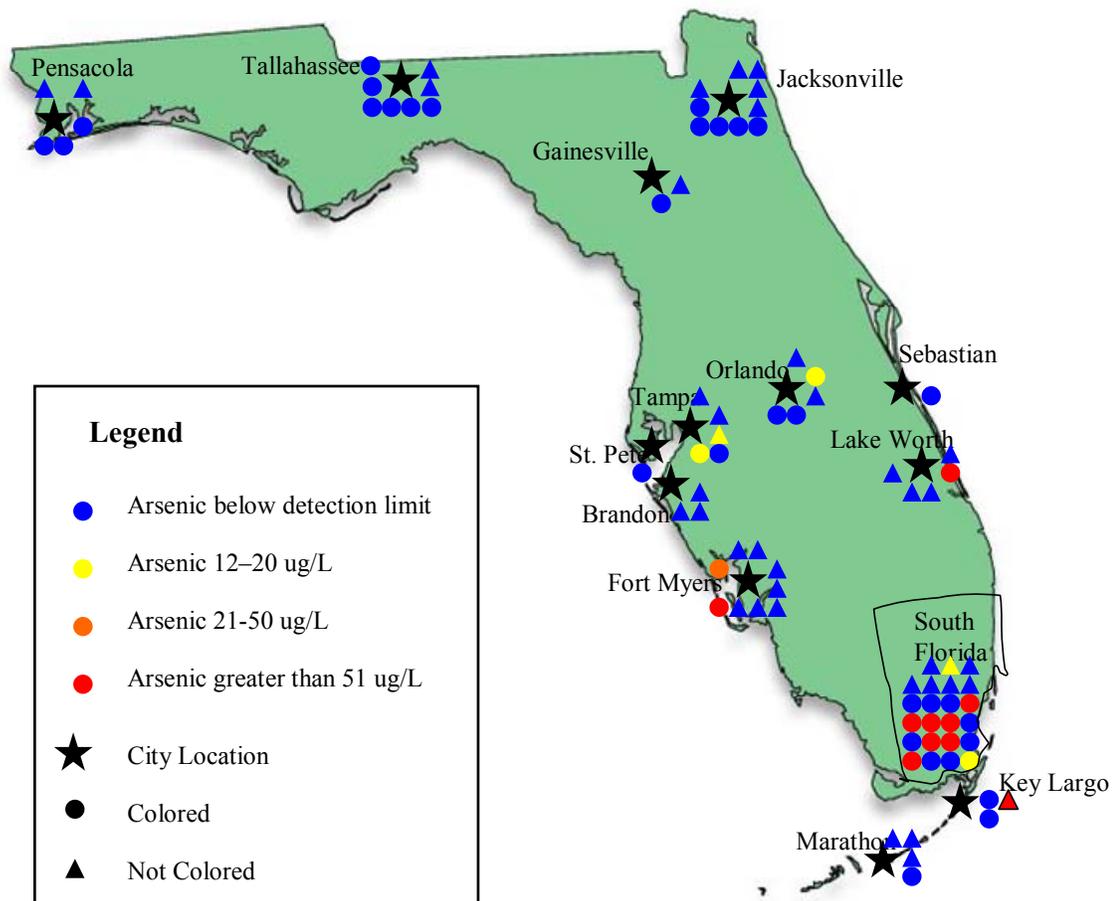


Figure II.7: Geographic Distribution of Mulch Samples Characterized by Various Levels of Leachable Arsenic as Measured Using the SPLP. Data points are included for the 84 wood mulch samples collected in Florida. South Florida includes Miami-Dade and Broward Counties.

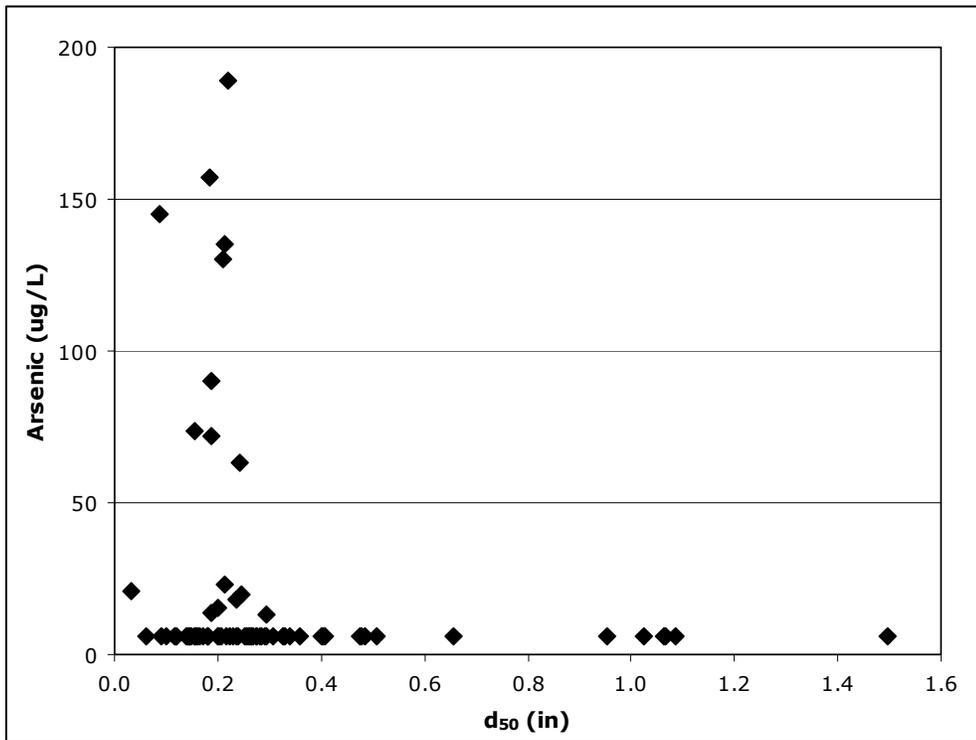


Figure II.8:  $d_{50}$  versus Arsenic SPLP Concentrations for all Mulch Samples

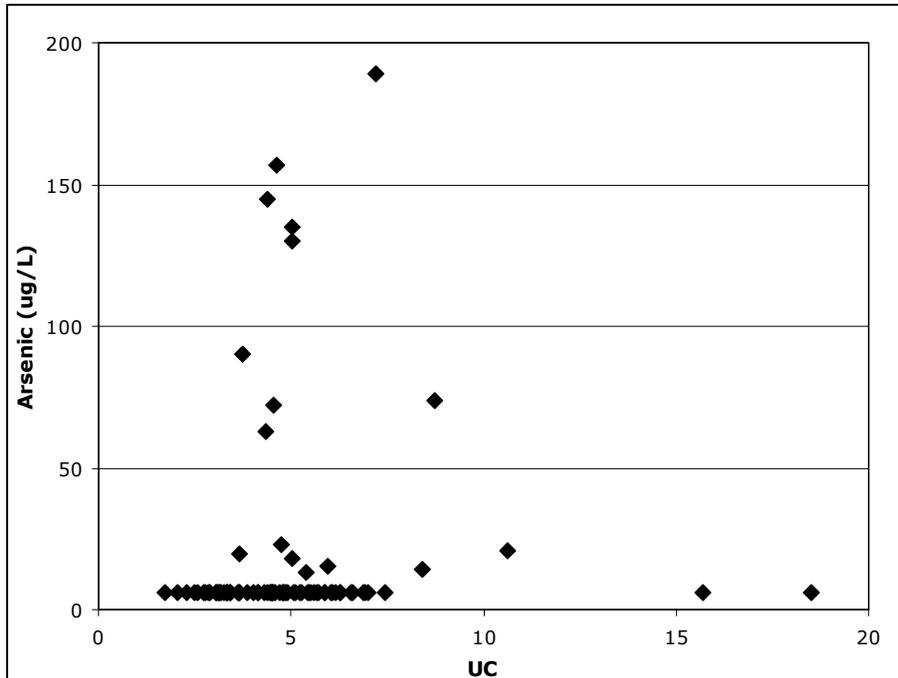


Figure II.9: Uniformity Coefficient (UC) versus Arsenic SPLP Concentrations for all Mulch Samples

## **II.4 “RECOVERABLE” METALS FROM MULCH AND FRACTION OF CCA-TREATED WOOD IN MULCHES**

As for leachable metals, the results for recoverable metals are described using a series of figures and tables. It is important to note that “recoverable” metals are defined by the method used for analysis. The method involved an ashing step (which may have resulted in the volatilization of some metals) and an acid digestion of the resultant ash. The first set of figures focus on describing the results for all metals and is organized by sample number (section III.4.a). Comparisons are also provided between metals (section III.4.b). Subsequent discussions focus on recoverable arsenic concentrations, and include an overall summary of the recoverable arsenic results in tabular format (section III.4.c), an emphasis on the geographic distribution of results (section III.4.d), and a comparison of total recoverable arsenic with the size distribution of the mulch (section III.4.e). The section closes with a summary focusing on an estimated percentage of CCA-treated wood within the samples that were found to contain elevated concentrations of arsenic, chromium, and copper (section III.4.f).

### **II.4.a “Recoverable” As, Cr, and Cu Concentrations By Sample Number**

In a similar fashion as for leachable metals, the results for recoverable metals were separated into two batches: samples collected primarily within South Florida plus the one playground mulch sample collected in Arizona (Figure II.10) and samples collected in the rest of Florida (Figure II.11). For the first set of samples, the results were consistent with the leachable metals concentrations. Recoverable metals were elevated for: a) all three of the playground mulches that were colored and contained plywood, and b) one of the three playground mulches (the one from Arizona) that was not colored and did not contain plywood. Total recoverable metals in the 4 playground samples with elevated concentrations was on the order of 100 mg/kg for each metal. The concentrations in the mulch sample collected from a residence, was also elevated with metal concentrations on the order of 10 mg/kg. Four of the 5 store-bought mulch samples that were colored and contained plywood were also characterized by consistently elevated arsenic, chromium, and copper concentrations. These concentrations were on the order of a 100 mg/kg for each metal. All of the remaining samples that did not contain plywood were characterized by metals concentrations consistently less than 10 mg/kg.

For the second set of samples, the majority of the samples were characterized by recoverable metals concentrations below 10 mg/kg. The samples with less than 10 mg/kg were characterized by exceptionally low and variable arsenic levels, perhaps due to some volatilization of the arsenic during the ashing step. Exceptions to the low recoverable metals concentrations include samples 72, 81, 84 and 94 which were 4 of 5 samples that were colored and contained plywood. One of the 32 non-colored samples (sample 74) in this set exceeded 10 mg/kg for each metal.

Overall a larger proportion of mulch samples exceeded 10 mg/kg recoverable metals for the first batch of samples relative to the second batch. Furthermore, the concentration of the metals in the first batch more frequently exceeded the 100 mg/kg threshold as well. So not only were more samples contaminated in the first batch, the level of contamination was higher in the first batch relative to the second. Also of note is that samples that contained recoverable metals in excess of 10 mg/kg consistently contained concentrations in excess for arsenic, chromium and copper, with the chromium concentrations slightly higher than the copper and arsenic.

#### **II.4.b Comparisons Between “Recoverable” Metal Concentrations**

The ratio of “recoverable” chromium to “recoverable” arsenic was consistent with the composition of CCA. CCA is produced in set ratios of As, Cr, and Cu (AWPA 2003). Three types of CCA have been produced over time. These include CCA Type A, Type B, and Type C. Type A and Type B are considered to represent older formulations and Type C is the common formulation today. The theoretical lines associated with CCA Types A, B, and C are superimposed on Figures II.12 and II.13. Furthermore, within Type C, the American Wood Preservers’ Association specifies acceptable ranges of metals for each formulation. The minimum and maximum allowable ratios of Type C preservative is also superimposed on these graphs.

Comparison of the data with the theoretical CCA lines, for Type A, B, and C, indicate that all the mulch samples with elevated chromium and copper concentrations, except for 1 sample, fell within the boundaries of typical CCA solutions (Figure 11.12). The best fit line of the chromium and copper data coincides with the theoretical line that corresponds to the maximum allowable chromium to copper ratio for Type C solutions. The consistency in the ratio of chromium to copper between the data and theoretical CCA lines provides strong evidence that the source of chromium, and copper contamination observed in the samples was due to the presence of CCA-treated wood.

Recoverable arsenic and chromium ratios were slightly below the theoretical ratio corresponding to Type C solutions, although the ratio was above the line corresponding to Type B CCA solutions. Such results suggest that a fraction of the arsenic was volatilized during the ashing step, assuming that the majority of the CCA-treated wood was Type C which was indicated by Figure II.12 above. This result is consistent with studies that indicate that among the 3 metals within CCA, arsenic is the most volatile and that at the temperatures used to ash the mulch samples some arsenic volatilization has been documented (Hirata et al. 1993; Helsen and Van den Bulck 2003; Helsen et al. 2003; Hata et al. 2003; Wu and Barton 2001). Thus the “recoverable” arsenic concentrations reported should be considered to represent possible low values due to possible volatilization of the arsenic during the ashing step. Please refer to Appendix G for experimentation focusing on quantifying volatilization during ashing.

#### **II.4.c Summary of “Recoverable” Arsenic Results in Tabular Format**

Of the 84 Florida wood mulch samples evaluated in this study, 13 were colored and contained plywood (Table II.9). Of these 13 samples, 69% were characterized by “recoverable” arsenic in excess of 50 mg/kg. Less than 10% of the mulch samples (that were not both colored and contained plywood) were characterized by recoverable arsenic concentrations in excess of 2.1 mg/kg (milligrams of arsenic per kilogram of unburned wood mulch). Although the number of samples is small (n = 4), the majority of the samples (n = 3) collected from “open bins” were characterized by recoverable arsenic concentrations in excess of 50 mg/kg. None of the 7 samples that were composed primarily of pine bark contained recoverable arsenic in excess of 2.1 mg/kg.

#### **II.4.d Geographic Distribution of “Recoverable” Arsenic Concentrations**

The geographic distribution of samples that exceeded thresholds for recoverable arsenic concentrations (Figure II.14) was very similar to the geographic distribution of those same samples that exceeded SPLP arsenic thresholds. In summary the majority of the “hits” were located in the south Florida area. Among the “hits”, colored mulch samples exceeded recoverable arsenic

thresholds more frequently than non-colored mulch samples. In addition to south Florida, notable “hits” among colored mulch samples were observed in Ft. Myers and Lake Worth. One sample from Orlando and two from Tampa also exceeded the 2.1 mg/kg threshold.

#### **II.4.e Relationships Between “Recoverable” Arsenic Concentration and Size Distribution Parameters**

As observed for SPLP arsenic concentrations, recoverable arsenic was not directly correlated with the mulch  $d_{50}$  value or the uniformity coefficient (Figure II.15 and Figure II.16). However, only samples that were characterized by a  $d_{50}$  less than 0.25 inches were characterized by elevated recoverable arsenic concentrations ( $> 2.1$  mg/kg). None of the samples that were characterized by a  $d_{50}$  greater than 0.25 inches contained elevated levels of arsenic. It is emphasized that some finely ground mulch samples were not characterized by elevated recoverable arsenic. However, only the finely ground mulch samples were characterized by elevated recoverable arsenic concentrations.

#### **II.4.f Fraction of CCA-treated Wood Within the Mulch Samples**

Results focusing on the fraction of CCA-treated wood contained within the mulch samples indicated that the majority of the mulch samples evaluated were characterized by less than 5% CCA-treated wood (Table II.10 and Appendix E). Sixty-nine percent of the samples that were colored and contained plywood were characterized by greater than 1% CCA-treated wood by weight. This is contrasted by the other 3 categories of mulch (no color and no plywood, no color and plywood, color and no plywood) for which less than 10% of the samples were characterized by 1% CCA-treated wood, by weight. The maximum fraction of CCA-treated wood observed was 15% (Sample 10). This sample was a red-colored open-bin sample from a nursery in southeast Florida. This sample also contained plywood, a small fraction of pinebark, and was characterized by a fine average mulch size ( $d_{50} = 0.18$  inches).

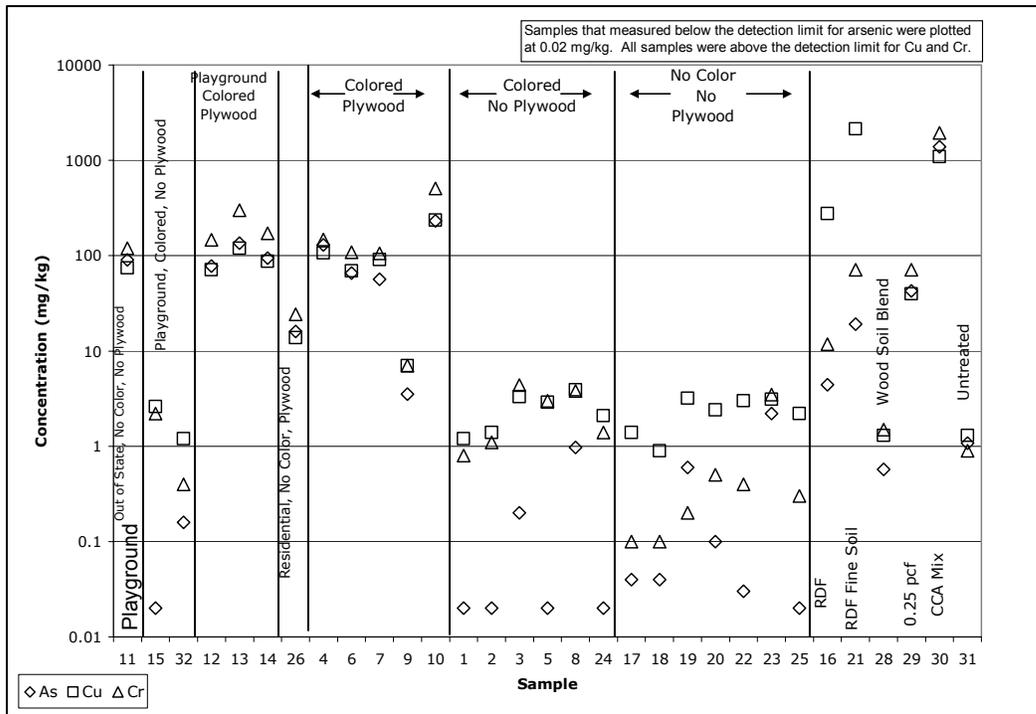


Figure II.10: Recoverable Metals Concentrations Versus Sample Number for Samples Collected in South Florida

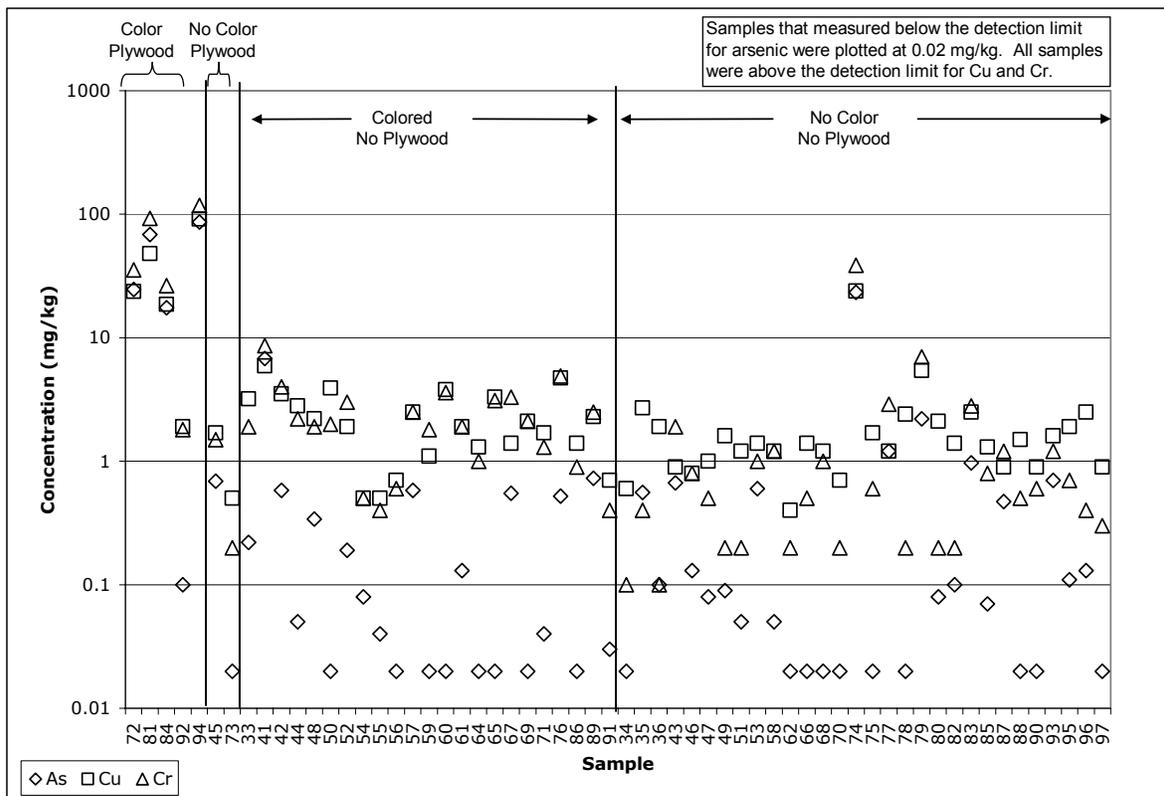


Figure II.11: Recoverable Metals Concentrations Versus Sample Number for Samples Collected Outside of South Florida

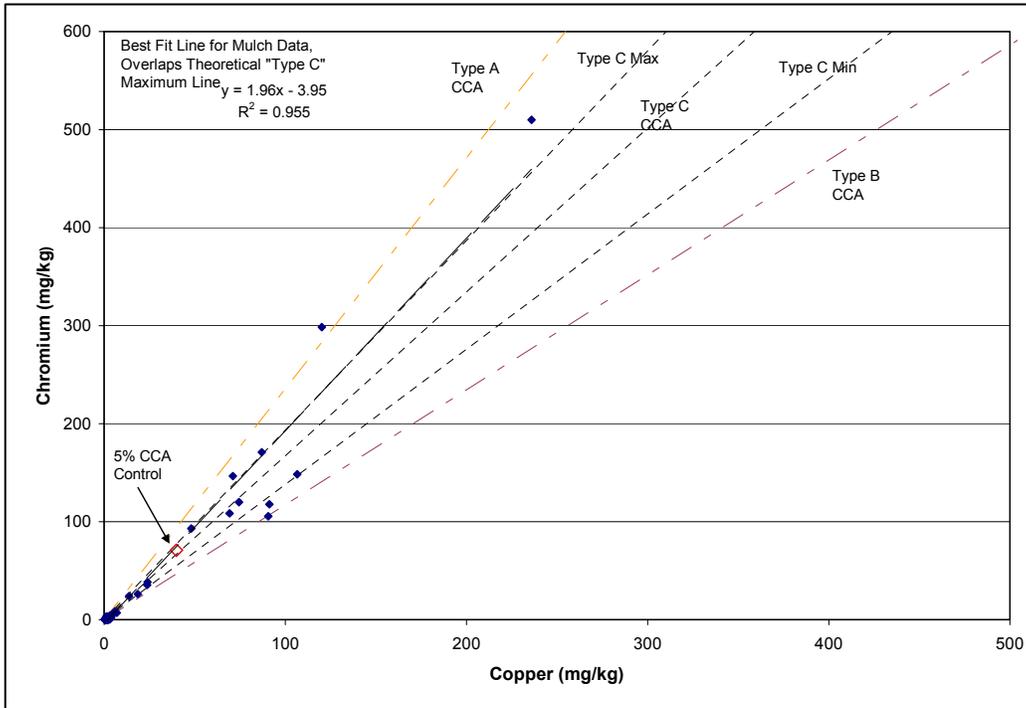


Figure II.12: Recoverable Copper Versus Recoverable Chromium for Mulch Samples

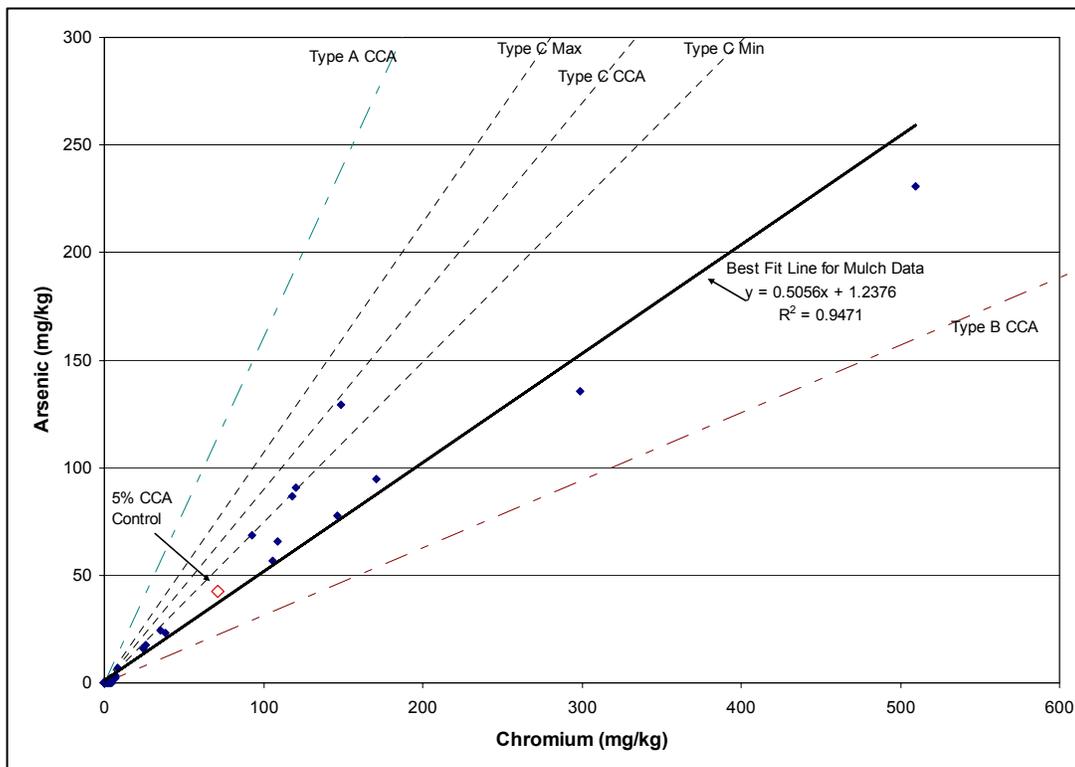


Figure II.13: Recoverable Chromium Versus Recoverable Arsenic for Mulch Samples

Category		Number of Samples in Category	Fraction of Samples in Category with Total Recoverable As Values Greater than Indicated			
Colored	Plywood		> 2.1 mg/kg <sup>a</sup> Arsenic	> 10 mg/kg Arsenic	> 50 mg/kg Arsenic	> 100 mg/kg Arsenic
		37	8%	3%	0%	0%
√		31	3%	0%	0%	0%
	√	3	33%	33%	0%	0%
√	√	13	92%	85%	69%	23%
Open Bin		4	75%	75%	75%	50%
Contain Some Pine Bark		47	13%	6%	4%	0%
Contain more than 95% Pine Bark		7	0%	0%	0%	0%

<sup>a</sup> mg of arsenic per kg of original mulch. 2.1 mg/kg was chosen as a threshold limit because it corresponds to Florida's Soil Cleanup Target Levels (SCTL) for Residential Areas (FDEP 2005)

Table II.9: Summary of Results for Recoverable Total Arsenic in Mulch Samples. (Florida Wood Mulch Samples Only, n = 84)

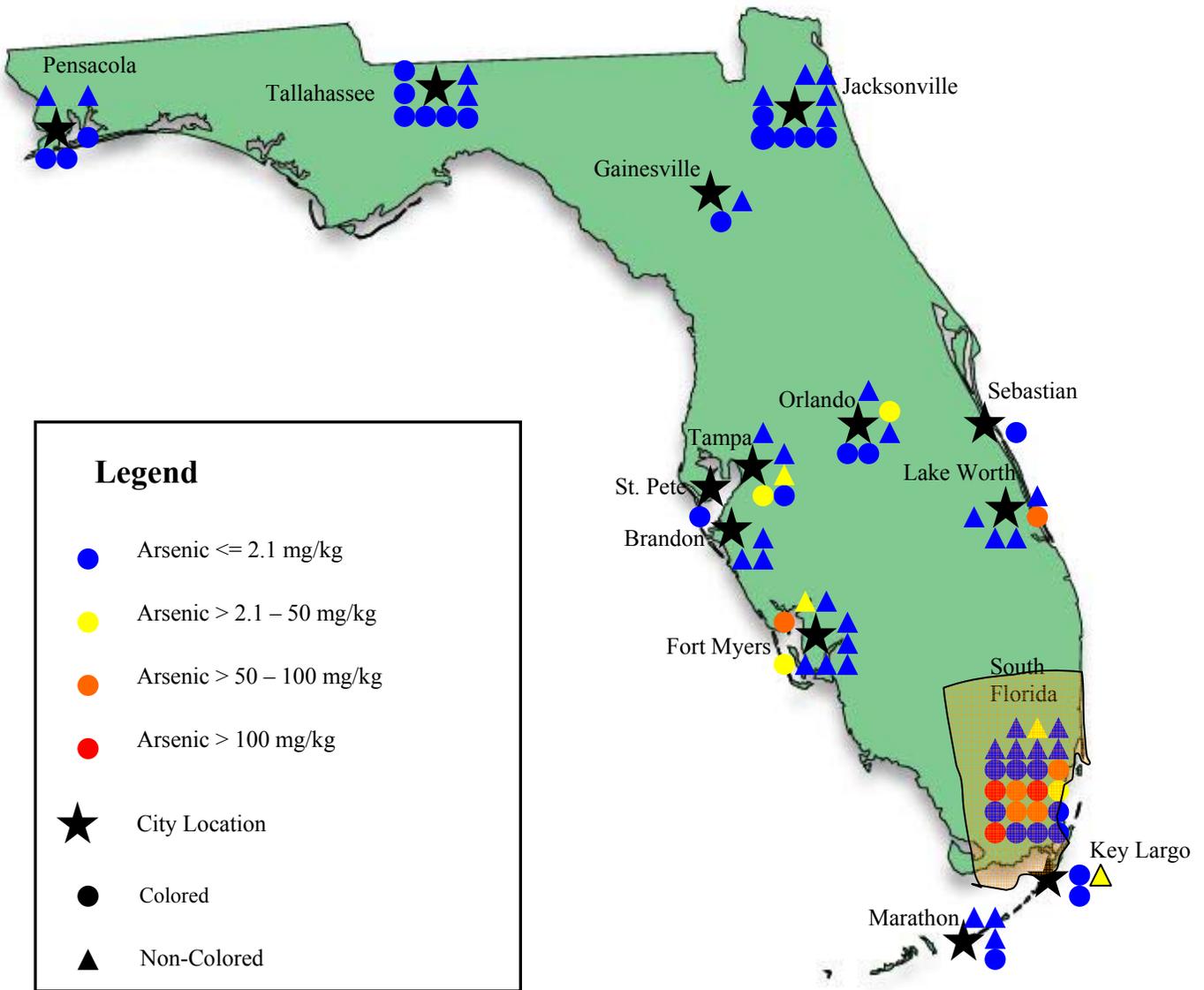


Figure II.14: Geographic Distribution of Mulch Samples Characterized by Various Levels of Total Recoverable Arsenic Within the Original Mulch Sample (milligrams of arsenic per kilogram of mulch). Data points are included for the 84 wood mulch samples collected in Florida. South Florida includes Miami-Dade and Broward Counties

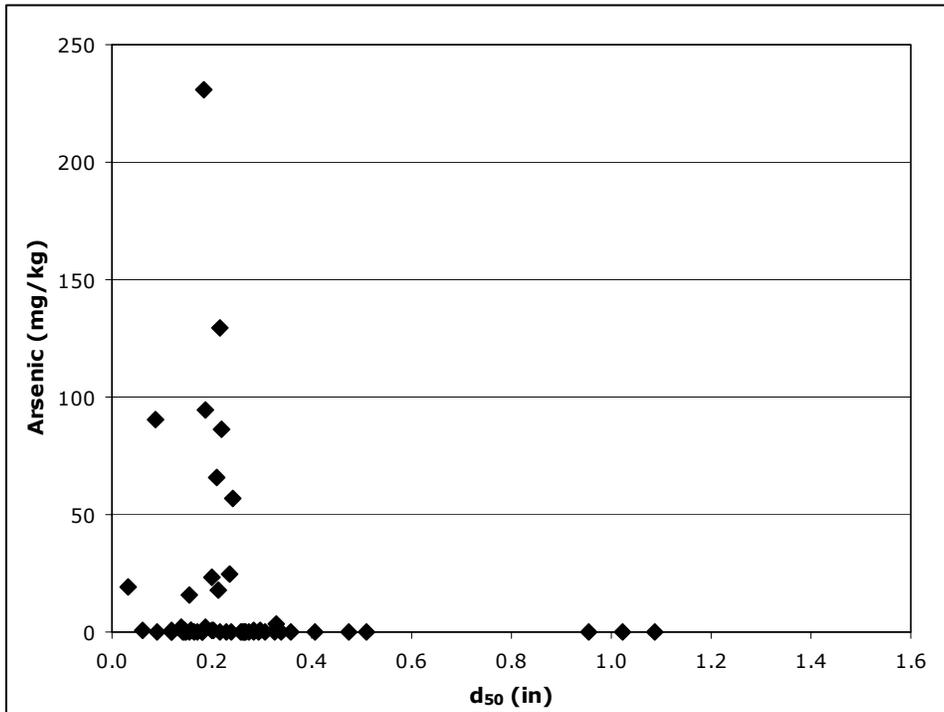


Figure II.15:  $d_{50}$  versus Recoverable Arsenic Concentrations for all Mulch Samples

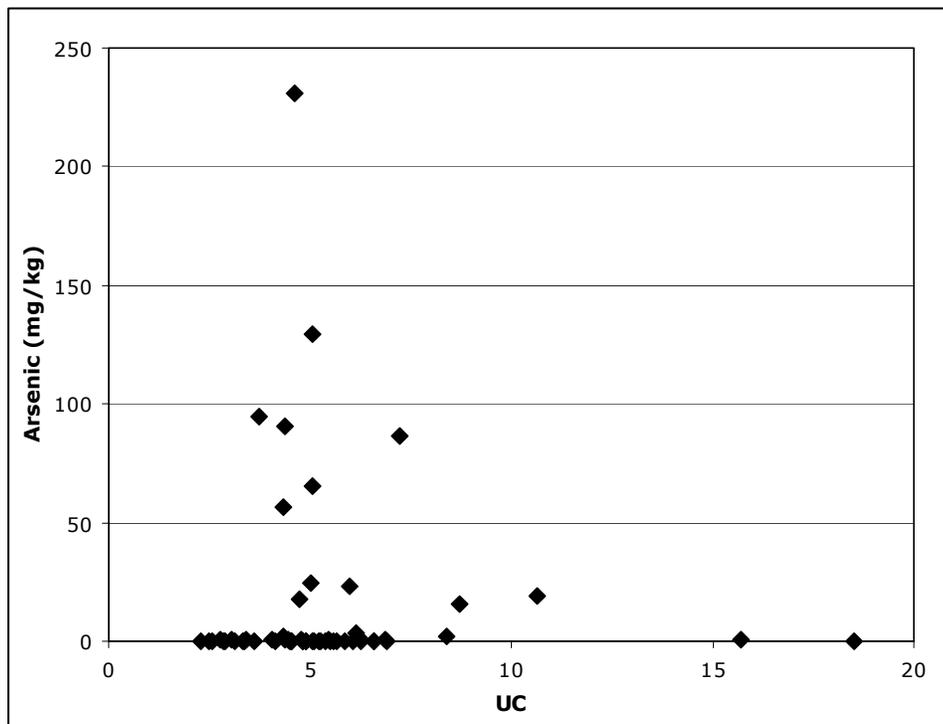


Figure II.16: UC versus Recoverable Arsenic Concentrations for all Mulch Samples

Category		Number of Samples in Category	Fraction of Samples in Category with %CCA Values Greater than Indicated			
Colored	Plywood		Detected	> 0.5% CCA	> 1 % CCA	> 5 % CCA
		37	70%	3%	0%	0%
√		31	58%	10%	6%	0%
	√	3	67%	0%	0%	0%
√	√	13	100%	77%	69%	9%
Open Bin		4	100%	75%	75%	50%
Contain Some Pine Bark		47	60%	4%	4%	0%
Contain more than 95% Pine Bark		7	29%	0%	0%	0%

Table II.10: %CCA in Treated Wood Samples

## **CHAPTER III**

# **IMPACT OF IRON-OXIDE COLORANT ON LEACHING OF METALS FROM CCA CONTAMINATED MULCH**

## CHAPTER III, IMPACT OF IRON-OXIDE COLORANT ON LEACHING OF METALS FROM CCA CONTAMINATED MULCH

This chapter focuses on describing the methods (Section III.1) and the results (Section III.2) from experiments designed to evaluate the impact of iron-oxide colorants on the leaching of metals from CCA-contaminated mulch.

### III.1 METHODS

Three mulch samples were prepared for this study. Each mulch sample was evaluated in pairs, with one dyed with the iron-oxide colorant and the other non-colored for a total of 6 colorant-mulch combinations (Table III.1). These combinations included two untreated wood samples (C000, N000), two - 100% treated wood samples (C100, N100), and two - 5% treated wood samples (C005, N005). The 5% wood samples were prepared by weighing 5% treated wood and 95% untreated wood. The 5% proportion was chosen because earlier studies as described in the previous chapter indicated that this proportion was representative of the upper bound of most contaminated mulch sold within the State of Florida.

Each colorant mulch combination was subjected to two tests: an SPLP test and a field leaching test using a series of observation boxes. The SPLP test is a laboratory test and the field observation boxes were placed outdoors for a period of several months and were subjected to natural rainfall and outdoor temperatures. Leachate samples were collected from these observation boxes to quantify the mass of metals leached over time. More details about the methods employed in this study are described in the subsections below including the experimental design (Section III.1.a) and leachate sample collection and analysis (Section III.1.b).

Colorant-Mulch Combination ID	%Untreated Wood	% CCA-Treated Wood	Colorant Used
N000	100%	---	None
C000	100%	---	Iron-Oxide
N100	---	100%	None
C100	---	100%	Iron-Oxide
N005	5%	95%	None
C005	5%	95%	Iron-Oxide

Table III.1: Colorant-Mulch Combinations Used for Experimentation

#### III.1.a Experimental Design

The experimental design involved: a) making the mulch from recycled C&D wood, b) determining the initial arsenic concentration of the mulch sample prior to experimentation, c) documenting the colorant characteristics and method of colorant addition, and d) construction of the observation boxes.

### *Preparation of Mulch Used in the Study*

Mulch was made from C&D wood obtained from a local wood recycling facility in Miami-Dade County, Florida. The wood from the recycling facility was brought to the University of Miami laboratories where it was sorted using the PAN indicator stain (Blassino et al. 2002) into copper treated and non-copper treated wood. The wood identified as non-copper treated was presumed to be untreated. A 55 horsepower industrial shredder was used to produce the mulch from the wood. Prior to introducing the wood into the shredder, the shredder was broomed clean to remove residual debris. First the untreated wood was shredded. The resultant mulch was collected on a large plastic tarp. The untreated wood was well mixed and then placed into a 130 L pre-acid washed plastic container. Once the untreated wood was processed and removed from the shredding location, the plastic tarp was wiped clean and the copper-treated wood was then shredded and processed in the same way as for the untreated wood. As a result of this process, two 130 L containers of mulch were produced, one containing untreated wood and the other containing treated wood. The samples used in the SPLP tests and for the observation boxes were prepared from the mulch stored in these containers.

### *Initial Arsenic Concentration in Mulch Samples Prior to Experimentation*

The initial arsenic concentration in the mulch samples prior to experimentation was determined using a modified procedure as established by Tolaymat et al. 2000, which requires drying and ashing of the samples. In brief, the mulch samples were dried in an oven for a period of 2 days and then ashed in a muffle furnace at 550°C for a period of 4 days. The modification of the method used by Tolaymat et al. 2000 involved decreasing the drying temperature to 65°C instead of 105°C. The lower temperature was chosen due to a safety concern of potential spontaneous ignition of a mulch sample at the higher temperature. The drying oven utilized in this study was not equipped to handle burning samples and so the drying temperatures utilized in this study were therefore decreased. Also, it is recognized that arsenic is a volatile metal. Spike tests conducted on mulch samples indicated that the majority of the arsenic (75%) is recovered in the ash. See Appendix G for more details concerning these spike tests.

Once ashed, the samples were digested using nitric acid and hydrogen peroxide according to a modified version of US EPA Method 3050B (US EPA 1996) and the digestates were then analyzed using an atomic absorption spectrometer (Perkin Elmer Model AA800) with flame atomization. The modification involved omitting the hydrochloric acid addition so that digestates could be alternatively analyzed by graphite furnace atomization in the event that concentrations were low. Shibata et al. 2004 compared digestates with and without the hydrochloric addition and found no significant differences in the metals recovery in sawdust samples from CCA-treated wood.

### *Colorant Characteristics and Method of Addition*

Mulch was colored with a red dye (Mulch Magic One Red, Becker Underwood, Ames, IA). The primary ingredients of the colorant utilized include iron oxide, water, and a resin package (Brent Packer, Becker Underwood, Personal Communication, Dec 2003). The moisture content of the colorant (35% water) was measured gravimetrically as part of the current study. According to the manufacturer the resin package serves as a binder which helps the iron oxide adhere to the wood chips. There are also trace ingredients within the colorant. One of these trace ingredients includes a preservative for the colorant when stored. This preservative helps to inhibit mold and other microbe

growth when the colorant is stored in solution.

Colorant addition to the mulch samples following basic instructions as provided by Becker Underwood. The instructions recommend adding 3 pounds of colorant to 200 ml water and mixing the colorant solution with a cubic yard of mulch. These instructions correspond to 1.78 kg of colorant per cubic meter of mulch (equation III.1).

$$Colorant / mulch(g / m^3) = \frac{3lb(colorant)}{yd^3(mulch)} \cdot \frac{0.453kg}{lb} \cdot \frac{yd^3}{27ft^3} \cdot \frac{ft^3}{0.0283m^3} = 1.78kg / m^3 \quad \text{eqn. III.1}$$

The mass of the mulch samples used for experimentation was 800 g. This mass of mulch corresponded to 0.00363 cubic meters. Thus the mass of colorant required for the mulch contained in each observation box was 6.45 g. Since the moisture content of the colorant was 35%, 9.92 g of wet colorant was added to the 800 g of mulch. Although the instructions indicate that 200 ml of water is to be added to facilitate mixing of the colorant and the mulch, it was found that 500 ml was needed to get the colorant to distribute evenly on the wood chips (Figure III.1). In summary, 9.92 g of liquid colorant were mixed with 500 ml of de-ionized water and this solution was added to 800 g of mulch.



Figure III.1: Diagram of Sample Preparation for Colorant Study

### *Construction of Observation Boxes*

The design of the observation boxes was finalized after making a set of prototypes. A total of six observation boxes were constructed. Each observation box consisted of the following materials (Figure III.2): a) a top reservoir consisting of a 7 L plastic container (23.5 cm x 34.0 cm top surface area), which held the mulch and which had an opening at the bottom for leachate to pass to the bottom reservoir, b) a bottom reservoir consisting of a 65 L plastic container; an opening was cut in the lid to allow leachate to collect at the bottom, c) 3 layers of geotextile (Mirafi 1160N, Pendergrass, GA) with a nominal opening size of 0.15 mm wrapped around the top reservoir; this geotextile, which is used in the construction of septic tank drainfields, was assumed to simulate the physical straining associated with a soil layer which would underlie mulches in the field and, d) a plastic net which was placed in the opening between the top and bottom reservoir to provide support for the geotextile. All reservoirs were calibrated in the range of 2 to 60 L with a 1 L graduated cylinder.

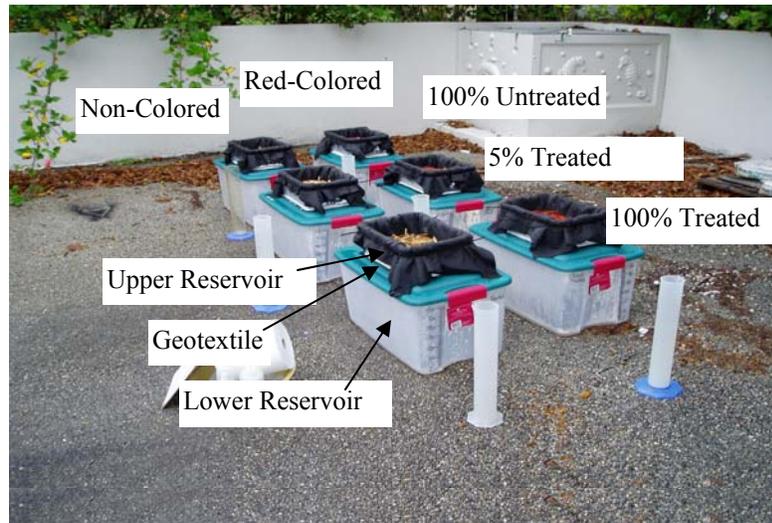


Figure III.2: Experimental Set-Up for Mulch Leaching Study

### III.1.b Leachate Sample Collection and Analysis

Each of the colorant-mulch combinations were evaluated in the laboratory using the SPLP test. Processing of the samples from the observation boxes, required rainfall data collection, leachate sample collection, leachate sample processing and analysis, and computing cumulative quantities of arsenic leached.

#### *Sample Processing for SPLP Analysis*

A set of 6 mulch samples were prepared in accordance with the combinations given in Table III.1. The mulch utilized came from the same batch used within the observation boxes. The SPLP procedure consisted of an initial extraction step, followed by filtration, sample digestion and analysis. The steps are the same as those outlined in section II.1.b. SPLP leachates were analyzed in triplicate using three separate aliquots of mulch, thereby representing replicates of the entire process. Sample C005 was analyzed in quintuplicate. Results shown in Appendix G show that reproducibility was extremely good with the coefficient of variation less than 5% for all samples evaluated with the exception of sample N005 for arsenic and chromium which were characterized by coefficient of variations in the 8 to 9% range. Results from matrix spike analysis indicate that about 80% of the copper, 85% of the arsenic, and 100% of the chromium were recovered. (See Appendix G for more details.)

#### *Rainfall Data Collection*

Rainfall depth was measured concurrently during leachate sample collection from the observation boxes using a gauge located within a few feet of the observation boxes. Rainfall depth was measured using a standard rain gauge made of plexiglass. Rainwater samples for pH measurement and arsenic analysis were collected using 120 mL pre-acid washed plastic containers

from the gauge each time a leachate sample was generated. Processing of rainfall samples for pH measurements and preservation were the same as that for leachate samples. Details concerning leachate sample processing are provided below.

#### *Leachate Sample Collection from Observation Boxes*

Prior to the collection of a leachate sample, the volume of leachate was read directly using either the calibrated reservoirs or, for sample volumes less than 2 liters, using an acid-washed graduated cylinder. A sub-sample of the leachate was then placed into a pre-acid washed 120 ml plastic bottle. After sample collection, the reservoirs were rinsed using de-ionized water and the residual water was wiped using a paper towel. This procedure was repeated three times before re-deploying the observation boxes.

The observation boxes were deployed on January 11, 2004. Leachate samples were collected daily after a rain event until 10 samples were collected. After the first 10 samples, samples were then collected once a week. Daily monitoring of the boxes occurred from January 11, 2004 through May 5, 2004. Weekly monitoring commenced thereafter and the results through June 30, 2004 are provided in this report.

#### *Leachate and Rainfall Samples Processing and Arsenic*

Upon collection within the 120 ml containers the samples were analyzed for pH (Orion pH meter model 525A). After the pH measurement, the samples were acidified by adding 1 ml of 1:1 nitric acid. The leachate samples were then digested using US EPA Method 7060A (US EPA 1996), which requires the addition of nitric acid and hydrogen peroxide. After digestion, samples were stored in a refrigerator until analysis. Analysis of the digestates was based upon the use of an atomic absorption spectrometer (Perkin Elmer Model AA800) with graphite furnace atomization and Zeeman background correction. All analyses of the digestates were run in duplicates. Monthly rainfall samples were also analyzed for arsenic. Rainfall samples were not digested prior to the analysis.

#### *Cumulative Arsenic Leached*

The percentage of cumulative arsenic leached out from the initial mass of arsenic in the mulch samples was calculated according to equation III.2.

$$\text{Cumulative leaching out (\%)} = \frac{\sum_{i=1}^n C_i \cdot V_i}{M_0} 100(\%) \quad (\text{eqn. III.2})$$

Where  $M_0$  is the initial mass of arsenic in a mulch sample (mg),  $C$  is the concentration of arsenic in the corresponding leachate sample (mg/L), and  $V$  is the volume of leachate measured within the observation box (L).

## III.2 RESULTS

The discussion of the results is separated into three sections. The initial arsenic content of the mulch samples is described first (Section III.2.a) followed by the results from the SPLP analyses (Section III.2.b). The last section focuses on the results observed from use of the observation boxes (Section III.2.c).

### III.2.a Results Associated with Sample Preparation (Initial Arsenic Content)

Analysis of the mulch after ashing showed that untreated wood mulch and treated wood mulch contained 1 mg/kg and 2,320 mg/kg of arsenic, respectively. Since the volume of mulch sample in the observation box was 0.8 kg, the initial masses of arsenic was 0.8 mg in the untreated wood mulch sample and 1,850 mg in the treated wood mulch sample. The initial mass of arsenic in the mixed wood mulch (5% treated and 95% untreated) was estimated as 93 mg based on these values.

### III.2.b Results from SPLP Analysis

Results from the SPLP analyses indicate that untreated wood mulch (both colored and uncolored) resulted in arsenic, chromium, and copper concentrations in the SPLP leachates below detection limits (Table III.2). The SPLP leachate concentrations from the 5% mixtures (5% treated and 95% untreated wood) were observed at intermediate concentrations, on the order of a hundred to a few hundred ug/L of arsenic, chromium, and copper, whereas the leachate concentrations for the 100% treated wood were characterized by several hundred to thousands of ug/L of metals. Although one would expect the leachate concentrations to increase by a factor of 20 due to the differences in metals concentrations between the 5% and 100% sample, this was not observed in all cases. It is likely that chemical saturation was reached in the SPLP extract solution for the 100% treated mulch sample which resulted in less than a 20 factor increase in leachate concentrations between the 5% and 100% treated wood sample.

Also of note is that a smaller amount of arsenic, chromium, and copper leached from the colored samples when compared to the non-colored samples. Apparently the iron-oxide colorant decreases the quantities of metals leached. For the 5% treated wood sample, the iron-oxide colorant resulted in a 60% decrease in the arsenic concentration, a 40% decrease in the chromium concentration, and a 30% decrease in the copper concentration. For the 100% treated wood sample, the iron-oxide colorant resulted in an 80 to 90% decrease in the metal concentrations.

As expected more iron leached from the colored sample relative to that from the uncolored sample. No distinct trend was observed between the fraction of CCA-treated wood in the samples and the amount of iron released in the SPLP leachate.

Sample ID	Sample Description	Arsenic (ug/L)	Chromium (ug/L)	Copper (ug/L)	Iron (ug/L)
N000	100% non-colored untreated mulch	< 12	< 5	4	1,370
C000	100% red-colored untreated mulch	< 12	< 5	< 4	8,700
N005	5% Non colored mixed mulch	920	180	100	500
C005	5% Red-colored mixed mulch	380	100	70	10,090
N100	100% non-colored treated mulch	9,850	2,620	2,430	790
C100	100% colored treated mulch	1,320	530	290	4,920

Table III.2: SPLP Results for Experimental Mulch Samples With and Without Iron-Oxide Addition

### III.2.c Results from Use of the Observation Boxes

Several different data sets were evaluated in conjunction with experimentation that utilized the observation boxes. These data sets included: a) rainfall and leachate volumes and pH, b) average arsenic concentrations of the rainfall and leachate, c) time series plots of arsenic concentrations, and d) mass balance analysis of the arsenic released.

#### *Rainfall and Leachate Volumes and pH*

A total 16 leachate samples were collected from each observation box during the monitoring period (January 11, 2004 ~ June 30, 2004), which corresponds to the dry season for South Florida. The total rainfall depth was 401 mm which was notably smaller than the sum of normal monthly precipitation (January through June) of 608 mm (National Climatic Data Center 2004). Two rainfall events, February 15 and March 27, were too small (< 5mm) to generate leachate and as a result the rainfall was entirely absorbed by the mulch. On June 30<sup>th</sup> the rain gauge was out of service for maintenance, however it rained on that day. The rainfall depth for June 30<sup>th</sup> (25 mm) was obtained from measurements recorded at Miami International Airport as documented by the South Florida Water Management District (SFWMD). The total rainfall of 401 mm corresponded to a 32.0 L volume (rainfall depth times surface area) for each observation box. The volume of leachate collected from each observation box varied from 25.7 L to 30.9 L (Table III.3). The difference between the rainfall volume and the measured volume is due to evaporation of moisture from the mulch during drying. The leachate volumes from non-colored untreated wood mulch (N000) were significantly smaller than the leachate volumes from non-colored treated wood mulch (N100) ( $p = 0.010$ ). No other statistical differences were observed in leachate volumes.

During the monitoring period, the average pH value of rainfall was 4.95 and leachate was 6.66 (6.24 ~ 6.84). The pH value increased significantly from rainfall to leachate ( $p < 0.001$ ). Among leachate from colored mulch, the pH values were statistically not different while among non-colored mulches, especially treated wood mulch and the others, were significantly different ( $p = 0.015$  (the non-colored mixed wood mulch vs. the non-colored treated wood mulch) and 0.060 (the non-colored untreated mulch vs. the non-colored treated wood mulch)). For the non colored mulch samples, the pH of the leachate decreased as the ratio of treated wood in the mulch increased. Such a trend is reasonable given that the most common wood treatment chemical, CCA, is prepared in an acidic solution.

*Average Arsenic Concentrations of the Rainfall and Leachate*

The concentration of arsenic in rainfall was consistently below 1 ug/L for the monthly samples evaluated. The average concentrations of arsenic in the leachate from untreated wood mulch were 3.9 ug/L for the non-colored mulch and 2.1 ug/L for the colored mulch. From the mixed wood mulch (5% untreated and 95% treated wood) significantly higher concentrations of arsenic were observed from the untreated wood mulch ( $p < 0.001$ ). The average concentration of arsenic in the leachate was 580 ug/L for samples with no color and 390 ug/L for the colored samples. For the mulch samples made from 100% treated wood, the average leachate arsenic concentrations was 8,000 ug/L for the non-colored sample and 5,200 ug/L for the colored samples. These concentrations were significantly higher than from the mixed wood mulch ( $p < 0.001$ ). The mean concentrations of arsenic in the leachate from the colored mulch were significantly smaller than the non colored mulch ( $p < 0.04$ ).

Sample ID	Sample Description		Total Volume	pH	Average As Concentration (ug/L)
Rainfall	Rainfall		401 mm 32.0 L	4.95	< 1
N000	Untreated	Non-Colored	27.0 L	6.71	3.9
C000		Colored	26.0 L	6.84	2.1
N005	Mix (5%/95%)	Non-Colored	25.7 L	6.63	578
C005		Colored	26.1 L	6.40	392
N100	Treated	Non-Colored	30.9 L	6.24	8,028
C100		Colored	29.3 L	6.68	5,198

Table III.3: Average Arsenic Concentrations in the Leachate. Rainfall and Leachate Volumes and pH included for Comparison

*Time Series Plots of Arsenic Concentrations*

A time series plot of the data (Figure III.3) emphasizes the differences in the arsenic leachate concentrations between the 100% treated wood mulch samples, the 5% treated wood mulch samples, and the untreated wood samples. Overall, the concentrations of arsenic leached from the colored samples were less than the concentrations leached from the non-colored samples. The fluctuation in arsenic concentrations showed almost the same patterns between the 100% treated wood samples and the 5% treated wood samples. In time, the leachate concentrations increased from the first set of leachate samples to the second set and then decreased gradually with some fluctuations in subsequent days. The peak leachate arsenic concentrations were measured as 22,700 ug/L (non-colored sample) and 15,300 ug/L (colored sample) for the 100% treated wood mulches. These values generally declined towards the end of the 6-month monitoring period to several 100's to several 1,000's of ug/L of arsenic. For the 5% treated wood samples, the peak concentrations were 2,200 ug/L for the non-colored sample and 1,700 ug/L for the colored sample. The concentrations declined to the few 100's of ug/L by the end of the 6 month monitoring period. The peak arsenic concentrations of the leachates for the untreated wood samples were in the 9 to 13 ug/L range. The concentrations declined to less than 1 ug/L towards the end of the monitoring period with the exception of one leachate from the non-colored mulch sample which measured at 10 ug/L.

The leachate concentrations between the colored and non-colored treated wood mulches were correlated,  $R^2 = 0.97$  (Figure III.4). On average the leachate concentration for the colored

mulch was about 30% less the leachate concentration in the non-colored mulch.

The mass of arsenic leached in time (Figure III.5) followed a similar pattern for each set of leachate samples. The mass leached was computed as the product of the leachate concentration and leachate volume. The variation in masses computed was dominated by the leachate volume since volumes of leachate varied more than the leachate concentration. Again the time series plots showed that the mass of arsenic leached was generally greater from the non-colored mulch samples than from the colored mulch samples. The mass leached by June 30<sup>th</sup> (after 6 months of leaching) was on the order of 100 mg for the 100% treated mulch samples, 10 mg for the 5% treated mulch samples and 0.05 mg for the untreated mulch samples.

*Mass Balance Analysis of Total Initial Arsenic Released*

The cumulative mass of arsenic leached generally higher for the non-colored samples as compared to the colored samples. This was observed for all three sample pairs including the untreated wood mulch. The total amount of arsenic leached varied from 0.05 to 0.07 mg from the untreated wood during the 171 day monitoring period. For the 5% treated wood sample, the total amount of arsenic leached varied from 10 to 13 mg and for the 100% treated wood sample the total amount of arsenic leached varied from 150 to 220 mg. The percent of the initial arsenic leached from the mulch samples was on the order to about 10%. Overall, the presence of the iron oxide colorant decreased the rate of leaching by about 20 to 30%. The mass leached between colored and non-colored samples was statistically different at 95% confidence limits.

	N000 Untreated, Non- Colored	C100 Untreated, Colored	N005 5% Treated, Non-Colored	C005 5% Treated, Colored	N100 100% Treated, Non-Colored	C100 100% Treated, Colored
Initial Arsenic (mg/sample)	0.8	0.8	116	116	1,852	1,852
Leached out (mg)	0.069	0.052	13	10	223	147
Fraction Leached (%)	9	7	11	9	12	8

Table III.4: Total Arsenic Released from Each Mulch Sample

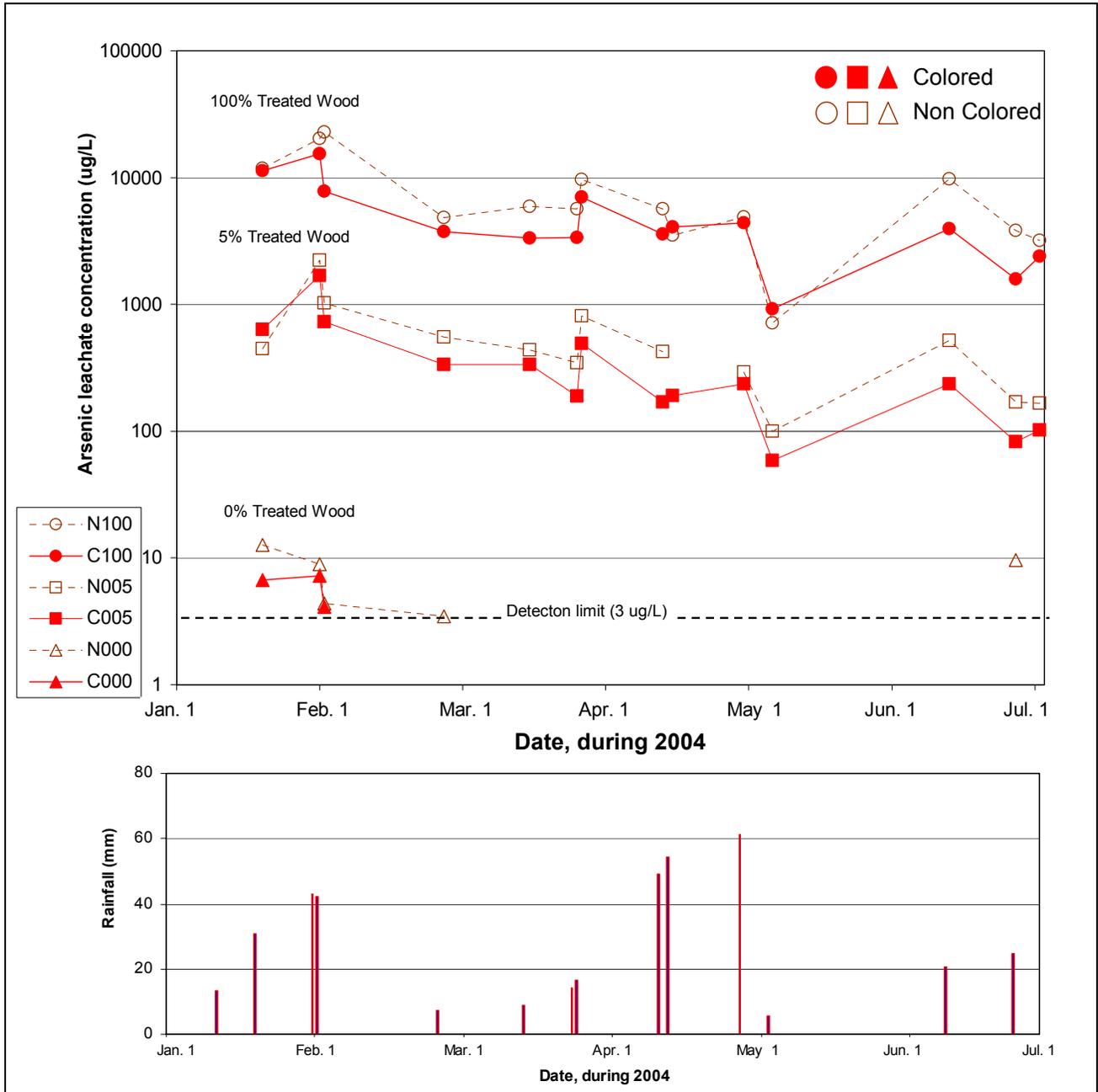


Figure III.3: Rainfall Volumes and Leachate Arsenic Concentrations for All Six Mulch Samples Versus Time

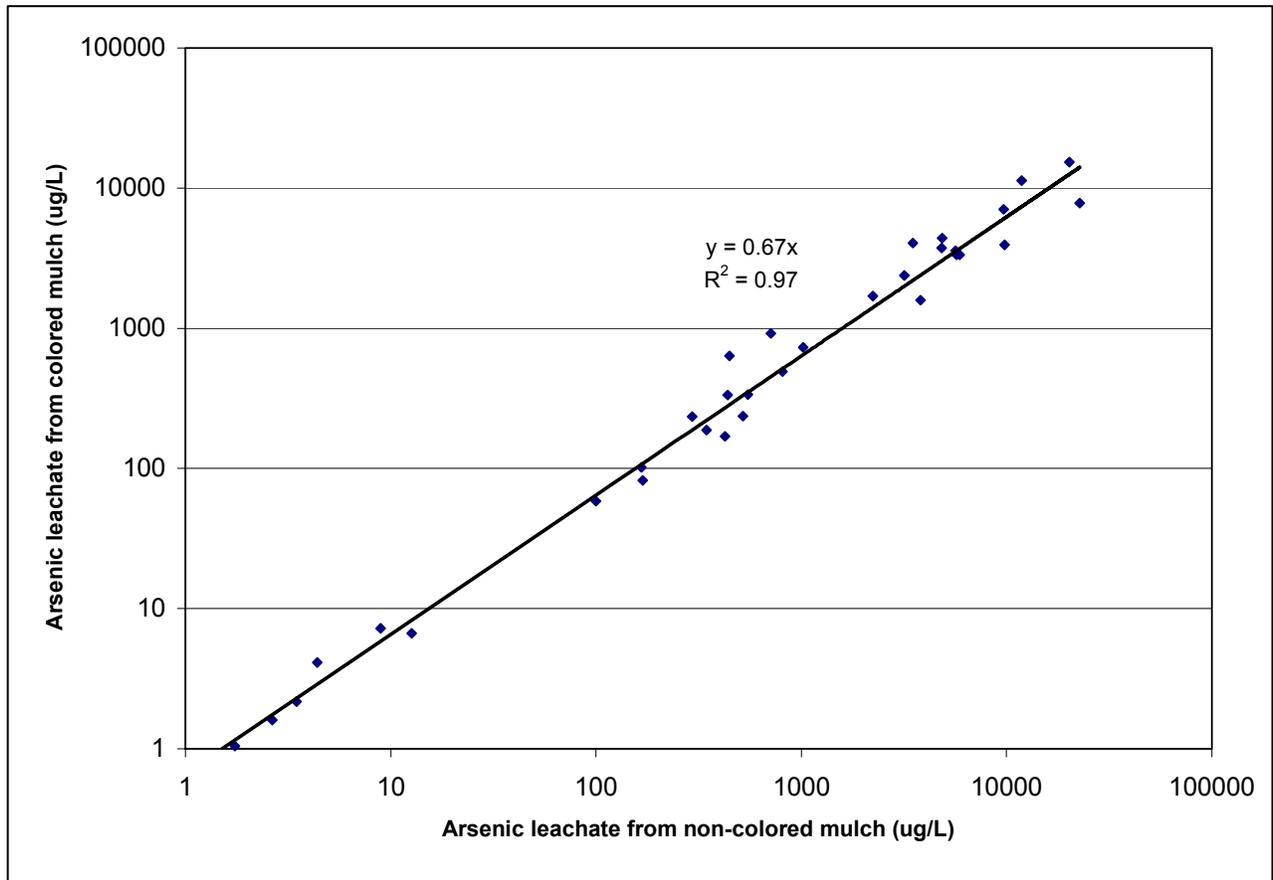


Figure III.4: Correlation Between Arsenic Concentration in the Leachate from Colored and Non-Colored Wood Mulches Containing Treated Wood.

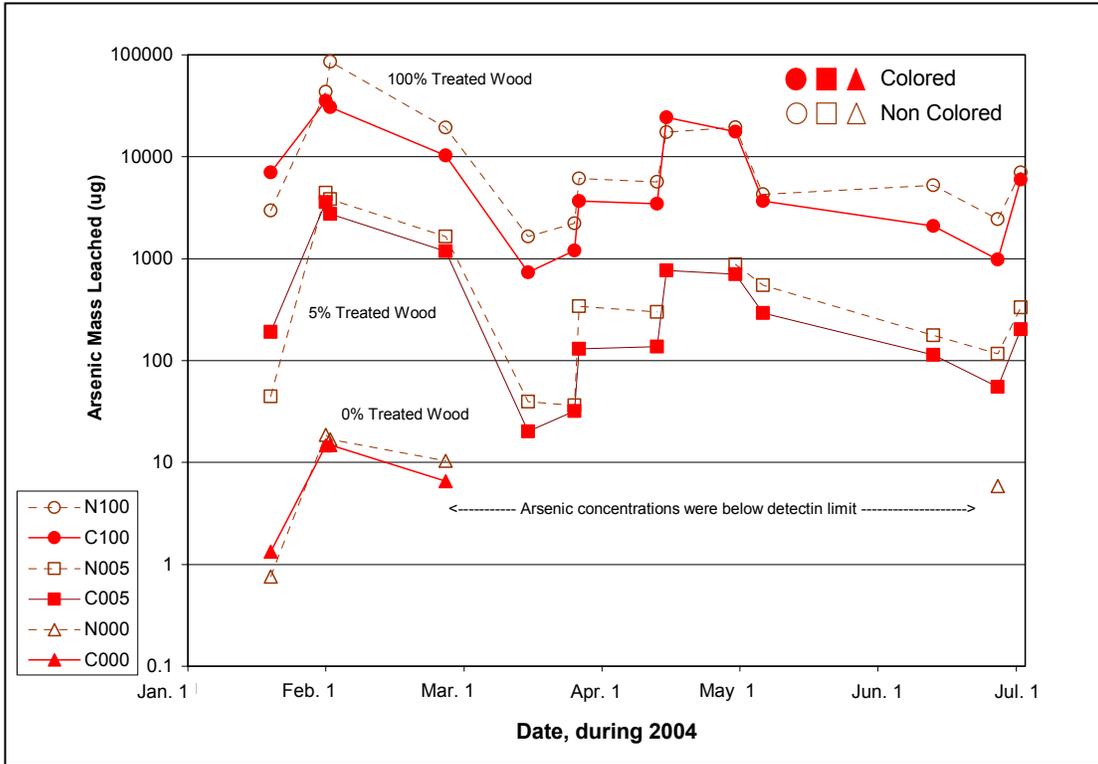


Figure III.5: Mass of Arsenic in Micrograms Released in the Observation Boxes On Each Sampling Date

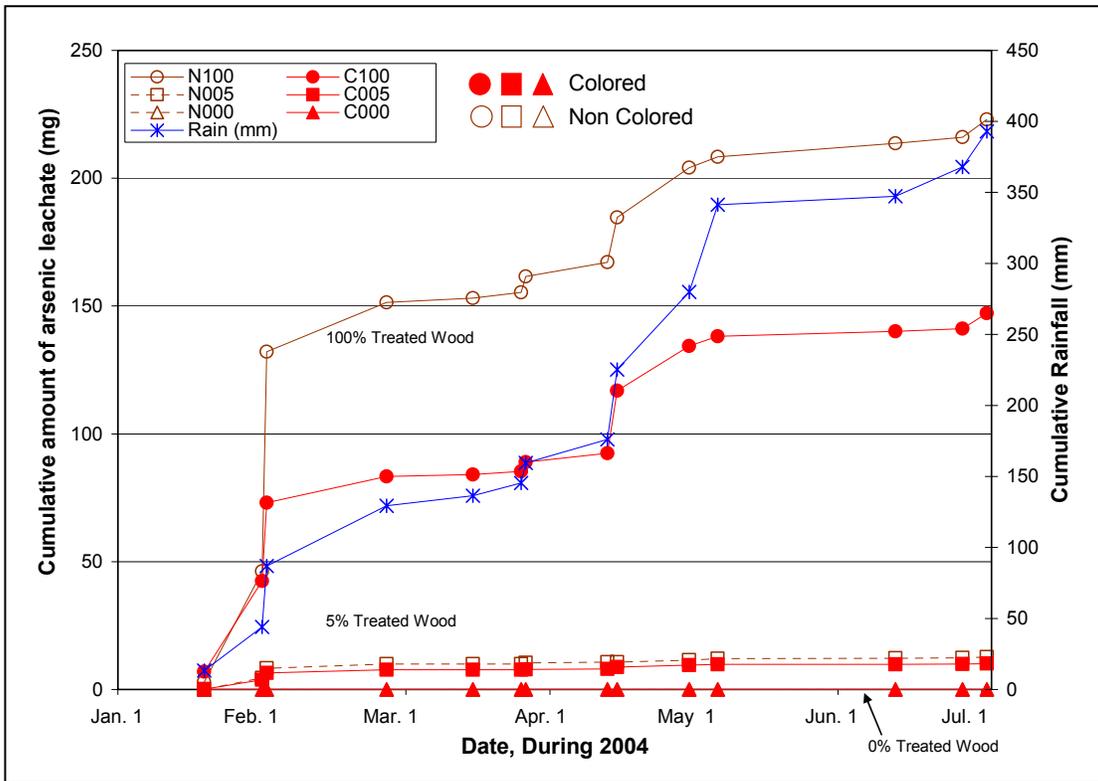


Figure III.6: Cumulative Arsenic in the Leachate from Six Mulch Samples and Cumulative Rainfall Versus Date

**CHAPTER IV,  
SUMMARY, RECOMMENDATIONS, AND  
ACKNOWLEDGMENTS**

## CHAPTER IV, SUMMARY, RECOMMENDATIONS, AND ACKNOWLEDGMENTS

### IV.1 SUMMARY & RECOMMENDATIONS

Mulch samples showing the highest probability of contamination with arsenic were those that were colored and which contained plywood. About 90% of these samples exceeded the residential Florida Soil Cleanup Target Levels for arsenic and almost  $\frac{3}{4}$  of these samples also exceeded the Florida Groundwater Cleanup Target Level for leachable arsenic. The presence of plywood in these samples is a strong indication that the samples were produced, in part, from recycled C&D wood. Recycled C&D (and not necessarily the plywood itself) is likely inadvertently contaminated with CCA and such results indicate that stronger efforts need to be made to assure that CCA does not contaminate recycled wood waste. The focus should not necessarily be on removing the plywood. *The focus should be on removing dimensional wood contaminated with CCA.* Results also showed that samples that were not colored and/or did not contain plywood would on occasion show elevated levels of leachable and recoverable metals in excess of regulatory guideline levels. About 10% of these samples (everything but the colored AND plywood) exceeded the 2.1 mg/kg Florida residential Soil Cleanup Target Level for arsenic. Only 2% of these samples also exceeded the current Florida Groundwater Cleanup Target Level (50 ug/L) for leachable arsenic.

Results from the observation boxes show that mulch made from 5% CCA-treated and 95% untreated wood leached arsenic at levels of 580 ug/L for non-colored mulch and 390 ug/L for colored mulch, on average, whereas mulch made from entirely untreated wood leached arsenic at concentrations less than 4 ug/L. Results from the SPLP analysis were consistent with the results from the observation boxes. A significant decrease in leachate arsenic concentration (by 30% on average) was observed from the colored mulch samples subjected to natural rainfall relative to the non-colored mulch samples. The use of iron-oxide colorants will thus help, at least in the short term, to decrease arsenic concentrations in the leachate from CCA-contaminated mulch.

Overall the results indicate that the presence of contaminated mulch at relatively low levels (5% by weight) results in leachate concentrations that exceed the current Florida Groundwater Cleanup Target Level (GWCTL) by a factor of 10. If the goal is to provide mulch that does not exceed the GWCTL, the mulch should contain less than 0.5% CCA-treated wood by weight. In general, between 1 and 5% of the mulch was contaminated with CCA for the majority of samples that were colored and contained plywood. One sample was characterized by a very high fraction of CCA-treated wood (15%). This sample, in addition to being colored and containing plywood, was an “open bin” sample from a plant nursery within southeast, Florida, which is consistent with the predominance of “hits” for arsenic observed from the more urbanized areas within the southern  $\frac{1}{2}$  of the State. This observation is likely associated with the predominance of C&D recycling facilities in these areas, which are economically viable due to limited landfill space and local demand for mulch. Efforts should focus on improving the sorting methods for CCA-treated wood at these facilities to assure that the mulch produced is essentially free of CCA-treated wood (< 0.5%). Regulatory initiatives should also be implemented to assure that all C&D facilities producing mulch are implementing improved sorting practices. Some within the mulch industry have also recommended the formation of a quality assurance group which would “brand” mulch as safe, depending upon the sorting practices implemented by the mulch producer.

## IV.2 ACKNOWLEDGEMENTS

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