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Studies on Weathered Waterborne Treated Wood: Leaching of Metals during Service and Metals Based Detection upon Recycle

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UNIVERSITY OF MIAMI

STUDIES ON WEATHERED WATERBORNE TREATED WOOD: LEACHING OF METALS DURING SERVICE AND METALS BASED SORTING UPON RECYCLE

By

A. Rasem Hasan

A DISSERTATION

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of the University of Miami
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STUDIES ON WEATHERED WATERBORNE TREATED WOOD: LEACHING OF METALS DURING SERVICE AND METALS BASED SORTING UPON RECYCLE

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Studies on Weathered Waterborne Treated Wood: (August 2009)
Leaching of Metals during Service and
Metals Based Sorting upon Recycle

Abstract of a dissertation at the University of Miami.

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Weathered waterborne treated wood is believed to behave differently than new wood during service regarding the loss of its metallic-based preservatives. Also, weathered preserved wood should be separated from the unpreserved wood upon recycle.

The first objective of this dissertation was to evaluate losses from weathered CCA-treated wood samples at different retention levels under normal field conditions and to compare leaching to new ACQ (as alternative to CCA). Results showed that arsenic leached at a higher rate than chromium and copper in all CCA treated wood samples, while copper leached the highest from the ACQ sample. Overall results suggest that the leaching rate of metals on a percent basis from in-service pressure treated wood may increase as the wood weathers; however due to lower retention levels of the metals in the wood as it ages the yearly mass of metals lost would be at similar or at lower quantities in comparison to new treated wood.

The second objective was to evaluate the use of automated X-ray fluorescence (XRF) systems for identifying and removing As-based and Cu-based treated wood within the recovered wood waste stream. A full-scale online automated XRF-detection, conveyance and diversion system was used for experimentation. At the different applied feeding rates

and belt speeds, online sorting efficiencies of waste wood by XRF technology were high (>70% for both treated wood and untreated wood). The incorrectly diverted pieces of wood were attributed to deficiencies in the wood conveyance systems and not to deficiencies in the XRF-based detection. Online sorting was shown to sort wood which would meet the residential soil cleanup target levels in Florida when an infeed is composed of 5% of treated wood pieces. Comparisons with other sorting methods show that XRF technology can potentially fulfill the need for cost-effective processing at large wood recycling facilities (> 30 tons per day).

Management of weathered CCA-preserved wood, due to its continuity of leaching metals and the need to remove it upon the recycle of wood, will likely continue until complete banning and removal from the environment, a process that may extend up to the next century.

DEDICATION

To my parents,

family,

and friends

ACKNOWLEDGMENTS

All praise be to Allah (SWT), and best prayer and peace be upon his worshiper and final messenger; Mohammad (SAW).

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The second project (sorting of wood based on metals' content) was funded by the Town of Medley through Florida Department of Environmental Protection, Innovative Recycling Grants Program. The authors of the manuscript thank the wood recycling facility that hosted this project and the many individuals from the wood recycling facility and the UM and the UF personnel who helped with the experimentation.

Specifically, I would like to thank my adviser Helena Solo-Gabriele for her help and support throughout my last two years in the Ph.D. program. Also, I would like to thank my committee: Lynne Fieber, Timothy Townsend, and Jacqueline James for reviewing the dissertation and comments during the proposal and dissertation defense. I thank Lynne Fieber for standing for my Ph.D. hooding.

TABLE OF CONTENTS

Page

List of Tables

List of Figures

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

This dissertation focused on two main studies conducted on weathered waterborne, As-based and Cu-based, preserved wood: Leaching of metals from weathered preserved wood and metals based sorting of recovered wood waste upon recycling.

Preserved wood tends to leach metals slowly during its service life. Leaching of metals from new preserved wood is covered in literature by many researchers (Kennedy and Collins, 2001; Taylor and Cooper, 2005; Dubey, 2005; Khan et al., 2006a; Shibata et al. 2007). As preserved wood weathers, leaching of metals is expected to continue, but not enough information is available in the literature regarding its rate and mechanisms.

At the end of service-life of preserved-wood, it will be collected together with unpreserved wood and considered for recycling purposes or disposal. As environmental agencies impose regulatory guidelines regarding the content of metals in the recycled products, contents of even low quantities of As-based preserved wood are most likely to fail the guidelines due to the stringent regulations for As. In Florida, the residential soil cleanup target level of As is 2.1 ppm for residential applications, and 12 ppm for commercial and industrial applications. The ground water cleanup target level is 0.01 ppm (FDEP, 2005), which is equal to the USEPA drinking water standards. Identifying preserved wood from unpreserved one is important for the success of recycling facilities, protection of human health and conservation of our environment.

Material presented in this chapter is an introduction to the dissertation, and serves as a literature review. General background is presented first, followed by three sections: the need for research, research objectives and approaches, and dissertation outline.

1.1.1 Wood

Wood is the first ever known construction material and source of energy to human beings. Its availability, variety, the high ratio of strength to weight, floatability, ease of fabrication, storage and transportation, all stand behind its continuity as a construction material (Milton, 1995), in addition to the human preferences for natural appearances to their domiciles, yards and parks. Lately, and due to the foreseen depletion of oil as an energy source and the global climatic change due to greenhouses gases, wood started to be considered again as a renewable energy source.

Wood is considered as a widely available and renewable material since it can be harvested from forests. The useful life of natural wood as a construction material depends on many factors, especially its species, age up to harvesting, in which both are determinants of wood strength. Local weather conditions (humidity, rainfall, frost and warmth) are determinants of wood erosion and abrasion and so cause deformations and weakness. Fire leads to complete damage of wooden structures and most importantly is the deterioration of wood due to uncontrolled attack and degradation by fungi, insects, termites and marine borers, where wood acts as food and shelter for these organisms (Milton, 1995).

1.1.2 Wood waterborne preservatives

Wood preservation is an old human activity. There is evidence that Greek and Roman applied oils and tars to the surface of wood pieces used to build their houses and bridges. Waterborne chemicals containing arsenic, chromium and copper are widely used as preservatives for wood in order to prolong their service life as construction materials (Dubey, 2004). In 1920, Chromated Copper Arsenate (CCA) was patented as wood preserving chemical, and the widespread use of this preservative occurred in the US by 1970. In the United States, CCA treated wood has been phased out for residential uses as of 2004 (USEPA, 2003). Other waterborne preservatives are acid copper chromate (ACC), ammonical copper arsenate (ACA), ammonical copper zinc arsenate (ACZA), chromated zinc chloride (CZC), alkyl ammonium compound (AAC), inorganic boron, alkaline copper quat (ACQ), copper bis (dimethyldithiocarbamate) (CDDC), ammonical copper citrate (ACC), and copper azole (CA), copper HDO (CX) and waterborne copper naphthenate (CuN-W) (AWPA, 2008) and micronized copper quat (MCQ) (Freeman and McIntyre, 2008).

Both CCA and ACQ treated wood are produced in set ratios of arsenic, chromium, and copper for CCA and copper and quat for ACQ. Three types of CCA have been produced over time. These include CCA Type A, Type B, and Type C (AWPA, 2008), and Types A, B, C, and D for ACQ. Type C is the common formulation of CCA used for products manufactured today consisting of 47.5% as CrO_3, 18.5% as CuO, and 34% as As_2O_5. ACQ Type A consists of 50% copper as CuO and 50% of DDAC as quat, while Types B, C and D contain 66.7% CuO and 33.3% quat, with differences among them regarding the quat structure and treating solutions. The industry permits some variation of the percentages within given tolerances (AWPA, 2008). The amount of chemical added, or retention level for both CCA and ACQ treated wood is dependent upon the intended use of the wood. The lowest retention level of 4 kg/m^3 (kilograms of CCA or ACQ chemical on an oxide basis per cubic meter of wood) is intended for wood used in above ground applications; the highest retention level of 40 kg/m^3 is intended for wood submerged in marine environments (AWPA, 2008).

1.1.3 Leaching of preservative metals from wood

Even though chromated copper arsenate (CCA) treated wood has been phased out from most residential applications in the US, large amounts of treated wood structures are still in service due to the prolonged service life of these products, that extends from 13 years for low retention levels (4 kg CCA/m^3) up to 40 years for high retention levels (40 kg CCA/m^3). Furthermore, additional amounts of CCA treated wood continue to be introduced in non-residential applications such as utility poles and marine structures. In spite of the phase out, leaching of metals from CCA treated wood continues to be a concern due to the release of arsenic, chromium and copper through weathering of wood in service (Khan et al., 2006a; Shibata et al., 2007) or disposal in monofills or MSW landfills (Khan et al., 2006b; Jambeck et al., 2007) or through releases during the reuse/recycling of wood (e.g., via ash produced from the treated wood used as an energy source or recycled treated wood used as landscaping mulch) (Jacobi et. al., 2007a; Shibata et al., 2007; Townsend et al., 2003). The alternatives to CCA used in the US (e.g., alkaline copper quat) contain higher levels of copper and are expected to leach copper at a higher rate relative to CCA (Dubey et al., 2005) due to the absence of a fixing agent as Cr in CCA. Release of metals from the waterborne-based preservatives is believed to behave differently in weathered products in comparison to newly manufactured ones.

1.1.4 Metals' based sorting of wood

At the end of wooden structures' service-life, wood will be removed and eventually disposed. The most common disposal route will be through the construction and demolition (C&D) waste stream (Solo-Gabriele and Townsend, 1999). As most of the wastes are gathered collectively upon disposal, waste wood (treated and untreated) ends up in mixed piles at C&D facilities. Detection of preserved wood and separation from the pile is commonly the next step upon further processing. The following is a literature review for sorting techniques practiced or researched at recycling facilities. Sorting of wood is a multistep process, includes handling of wood, detection of preserved wood and diversion for separation from the unpreserved ones.

1.1.4.1 Visual Sorting

Visual sorting has been found to be a useful technique for cases that the source of wood is known and end tags can be seen. The efficiency of preserved wood detection in such cases can be 100%. But for cases of unknown sources or very weathered wood, dirty or painted wood, the efficiency will drop significantly to about 17% (Jacobi et al., 2007b) to 50% (Blassino et al., 2002), depending on the characteristics of the piles.

1.1.4.2 Chemical stains

Chemical stains are a useful tool for identifying preserved wood within C&D wood waste. PAN and Chromazurol S (CS) are chemical stains that contain active chelating agents capable to react with Cu under normal ambient conditions and undergo a distinctive color change. When PAN stain is applied to the wood, the wood stains a magenta color if treated with copper and orange if untreated and in case of (CS), a blue color if treated and pink otherwise. PAN indicator was faster (5-12 s) in detecting Cu-treated wood than CS (45-63 s), but CS was more reliable. The color change was faster when applied on dry pieces relative to wet and longer times might be needed in the field for a distinctive color change (Sawyer and Irle, 2005; Blassino et al. 2002). Both stains can be applied by brush as a most economic method, can be sprayed or applied by a weed stick (that used for applying weed killers without harming the surrounding plants) (Sawyer and Irle, 2005). Jacobi et al. (2007b) used the visual sorting and PAN stain for sorting large quantities of wood, and found that both methods work very well for source separated wood, but for comingled wood, the efficiency drops to ~50%. Also, PAN stain may react with dirt on the outside of the wood and provide false indications. They concluded that PAN stain is not recommended for sorting large quantities of commingled waste, the case mostly found in C&D recycling facilities. Personnel training plays a major role in enhancing the efficiency (Jacobi et al., 2007b).

1.1.4.3 As-test kits

Because the targeted metal is copper, stains are not capable of distinguishing between CCA and other copper-containing preservatives. To differentiate between Cu (non arsenical)-treated such as ACQ and both Cu- and As-treated, such as CCA, Shalat et al. (2005) developed a method based on an As-test kit that is commercially available for analyzing As in drinking water. The modification included the addition of wood's sawdust with deionized water to the kit test tube, and then mixing with test reagents (Zn and HCl). The reaction undergone in the test tube converts the As (if the sawdust was originally from As-treated wood) into arsine gas, which then reacts with another reagent, Hg_2Br_2, that leads to the conversion of color from white into dark (brown to black). This method has several drawbacks: it is time consuming (30-45 min) and produces a toxic gas (Solo-Gabriele et al., 2005). this results in the unsuitability of this method for wood recycling streams. Omae et al. (2007) developed a non-toxic and faster method for detcting As in wood; the method was patented and produced commercially as test kit (http://arsenichometest.com). The method was modified from a standard method using stanous chloride for the analysis of phosphate in water. Both As-test kits require a longer time than the Cu-stains, but are useful to differntiate between As-based preserved wood and other inorganic (non aresenical)-preserved wood. Costs of these kits range from US$15-200, and can be used for almost 100 tests.

1.1.4.4 LIBS

Laser Induced Break-down Spectroscopy (LIBS) technology was found as a useful tool for identifying treated wood based on its Cr content, and it depends on targeting wood pieces with a laser beam through a series of mirrors and lenses that create a small microplasma on the surface of the targeted piece that causes a vaporization of the surface material, due to high temperature produced within the plasma (up to 20,000 ^oC), the vaporized atoms emit energy in the form of light with a wavelength that is a characteristic of the targeted element (Moskal and Hahn, 2002; Solo-Gabriel et al. 2004). In spite of the fact that LIBS technology was able to detect a wide range of CCA treated wood (efficiency as 92-100%), the technology did not prove reliable for the detection of severely rotted and completely wet wood (Hahn et al., 2002). This is a significant drawback, given the fact that piles of wood are not easy to cover at C&D facilities and rain can easily percolate those piles and wet the wood. In addition, detection of preserved wood by LIBS is optimal when most of the plasma emitted is collected. This requires that the surface of the subjected wood piece is situated at the laser focal point, and this may not be the case for all times providing the fact of different shapes, sizes and surface conditions of waste wood.

1.1.4.5 XRF

Atoms fluoresce at specific energies when excited by X-rays (Kalnicky and Singhvi, 2001). X-rays are relatively short wavelength, high energy electromagnetic radiation that can be produced by applying voltage on an evacuated tube that contains a radiation source, an anode made of pure element, and a cathode filament usually of tungsten (Lifshin, 1999). X-ray energy is inversely proportional to its wavelength and the relation is $E = 1.24/\lambda$, where E is energy in KeV and λ is the wavelength in nm (Michette and Buckley, 1993; Lifshin, 1999).

X-ray fluorescence (XRF) is based upon the use of a high energy X-ray source that emits X-rays that knock electrons out of the innermost shell of atoms in the treated wood and changing the atoms into unstable ions. More energetic electrons from outer shells will move into the newly vacant spaces in the inner shell in order to reach the lowest stable energy state and so releasing the extra energy possessed before. The emitted energy is equal to the difference in energies between the innermost shell and the outer ones, thus it is a characteristic of the element fluorescing. Emitted energy as photons are then detected by an X-ray detector that converts the energy emitted into an electronic measurable signal. The count of emitted energies is proportional to the concentration of the metal in the wood and is simulated by a spectrum representing the number of counts versus energy in KeV (Michette and Buckley, 1993; Lifshin, 1999) where the targeted metals will appear as peaks in the spectrum at their excitation energy range according to their atomic structure.

The first technology to be developed and used for wood detection is the handheld XRF. The handheld XRF technology can analyze for the As, Cr, Cu and other metals at the same time and within 2-6 s and was found to have some advantages over the laser technology (Solo-Gabriele et al., 2004), providing that the cost for implementing both systems are almost similar (Solo-Gabriele et al., 2001). Block et al. (2007) found that XRF technology is capable to penetrate wood to a depth of 1.2-2.0 cm when the XRF machine is placed on the surface of the wood. The handheld XRF units were found to be the technology of choice due to their ability to detect preservative treatment, even when the wood was dirty and wet (Jacobi et al. 2007b). Efficiency of detection of wood preservatives can easily reach 100% regardless of the wood surface conditions.

1.2 NEED FOR RESEARCH

The research presented in this dissertation is continuity and progress for a line of research activities conducted on the environmental impacts of pressure treated wood by three universities in Florida; University of Miami, University of Florida and Florida International University. The research work composed of two main parts (Figure 1.1). The first part of this research evaluates metals leaching from weathered treated wood. The second part concerns the introduction and evaluation of XRF-technology for online sorting of preserved wood from recovered wood waste upon recycling.

1.2.1 Research part 1

Khan et al. (2006a) studied leaching of As from a new low-retention CCA-treated deck and characterized the loss of As as 5% after one year. A model was built to forecast the quantities of arsenic produced, disposed and leached from treated wood during service. The model was based on average retention levels of CCA-treated wood in Florida and utilized a constant leaching rate for lumbers calculated from their one-year study of new wood. Shibata et al. (2007) continued the Khan et al. (2006a) deck study for three years and concluded that the rate of As and Cr leaching decreased as wood weathers over the years of study. Dubey (2005), by using a deck study, also observed that Cu leached from new ACQ wood at a rate seven times higher than the rate from new CCA. Townsend et al. (2004; 2005) conducted laboratory leaching tests on new and weathered wood using toxicity characteristics leaching procedure (TCLP) and synthetic precipitation leaching procedure (SPLP) (new and weathered). The results of their study found that weathered wood does leach preservative elements at a similar magnitude as new, un-weathered wood. Similar results have been reported by Stook et al. (2004; 2005) for batch leaching experiments of ACQ-treated wood. Khan et al. (2004) also used the TCLP and SPLP to compare As leaching from new and weathered wood and found that weathered wood leached more As and they attributed the greater leaching to natural chemical and biological transformations during the weathering process. Thus batch leaching tests conducted in the laboratory suggest that the weathering process increases leaching rates, but this is yet to be shown under natural field conditions.

1.2.2 Research part 2

Section (1.1.4) summarized the different sorting techniques developed during the past ten years. These methods can range from laborious, manual, lengthy, single targeted metal methods such as visual inspection, stains and test kits, to automated, fast, multiple targeted metals and expensive technological wise methods such as LIBS and XRF. Most of the manual methods are cheap in capital cost, but very expensive in labor cost. Stains represent the most popular augmentation technology for visual sorting, and were found suitable for facilities that process <0.5 tons of waste wood (Jacobi et al. 2007b). Solo-Gabriele et al. (2004), studied the LIBS and XRF technologies in semi-automated operation for sorting waste wood, and concluded that "A follow-up study should be initiated to test XRF and LIBS technologies, under full-scale day-to-day sorting for the purpose of further documenting and fine-tuning their performance." And regarding the capital cost of the XRF system as US$ 50,000, they recommended: "Such an investment is highly recommended in a subsequent full-scale study of XRF technology for sorting C&D waste." And finally they concluded: "Commercialization of both technologies can occur once performance is improved and demonstrated through full-scale operation." No online-automated system has been evaluated before for sorting preserved wood. In addition, no tracking of the metals masses diverted by sorting has been reported in the literature.

Hence, this research was conducted to cover the gap for more depth in understanding of the metals' leaching behaviour from weathered wood, and to investigate the performance of the online-automated-XRF system for sorting preserved wood from recovered wood waste.

1.3 RESEARCH OBJECTIVES AND APPROACHES

The first objective of this dissertation was to evaluate metals loss from CCA-weathered treated wood under normal field conditions, to study the mechanism of leaching, and to compare the leaching rate to leaching from new wood.

For comparison, rainfall and rainfall leachate samples were collected from 5 different wood types, weathered chromated copper arsenate (CCA) treated wood at low, medium and high retention levels, new alkaline copper quat (ACQ) treated wood and new untreated wood which was used as a control. Measurements included weekly rainfall depth, pH, and the concentration of arsenic, chromium and copper in the rainfall and rainfall leachate. Metals losses were evaluated by:

- Metals’ concentration in leachate collected after rainfall contacted wood samples.
- Metals’ mass leached from wood samples over the period.
- Cumulative mass leached over the period.
- Cumulative mass leached with cumulative rainfall.
- Mass ratios of leached metals.
- Percentage losses of metals from wood samples.
- Metals’ leaching rates in $mg/(m^2 \cdot d)$.
- Comparison of results with reported values in the literature. A comparison of results was conducted with other researchers including Khan et al. (2006a) and Shibata et al. (2007), who conducted their research at the same location as this research (Coral Gables, FL), Taylor and Cooper (2005), for a research conducted in Ontario, Canada, and Kennedy and Collins (2001) for a research conducted in

Queensland, Australia. These studies used for comparison covering three different locations in the world with distinctly different climates.

The second objective was to introduce, optimize and evaluate the use of automated X-ray fluorescence (XRF) systems for sorting As-based and Cu-based treated wood within the recovered wood waste stream. Online sorting of wood comprise three processes: conveyance, detection and diversion of wood. The introduction of the system was done by proposing a design for conveyance and detection systems. The design was based on the use of a full-scale unit for experimentation. This unit consisted of two large motorized belt conveyors, an XRF-detection chamber mounted in the top of one of the conveyors and a pneumatic slide-way diverter.

The optimization of the XRF-detection system was done by calibration of two main parameters, operational threshold (OT) and measurement time. These two parameters where optimized utilizing treated wood pieces and analysis of collected spectrums for the OT calibration, and calculations of sorting efficiencies and mass recoveries of targeted metals for the measurement time calibration. The optimization of the conveyance system was done for two parameters, conveyor belt speed and wood feeding rate, and evaluated through a randomized block design. The experiments utilized two main sets of infeed wood each of 1000 pieces. The first is of 50:50, and the second is 95:05 composition of untreated to treated wood. Treated wood pieces included: As-based, Cu-based, and others. The evaluation of the system was done by the calculation of:

- Sorting efficiencies for treated and untreated wood by number of pieces.
- Sorting efficiencies for each type of treated wood by number of pieces.
- Sorting efficiencies for treated and untreated wood by weight of pieces.

- Sorting efficiencies for each type of treated wood by weight of pieces.
- Mass recoveries of As, Cr and Cu in treated wood from the recycle stream of untreated wood.
- Mass recoveries of As, Cr and Cu in each specific type of treated wood from the recycle stream of untreated wood.
- Sorted piles' composition based on number of pieces.
- Sorted piles' composition based on weight of pieces.
- Untreated pile composition by mg of metals per total weight of wood by kg.

1.4 DISSERTATION OUTLINE

The goal of this dissertation is to contribute to the knowledge of leaching behavior of preservative metals from weathered wood and to introduce and evaluate the performance of XRF-based technology for online automated sorting of preserved wood from recovered wood waste. The dissertation contains five chapters:

- Chapter 1 (this chapter) is an introduction and provide a background about both topic, in addition to describing the motive behind this research, objectives and approaches of the current research.

The subsequent chapters 2, 3 and 4 are the main body of the dissertation and comprise three manuscripts prepared for publication with titles similar to the chapters.

- Chapter 2, Field scale leaching of arsenic, chromium and copper from weathered treated wood. Manuscript authors are: Hasan, A. R.,[a] Ligang Hu,[c] Helena Solo-Gabriele,[a] Lynne Fieber,[b] and Yong Cai[c,d]. Manuscript submitted for the journal of *Environmental Pollution.*

- Chapter 3, XRF technology for online detection of preserved wood waste. Manuscript authors are: Hasan, A. R.,[a] John Schindler,[f] Helena Solo-Gabriele,[a,] and Timothy Townsend[e]. Manuscript to be submitted for consideration by the *Journal of Hazardous Materials*.
- Chapter 4, Sorting of recovered wood waste by automated XRF technology. Manuscript authors are: Hasan, A. R.,[a] Helena Solo-Gabriele,[a,] and Timothy Townsend[e]. Manuscript to be submitted for consideration by the Journal of *Waste Management*.
- Chapter 5 is a summary, conclusions and recommendations for the dissertation.

Appendices include supplemental information for chapter 2, 3 and 4. And finally, the list of references for all cited literature.

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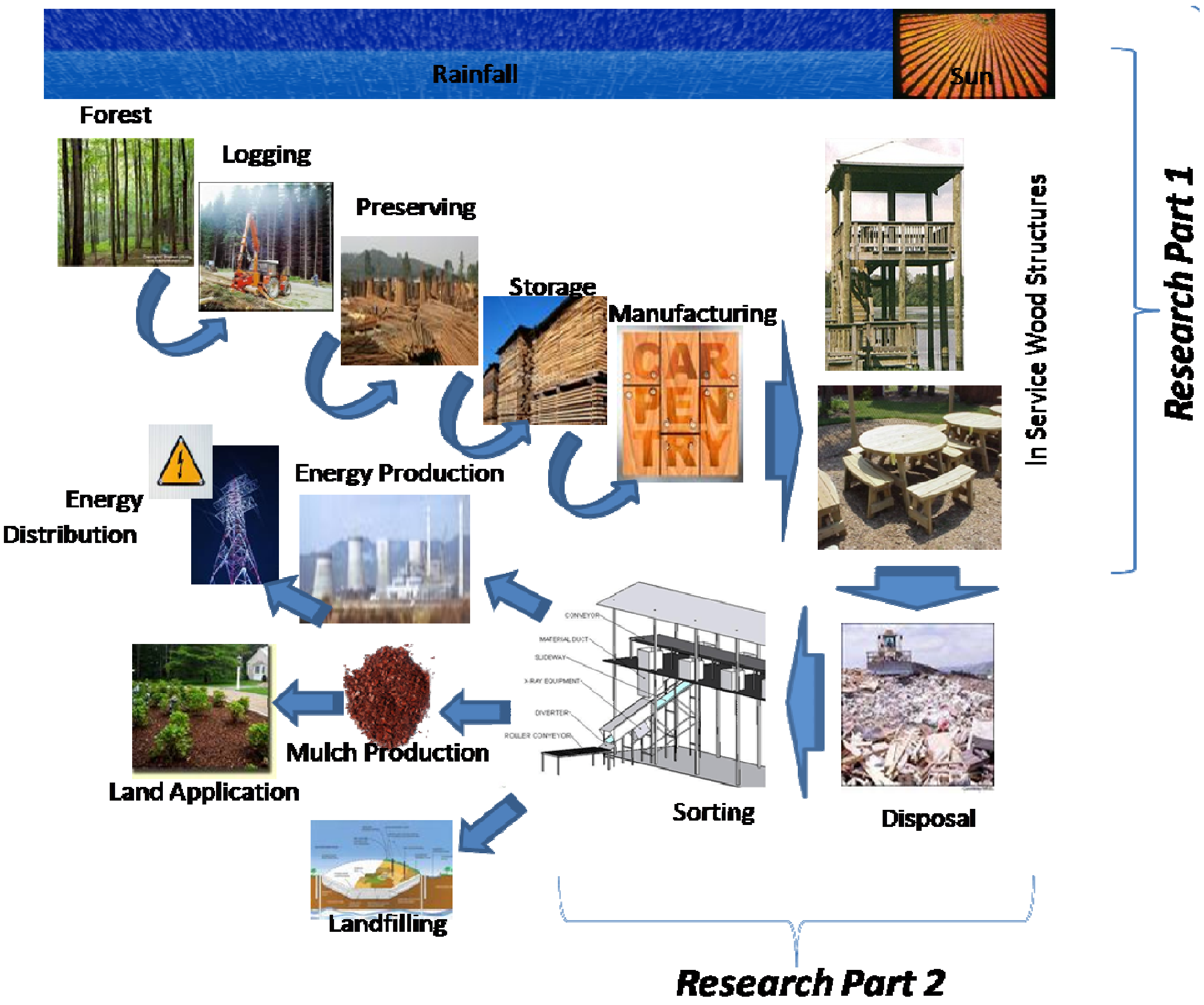


Figure 1.1 Research conducted on two subsequent stages during the wood life cycle.

CHAPTER 2

FIELD-SCALE LEACHING OF ARSENIC, CHROMIUM AND COPPER FROM WEATHERED TREATED WOOD

2.1 CHAPTER INTRODUCTION

Chromated copper arsenate (CCA) treated wood has been phased out from most residential applications in the U.S. as of 2004. However, large amounts of treated wood products are still in service due to continued use for non-residential applications and their prolonged service life that extends from 10 years to 40 years depending on its intended use and the retention level of treatment (Alderman et al., 2003; Cooper, 1993; Jacobi et al., 2007a; McQueen and Stevens, 1998; Solo-Gabriele and Townsend, 1999). As a result, leaching of metals from CCA treated wood continues to be a concern through the slow release of the metals during the weathering process. The alternatives to CCA in the US (e.g. alkaline copper quat, ACQ), are wood preservative formulations that contain Cu, and in the case of ACQ, contain another active ingredient of quaternary ammonium compounds such as DDAC (didecyldimethyl ammonium chloride or carbonate compounds).

Both CCA and ACQ treated wood are produced in set ratios of As, Cr and Cu for CCA and Cu and quat for ACQ. Three types of CCA have been produced over time with type C (47.5% as CrO_3, 18.5% as CuO, and 34% as As_2O_5) as the most common formulation used for products manufactured today. The most common formulation of ACQ contains 66.7% CuO and 33.3% quat (AWPA, 2008). The amount of chemical added, or retention level for both CCA and ACQ treated wood, is dependent upon the intended use of the wood. The lowest retention level of CCA treated wood (4 kg/m^3;

kilograms of CCA chemical on an oxide basis per cubic meter of wood) is intended for wood used in above ground applications; the highest retention level of 40 kg/m^3 is intended for wood submerged in marine environments (AWPA, 2008). At the lowest retention level of CCA, the amount of As, Cr and Cu within the wood (in g of metal per kg of wood) are 1.7, 1.9, and 1.2, respectively, with concentrations increasing by a factor of 10 at the highest retention level (Jacobi et al., 2007a; Khan et al., 2006a). Copper concentrations (in g of Cu per kg of wood) in ACQ correspond to 3.28 at the lowest retention level (4 kg/m^3) and 13.3 g/kg at the highest retention level (16 kg/m^3).

Concerns about the safety and environmental impact of wood preservatives have increased in recent years. Arsenic and chromium are considered human carcinogens and Cu can be toxic to aquatic organisms (Flemming and Trevors, 1989; Stook et al., 2004; Dubey et al., 2007). Metals release from treated wood has been reported by many researchers during the wood service life (Khan et al., 2006a; Shibata et al., 2007), during disposal (Khan et al., 2006b; Jambeck et al., 2006; Moghaddam and Mulligan, 2007) and from recycled forms such as mulch (Jacobi et al., 2007a; Shibata et al., 2006). Shibata et al. 2007 summarized other researchers' results of bulk metal loss rates ranging from an average 25% lost after 20 to 43 years of exposure in temperate Sweden (Evans and Edlund, 1993) and 22% after 44 months in tropical Hawaii (Jin et al., 1992) and 5% in 1 year in southern Florida (Khan et al., 2006a). Few studies document loss rates on a year to year basis and all of these studies evaluated new wood. For these studies, roughly 5% of As was shown to leach from the wood in 1 year (Kennedy and Collins, 2001; Khan et al., 2006a) resulting in As leachate concentrations between 0.1 and 8.4 mg/l (Khan et al., 2006a). No studies exist on yearly leaching rates for weathered wood. The contribution of weathering to release of CCA components from treated wood is largely unknown, but there is substantial information available on the mechanisms of surface degradation (Lebow et al., 2003, Williams et al., 2001) to suggest that leaching rates may change as a function of weathering. Leaching rates are important in assessing the potential impacts of existing wood structures constructed prior to the phase-out of CCA-treated wood for residential purposes. Townsend et al. (2005) studied the leaching of naturally weathered treated wood using laboratory batch tests such as the Toxicity Characteristic Leaching Procedure (TCLP), Synthetic Precipitation Leaching Procedure (SPLP) and Waste Extraction Test (WET). These studies showed that the toxicity characteristic threshold of As (5 mg/l) was exceeded in most of their experiments. Khan et al. (2004) also used the TCLP and SPLP to compare As leaching from new and weathered wood and found that weathered wood leached more As and they attributed the greater leaching to natural chemical and biological transformations during the weathering process. Thus batch leaching tests conducted in the laboratory suggest that the weathering process increases leaching rates, but this is yet to be shown under natural field conditions.

The objectives of the current study presented in this chapter were to evaluate leaching rates from weathered CCA-treated wood. Experiments were designed to evaluate the impacts of different retention levels of CCA and to compare leaching rates of weathered CCA-treated wood to leaching of new ACQ-treated and untreated wood. In an effort to evaluate the potential impacts of aging on leaching rates, results from the current study using weathered wood samples were compared to results from earlier studies which utilized new CCA-treated wood.

2.2 EXPERIMENTAL METHODS

2.2.1 Rainfall leachate collection system

Six separate leaching systems were constructed and set up outdoors within an open area located at the University of Miami, Coral Gables, FL, USA (Figure A.1). Each system was composed of an uncovered tank (Heavy Duty Polyethylene, US Plastic type Tamco® 6325, Lima, OH, USA) with interior dimensions of 91.4 cm x 61.0 cm open area and 76.2 cm high. Each tank was supported on an aluminum frame base with an average height of 0.6 m from the ground and horizontal inclination of 5^o. Rainfall leachate was captured in the tank and flowed by gravity via tubing (12.5 mm in diameter) to a 70 L covered reservoir. The reservoir was scaled in units of 1 L and was covered in dark plastic to minimize the impacts of evaporation and UV light. Each wood sample placed within the tank was supported by a frame made of PVC. A plastic screen of 2 mm mesh size was placed below the wood samples to prevent vegetative debris from accumulating in the bottom of the tank. Rainfall depth and rainfall samples were collected from a standard rain gauge made from Plexiglas. A correlation relation was established between rainfall depth (cm) and volume collected in tanks in order to calculate the volume in the tanks whenever they overflowed due to large rainfall events.

2.2.2 Wood samples' characteristics

Six different types of Southern Yellow Pine wood samples were used for the study (Table A.1); the surface area exposed to rainfall (about 2100 cm^2) was consistent between samples and corresponded to a ratio of 5:2 (total rainfall capture area relative to the wood surface area). One sample consisted of two new untreated boards (UW) and a second sample consisted of three new ACQ treated boards (ACQ). Both of these samples were purchased from a retail store in Miami, FL, USA. The remaining four samples were weathered CCA-treated wood samples and included replicates of low CCA-concentration treated wood boards (La-CCA and Lb-CCA) consisting of three boards each, medium concentration treated wood posts (M-CCA) consisting of four boards, and a high retention level (H-CCA) marine piling. Low and medium weathered wood pieces were obtained from a residential fence that was 14 years of age at the time of this study. This fence was never painted but sealed twice with a clear water sealant. The weathered marine piling was manufactured in 1982 according to the date stamp on the piling and was thus 25 years old at the time of the initiation of this experiment. All wood samples in this study were sealed along the cut-edges to minimize end-effects on leaching rates.

Initial concentrations of As, Cr and Cu in wood, and consequently retention levels, R_x, (Table 2.1), were determined by analyzing the sawdust produced during cutting wood pieces to the specified dimensions, except for the marine piling, where sawdust was collected from 40 holes drilled to 1.5 cm distributed equally on the outer surface of the piling. Drill holes were filled with wood sealant to minimize the effects of these holes on leaching. Sawdust samples were digested according to the U.S. EPA method 3050B (U.S. EPA, 1996), and the concentration of As, Cr, and Cu were measured by graphite furnace atomic absorption spectrometry (GFAAS, Model AAnalyst-600, Perkin Elmir, Shelton, CT, USA).

Total amounts of each of the three elements within each sample were calculated for each wood type as a product of each elemental concentration in wood sample times the mass of the wood, except for the mass of H-CCA, where the mass used corresponded to the volume of wood providing a CCA-depth of penetration equal half the piling diameter, as visual inspection showed that the CCA chemical did not penetrate the entire cross section.

2.2.3 Water sampling and analyses

Water samples were collected from each of the six leaching systems and the rain gauge on a weekly basis for one year starting on April 11, 2007. The first week of sampling (April 18) was carried out before the installation of wood pieces to obtain background concentrations of the systems without the wood and data showed no measurable contribution of As, Cr and Cu prior to wood installation. Immediately upon collection, water samples were analyzed for pH (Model 525A, Orion Research Inc., Beverly, MA, USA). Samples for As, Cr and Cu were collected in high density polyethylene bottles pre-washed with acid. Those samples were filtered through 0.45 µm pore-size membranes before analysis, and metal concentrations for each metal within the water samples were determined either by inductively coupled plasma mass spectrometry (ICP-MS, Elan DRCe, Perkin Elmer, Shelton, CT, USA) or by GFAAS using the same instrument listed earlier in the current paper. Detection limits by ICP-MS were 0.12, 0.1 and 0.1 µg/l for As, Cr and Cu, respectively, and by GFAAS were 3.3, 3.3 and 3.8 µg/l for As, Cr and Cu, respectively. For computation purposes, samples below the detection limit were set at the detection limit.

2.2.4 Analysis of data

Mass losses of metals were computed as the product of the measured concentration and the volume of water within the reservoir at time of collection. Mass of CCA leached was computed by converting metal mass to its corresponding oxide as given in the CCA solution (e.g. As to As_2O_5, Cr to CrO_3, and Cu to CuO). Percentage of mass leached was computed for each metal as the percentage ratio of total leached metal over the experimental period to the initial mass retention of the metal in the wood samples. The percentage of CCA leached was evaluated in the same way, as the sum of leached metal oxides to the initial retention of CCA.

Correlation p and R^2 values were evaluated by Pearson method. Significant differences were evaluated by one way ANOVA on ranks using the Tukey test at p value less than 0.05.

2.3. RESULTS AND DISCUSSION

2.3.1 Rainfall and pH

A cumulative amount of 176 cm of rainfall was measured during the sampling period, divided as 136 cm during the wet summer season (end of April up to end of October) followed by 40 cm during the following six months (dry season). In general rainfall leachate samples were mostly in the acidic range ($pH<7$) with the pH of the leached water higher than that of the background levels of rain and inversely proportional to the volume of leachated water (R^2 of 0.42-0.5) (Figure A.2), supporting that wood buffers the pH of the rainwater (Shibata et al., 2007).

2.3.2 Concentrations of leached metals

Metal concentrations in the rainfall and in the leachate from the UW and ACQ samples were mostly below or around the detection limits (except for Cu from the ACQ). The average As, Cr, and Cu concentrations measured in the rainfall and in the leachate from the UW and ACQ samples were on the order of a few micrograms per liter with the exception of Cu for ACQ which measured at 640 µg/l, on average. Leachate concentrations of As, Cr and Cu from the four CCA-treated wood samples oscillated over time between minimum and maximum values (Figure A.3) which were significantly different ($p<0.001$) between retention levels and from levels observed in rainfall, and in leachate from UW. Also, CCA-leachate concentrations had averages that were proportional with their retention level in the wood samples (Table 2.2). The average measured concentration in the leachate collected from the La-CCA and Lb-CCA were approximately 100 µg/l for As and approx. 30 µg/l for Cr and Cu, while for M-CCA, As measured at approx. 900 µg/l, with Cr and Cu measuring at about an order of magnitude less (90 and 65 µg/l, on average, respectively). The metal concentrations in the leachates from the H-CCA sample were the highest (As - 2000 µg/l, Cr - 400 µg/l and Cu - 400 µg/l, on average). In all cases As leached the most with the average concentration of As 3 - 4 times higher than that of Cr and Cu from the L-CCA samples, 5 - 6 times higher for the H-CCA sample, and 11 - 14 times higher for the M-CCA sample. The replicates, La- and Lb-CCA, had similar leaching trends and bounds (Figure A.3) with no significant differences between these replicates whose coefficients of variation (calculated for each metal as the ratio of the standard deviation of the difference between La and Lb-CCA to the mean of both La and Lb-CCA weekly concentrations) measured at 21, 15, and 18%

for As, Cr and Cu, respectively, which support the similar behavior of metals leaching among wood pieces of same original retention, age, and use.

The Cu concentrations in the leachates from the ACQ sample averaged 640 µg/l and were high in comparison to the leachates from the CCA samples (65 µg/l for the M-CCA sample and 410 µg/l for the H-CCA sample). This is significant especially considering that the M-CCA sample contained twice, and H-CCA contained 23 times the Cu mass of the ACQ sample. An apparent wash off effect was observed from the ACQ sample, with higher leaching levels observed during the first three months (900 µg/l) relative to those observed later (530 µg/l). This trend is consistent with studies that focused on leaching from new treated wood (Khan et al., 2004; Dubey et al., 2005).

Results also showed no strong relationship between rainfall depth and metal concentration in the leachates when considering the data on a week-by-week basis (Figure 2.1 for M-CCA and ACQ). However, when data were combined into seasonal categories (wet versus dry seasons) distinct differences were observed. In general, higher average concentration of leached Cr observed in the wet season relative to the dry season; this difference was more pronounced at higher retention levels from the CCA treated samples (Figure 2.2). Arsenic and Cu behaved differently, at the low retention level samples, average concentrations of As and Cu were higher in the dry season, as retention level increase, average concentrations of arsenic shifted to be higher in the wet season followed by the same shift of Cu just at the highest retention level. For example, the average metal concentrations for the H-CCA samples were consistently higher during the wet season in comparison to the dry season (23, 43 and 31% greater for As, Cr and Cu, respectively). M-CCA followed the same trend as H-CCA for As and Cr with 17% and

36% increases in concentration from the wet to dry season; the average Cu concentration from M-CCA decreased from the wet to dry season by 13%. In contrast, Cr concentration from L-CCA showed an increasing trend from wet to dry seasons (29 ± 2.4% increase), while the As and Cu concentrations from L-CCA showed a decreasing trend from wet to dry season (13 ± 5.3% and 37 ± 0.3% , respectively) (Figure 2.2).The ACQ sample was observed to exhibit higher average Cu concentration during the wet season relative to the dry season (Figure 2.2). Apparently, the manner in which As and Cu leach changes as the retention level of metals in the wood decreases. When metals are in abundance, high rainfall promotes the transport of metals to the surface of the wood allowing for a large loss of metals during subsequent rainfall events. When metal retention levels are lower such as in L-CCA, metal transport to the wood's surface by high rainfall may be limited, resulting in a dilution effect within the collected rainfall leachate. Chromium leaching from treated wood is believed to be more responsive to prevailing moisture conditions relative to As and Cu at the different retention levels of chemicals.

2.3.3 Masses of leached metals

For a given sample, the mass of metals leached (the product of rainfall volume and concentration of metal in the leachate) was primarily dependent on rainfall volume with increases in metal mass leached as rainfall volume increased ($p<0.001$; Figure A.4 for H-CCA and ACQ). Concentration of metals in the leachate played a secondary role in influencing the mass of metals leached ($p<0.0014$ for H-CCA and not significant for other wood samples). The correlation between metals' mass leached and rainfall was higher with higher CCA-retention (R^2: 0.7-0.8 for L-CCA, 0.80-0.82 for M-CCA and

0.88-0.92 for H-CCA) (Figure A.4 for H-CCA and ACQ). The higher leaching of metal masses from wood associated with larger collected volumes of leachate may have also been facilitated by a slight shift of the leachate pH towards the acidic range with larger rainfall volumes, in a fashion similar to that reported by Taylor and Cooper (2005). Although Figure A.4 shows that metal leached is reduced with increasing pH value, the correlation between the factors was not significant.

The masses of leached metals were significantly dependent on the original retention levels of wood ($p<0.001$). The H-CCA leached As, Cr and Cu (2386, 548 and 418 mg, respectively over the experimental period) more than 20 times higher than L-CCA (99.3 ± 8.10, 27.4 ± 0.64 and 19.9 ± 1.6 mg, respectively), while M-CCA leached As, Cr and Cu (880, 87.8 and 44.2 mg, respectively) 8 times more As and 2 – 3 times more Cr and Cu relative to L-CCA. Masses of metals leached during the wet season were higher than during the dry season (Figure 2.3). Roughly 70 to 80% more metals were leached during the wet season from the CCA wood samples in comparison to the dry season. For the ACQ sample, 84% more Cu leached during the wet season in comparison to the dry season.

Leaching of As and Cu was significantly correlated with the amount of Cr leached for all CCA-treated wood samples ($p<0.001$; R^2: 0.8-0.95). Chromium compounds act as fixing agents for both As and Cu in CCA treated wood. Loss of Cr from the wood may have led to higher loss of As and moderate loss of Cu (Figure 2.4 for the H-CCA wood sample). According to manufacturer requirements, the As/Cr and the Cu/Cr ratios in new wood should have been at 0.89 and 0.63, respectively. This manufacturer ratio is in contrast to the ratios observed in the leachate for all CCA samples. For all CCA samples, the As to Cr mass ratios was always higher than 5, while the Cu to Cr mass ratios oscillated around 1.

This loss impacts the mass ratios of metals contained in the wood. At the beginning of the experiment, the mass ratios of Cu to Cr in the wood fiber were 0.67, 0.59 and 0.50 for the L-CCA, M-CCA and H-CCA, respectively, which was near the expected ratio of 0.63. After one year of experimentation, the Cu to Cr ratios in the CCA-wood samples were kept at the same level. The mass ratios of As to Cr in the wood fiber for L-CCA, M-CCA and H-CCA was measured at 0.28, 0.54 and 1.43, suggesting a preferential depletion of As relative to Cr at the different retention levels. The difference in metals ratios between these samples may be due to the different retention levels of the original samples. The L-CCA and M-CCA samples were of lower retention level and their As/Cr ratios were generally lower whereas the H-CCA sample was characterized by an exceptionally high retention level. In order to see changes in As/Cr ratios in the H-CCA samples, a large amount of metals need to leach and perhaps the fraction leached to date (25 years) was not a significant fraction of the amount originally contained in the wood, whereas the amount leached from the L-CCA and M-CCA samples was significant relative to the original retention level allowing for a significant reduction of the As level in the wood fiber relative to Cr. After one year of experimentation, the As to Cr ratios in the CCA-wood samples were reduced due to the higher loss of As relative to Cr, and evaluated as 0.25, 0.50 and 1.42, for L-CCA, M-CCA and H-CCA, respectively.

The new ACQ wood sample had very low As and Cr contents as expected and the amount of Cu leached was 672 mg over the experimental period; 1.6 times and 15 times more than the Cu leached from the H-CCA and M-CCA samples. The factors that influenced Cu mass leaching from the ACQ sample was primarily the rainfall volume ($p<0.001$) and secondarily the Cu concentration observed in the leachate ($p<0.033$).

2.3.4 Cumulative masses of metals leached

Cumulative leaching data (Figure 2.5 for the M-CCA) showed that As leached the highest when compared to Cr and Cu. The cumulative mass of leached metals from all samples evaluated is highly correlated ($p<0.001$) to the cumulative rainfall (Figure A.5, R^2: 0.94-0.99). In general, initial leaching was low for the first month of the experiments (except for ACQ, Figure 2.5) and followed by several sudden increases. These sudden increases did not occur during major rainfall events but rather occurred during weeks of low to moderate rainfall depths that follow major rainfall peaks. According to Taylor and Cooper (2005) large rainfall events (in terms of duration or intensity) lead to a deeper water-penetration level of wood where solubilisation of metals occurs. After the rainfall period, metals diffusively migrate to the surface of the wood, precipitate as water evaporates from the wood, and become available for the next rainfall period to achieve a jump in the cumulative mass leaching curve. The sudden increases observed in mass leached are consistent with the explanation provided by Taylor and Cooper (2005) and suggest that leaching of metals from preservative treated wood is a dynamic process which involves continual solubilisation of metals. This process provides an over-abundance of metals at the wood's surface, especially when the wood is new and contains high metal retention levels.

2.3.5 Metals' leaching percentages and rates

Normalized leaching percentage is defined as percentage mass lost per cm of wood depth. Normalized leaching rate is equivalent to mass flux (mass lost per time per area).

Annual CCA leaching percentages measured in this study ranged from 1.5%/cm for the L-CCA samples to 0.02%/m for the H-CCA sample. On a total mass basis, these corresponding rates resulted in 3 mg/d of CCA leached per square meter of the L-CCA sample relative to 57 mg/d of CCA leached per square meter of H-CCA (Table 2.3). Consistencies were observed when comparing these levels with the yearly values published in the literature for new CCA-treated wood. In this study, the percentage of metals' masses leached was inversely proportional to the retention level of the CCA-treated wood samples which was consistent with the results of Taylor and Cooper (2005). The lowest retention of weathered wood (L-CCA characterized by a retention level, R_x of 2.69 kg/m^3) leached 6.3%/cm of the As during one year which was more than two times the amount reported by Khan et al. (2006a) for leaching of new wood, and similarly almost two to four times of the As loss from new wood as reported by Shibata et al. 2007, who reported 3.5%/cm after 1 year, 1.5%/cm during year 2 and 1.5%/cm during year 3 (R_x of samples used in these studies were 3.5 kg/m^3). All three of these studies were conducted at the same location at the campus of the University of Miami, with no significant difference in rainfall depth. Thus, the results from this study suggest that the As leaching percentages for weathered wood are roughly double that of new wood at the lower retention levels. For the medium retention, As leached at a rate of 0.8%/cm from M-CCA (R_x of 4.79 kg/m^3) which was similar to the rate observed for the new wood evaluated by Taylor and Cooper (2005) (0.7%/cm for R_x of 5.52 kg/m^3). Of note the rainfall depth in the Taylor and Cooper (2005) study was about 1/3 of the amount measured in the current study and so differences were not observable due to the differences in weather conditions in the comparative studies.

Chromium percentage leaching as measured by Kennedy and Collins (2001) was at 0.5%/cm for one year whereas Shibata et al. (2007) also measured 0.5%/cm during the first year and then 0.1%/cm during the second and third years of their study. The percentage leached during these other studies was comparable to the Cr leaching rate measured in the low retention level wood in the current study (0.48%/cm). Copper percentage leaching in the current study also measured at near 0.5%/cm for the lower retention (similar to Kennedy and Collins, 2001) and decreased with higher retention levels. The decrease in percentage leached with increasing retention level was consistent with observations of Taylor and Cooper (2005).

In the current study, the annual amount of As mass leached for L-CCA, M-CCA, and H-CCA was 99, 880, and 2386 mg, respectively. The total masses leached when averaged on a daily basis show an As loss rate of 1.3, 11.5 and 31 mg/d per 1 m^2 of horizontal surface area for the low, medium and the high retention levels (Table 2.3), showing a strong increasing trend for the mass leached with increasing retention levels. The As mass leached from the L-CCA samples were comparable with those measured by Shibata et al. (2007), Khan et al. (2006a) and Kennedy and Collins (2001). Despite, the increase in percentage leaching as wood weathers, As mass leached was slightly higher for the new wood. The explanation for these trends is twofold. First, new wood has higher metals' retention, and a significant wash-off effect is observed for new wood when it is first put into service. Thus new wood releases a larger mass when first put into service because of the greater amount of metals in the wood and the release of metals that have accumulated. Second, new wood has a larger retention of metals in the wood. The larger retention results in a greater amount of metal mass in the wood fiber (divisor) which contributes to the lower percent leaching for new wood relative to weathered wood. Mass leaching of Cr appears to be similar between weathered wood and new wood. Chromium leached from new wood at 0.45 (mg/(d·m^2)) (Shibata et al. 2007) and at 0.36 (mg/(d·m^2)) from the weathered low retention in the current study. Chromium leaching rates were not as easily comparable to Taylor and Cooper (2005), due to the difference in the field environment and rainfall depths of both experimental locations. Copper mass leached from weathered wood is comparable to that observed by Kennedy and Collins (2001) for new wood and the yearly mass loss observed in the current study were lower than those observed by Taylor and Cooper (2005).

The total amount of Cu lost from the ACQ-treated wood sample was the highest (2.5%/cm) among all wood pieces in the experiment. This was observed regardless of the fact that the ACQ sample was characterized by half the wood volume and contained half the amount of Cu of the M-CCA sample. The mass loss of Cu from the ACQ was very high (8.77 mg/(d·m^2)). Dubey (2005) also observed that Cu leached from new ACQ wood at a rate seven times higher than the rate from new CCA. Similar results have been reported by Stook et al. (2004; 2005) for batch leaching experiments. This result suggests that Cu is not as strongly fixed in ACQ-treated wood in comparison to CCA-treated wood, thus potentially resulting in shorter service lives of wood products treated with this Cu-based alternative.

2.4 SUMMARY

The results from this study emphasize that leaching of metals from treated wood is driven by rainfall. The concentration and masses of leached metals is highly dependent on the retention level of the treated wood with higher retention levels resulting in higher concentrations in leachates and a greater mass of metals lost. The results from this study support that the mechanism of leaching is associated with the transport of metals from the interior portions of the wood towards the surface where sudden increases of metals lost were observed at a one week delay from maximum rainfall amounts. Furthermore, we observed that at low retention levels of CCA, the As and Cu concentrations were diluted presumably due to a limitation in the amount of metal transported to the surface whereas for high retention levels increases in metal concentrations were observed during the wet season. On the contrary to As and Cu in CCA, leaching of Cr from CCA wood and Cu from ACQ are more responsive to the prevailing moisture conditions. Comparing leaching rates observed in the current study with earlier work which evaluated leaching of new CCA-treated wood under field conditions suggests that weathering can increase leaching rates of As on a percent leached basis (mass leached per mass in wood); however, because the retention of metals in the wood decreases over time, the mass of metals leached would decrease. In spite of the decrease in total mass leached, metals leaching from treated wood are expected to continue over the service life of wood, and the leaching mechanism is expected to change as wood weathers due to loss of Cr fixation, cracking of wood, and deterioration of the wood fiber.

Since the initiation of the field work associated with this experiment, the wood treatment industry has developed a new micronized formulation for a Cu-based preservative (MCQ), which is believed to leach Cu at a slower rate relative to the early ACQ formulations as indicated by wood efficacy tests (Freeman and McIntyre, 2008). Of interest would be to evaluate new and weathered micronized Cu treated wood under natural field conditions to evaluate Cu leaching rates and to provide a comparison with values published in the literature for other wood preservative formulations.

Figures related to other wood samples that were not mentioned in this chapter of Appendix A, can be found as extra supporting information in Appendix B.

Table 2.1 Initial concentrations and quantities of As, Cr and Cu in the wood samples prior to installation in the leaching experiments. R_x corresponds to retention level of the chemical in the wood.

Label	Concentration of metal in wood sample (g/kg)			Mass contained in wood sample (g)			Meas.[a] R_x (kg/ m^3 wood)	Rated[b] R_x (kg/ m^3 wood)
	As	Cr	Cu	As	Cr	Cu		
UW	0.04	0.04	0.03	0.16	0.16	0.12	NA	NA
ACQ	N.A.	N.A.	1.78	N.A.	N.A.	7.64	1.14	4.0
L-CCA	0.455	1.65	1.10	0.88	3.18	2.12	2.69	4.0
M-CCA	1.44	2.68	1.57	13.3	24.8	14.5	4.79	9.6
H-CCA	20.7	14.5	7.30	375	262	132	35.4	40

NA = Not applicable

[a] Based on lab analysis. For the L-CCA, M-CCA, and H-CCA samples the R_x value corresponds to kg of CCA – oxide basis per cubic meter of wood. For the ACQ sample the R_x value corresponds to kg as CuO per cubic meter of wood. The density of wood used for computations was 511 kg/m^3.

[b] From manufacturer-intended use.

Table 2.2 Concentrations and masses of As, Cr and Cu from rainfall and leachate samples evaluated in this study based on weekly collected data.

			Rain	**UW**	**La-CCA**	**Lb-CCA**	**M-CCA**	**H-CCA**	**ACQ**
As	**Conc. (µg/l)**	Average	0.47	0.57	108	127	934	2101	1.03
		Std. dev.	0.72	0.94	63.0	70.6	396	1103	1.83
	Mass (mg)	Sum	0.003	0.77	105	93.6	880	2386	1.39
		Average	0.00007	0.02	2.33	2.08	19.6	53.0	0.03
		Std. dev.	0.0001	0.07	2.99	2.42	26.1	79.3	0.10
Cr	**Conc. (µg/l)**	Average	0.70	0.43	25.5	29.6	86.1	424	1.00
		Std. dev.	1.20	0.54	11.61	14.6	52.4	321	1.81
	Mass (mg)	Sum	0.01	0.57	27.8	26.9	87.8	548	1.71
		Average	0.0002	0.01	0.62	0.60	1.95	12.2	0.04
		Std. dev.	0.001	0.04	0.81	0.69	2.64	19.9	0.10
Cu	**Conc. (µg/l)**	Average	7.62	4.48	32.1	35.7	65.5	362	637
		Std. dev.	21.0	5.28	24.4	30.5	39.0	175	317
	Mass (mg)	Sum	0.02	1.64	21.0	18.8	44.2	418	672
		Average	0.0004	0.04	0.47	0.42	0.98	9.28	14.9
		Std. dev.	0.001	0.05	0.49	0.38	1.11	15	25.6

Table 2.3 Comparison of leaching data between new treated wood as reported in the literature and weathered wood from this study. Percent leaching correspond to the fraction of chemical leached during a period of one year.

Reference	Type of wood[a]	R_x	Rainfall	As leached		Cr leached		Cu leached		CCA leached	
		kg/m^3	depth cm	%	mg/d·m^2	%	mg/d·m^2	%	mg/d·m^2	%	mg/d·m^2
Kennedy and Collins (2001)[b]	new, CCA	3.00	60	4.0	1.40	1.2	0.58	1.3	0.52	1.96	3.92
Kennedy and Collins (2001)[b]	new, CCA	3.16	60	4.4	2.10	0.9	0.50	1.2	0.34	2.18	4.60
Taylor and Cooper (2005)[c]	new, CCA	5.52	68.5	2.50	3.93	0.30	0.51	1.90	1.95	1.40	8.37
Taylor and Cooper (2005)[c]	new, CCA	13.94	68.5	0.60	1.65	0.10	0.35	1.00	2.24	0.40	6.04
Khan et al. (2006a)	new, CCA	3.50	159	5.12	2.06	NA	NA	NA	NA	NA	NA
Shibata et al. (2007) (1st yr)	new, CCA	3.50	167	6.95	3.47	1.00	0.45	NA	NA	NA	NA
Shibata et al. (2007) (2nd yr)	new, CCA	3.50	112	3.03	1.41	0.20	0.09	NA	NA	NA	NA
Shibata et al. (2007) (3rd yr)	new, CCA	3.50	137	3.02	1.36	0.20	0.09	NA	NA	NA	NA
This study, L-CCA	weathered, CCA	2.69	176	11.3	1.29	0.86	0.36	0.89	0.25	2.66	2.98
This study, M-CCA	weathered, CCA	4.79	176	6.60	11.5	0.35	1.14	0.30	0.58	1.59	19.0
This study, H-CCA	weathered, CCA	35.4	176	0.64	31.1	0.21	7.15	0.24	5.45	0.35	56.8
This study, ACQ	new, ACQ	1.14	176	NA	NA	NA	NA	9.49	8.77	NA	NA

[a] All data presented in this table correspond to Southern Yellow Pine except for Kennedy and Collins (2001) where wood samples were Radiata Pine.

[b] Data are for 300 days in 2000-2001, R_x was calculated as a match for the H3 Australian standards (AS 1604.1, 2005) and after personal communication with the authors.

[c] Data are for samples of Southern Yellow Pine treated with CCA-wood and with no water repellent or wash treatment.

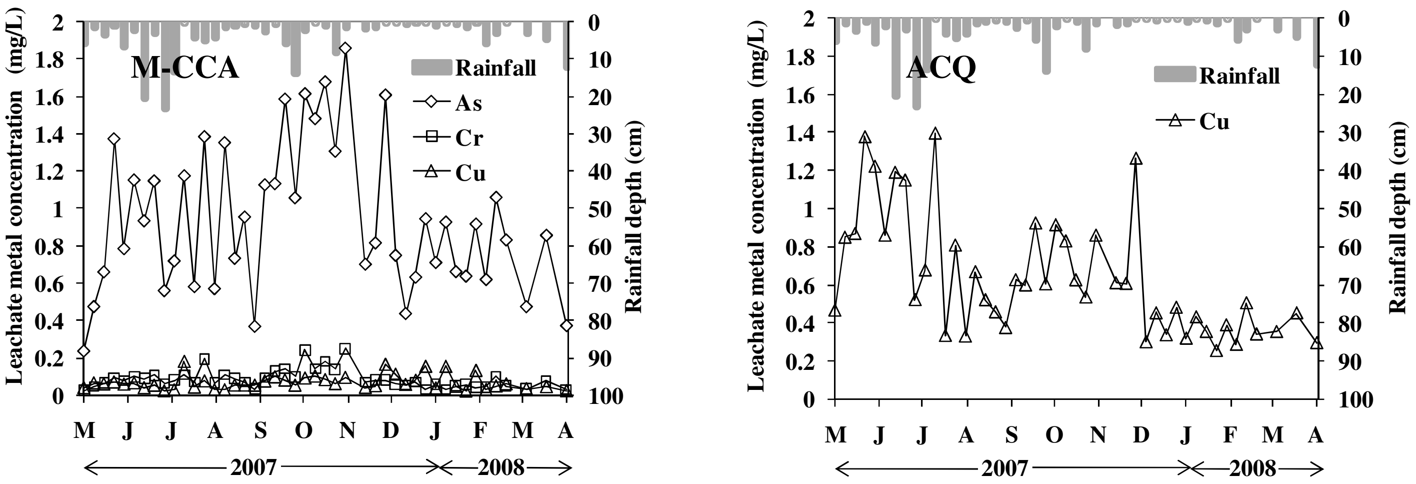
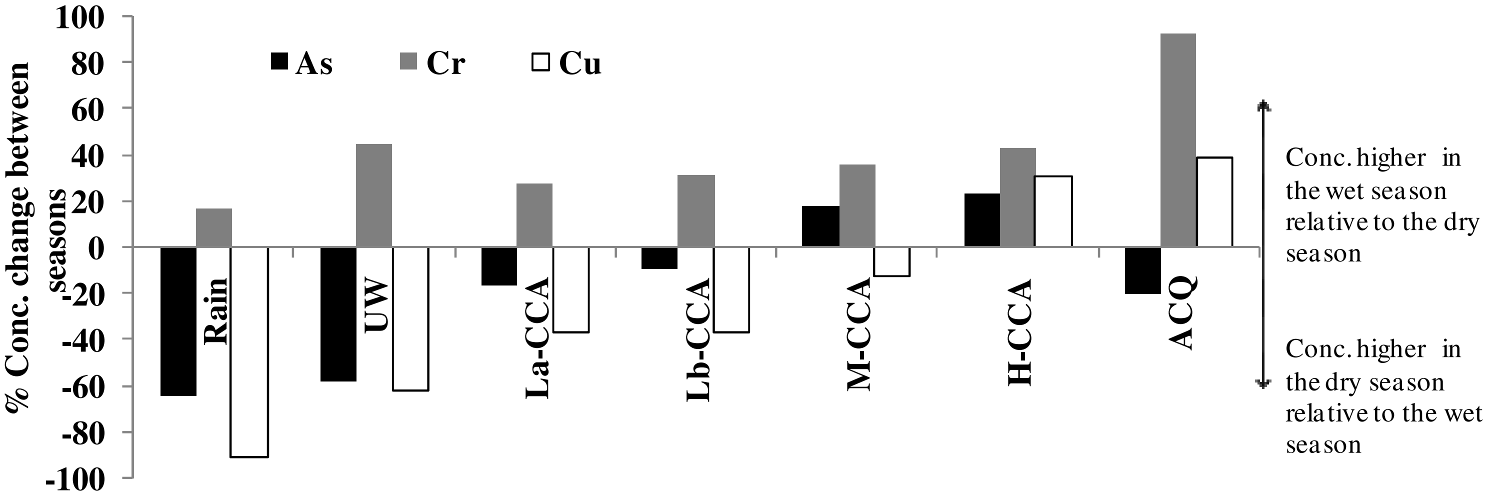


Figure 2.1 Time series plots of rainfall and metals' concentrations in leachates for M-CCA and ACQ treated wood samples.



Conc. higher in the wet season relative to the dry season

Conc. higher in the dry season relative to the wet season

Figure 2.2 Percentage change of average measured concentration of As, Cr and Cu from wet season relative to dry season over the experimental period. Percent change is defined as the average concentration during the wet season minus the average concentration during the dry season divided by the highest seasonal concentration. The ACQ wood sample was low in As and Cr level, so the high percentage change of Cr reflects losses of only minute values. The same can be said for As and Cu in rain.

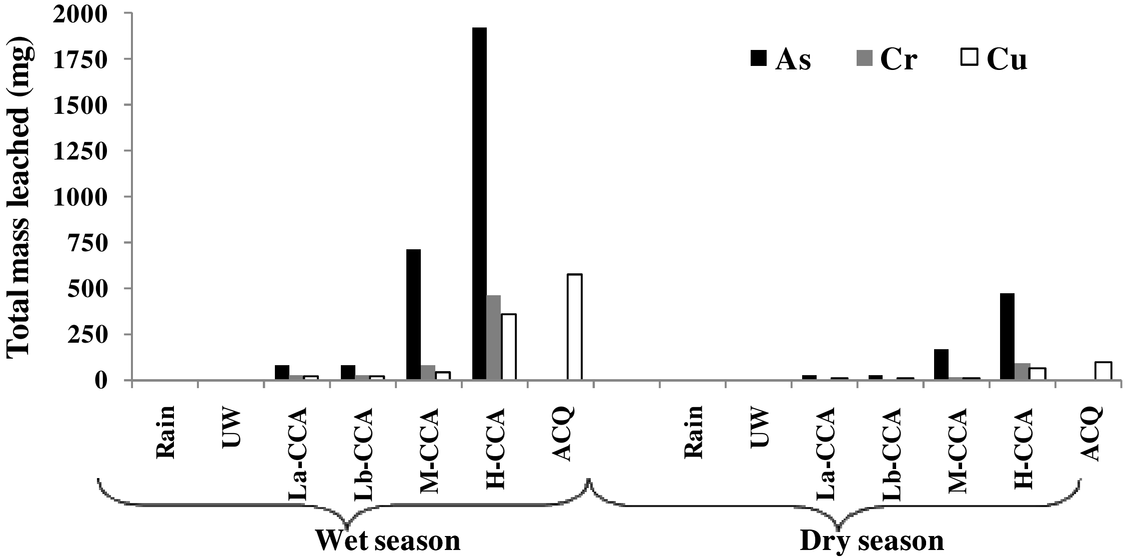


Figure 2.3 Total mass of As, Cr and Cu leached during the wet and dry seasons.

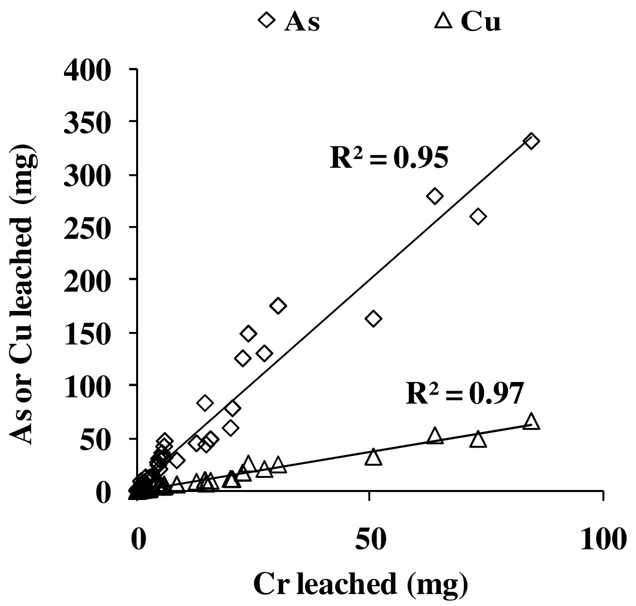


Figure 2.4 Mass Leached of As and Cu relative to the mass leached of Cr for H-CCA.

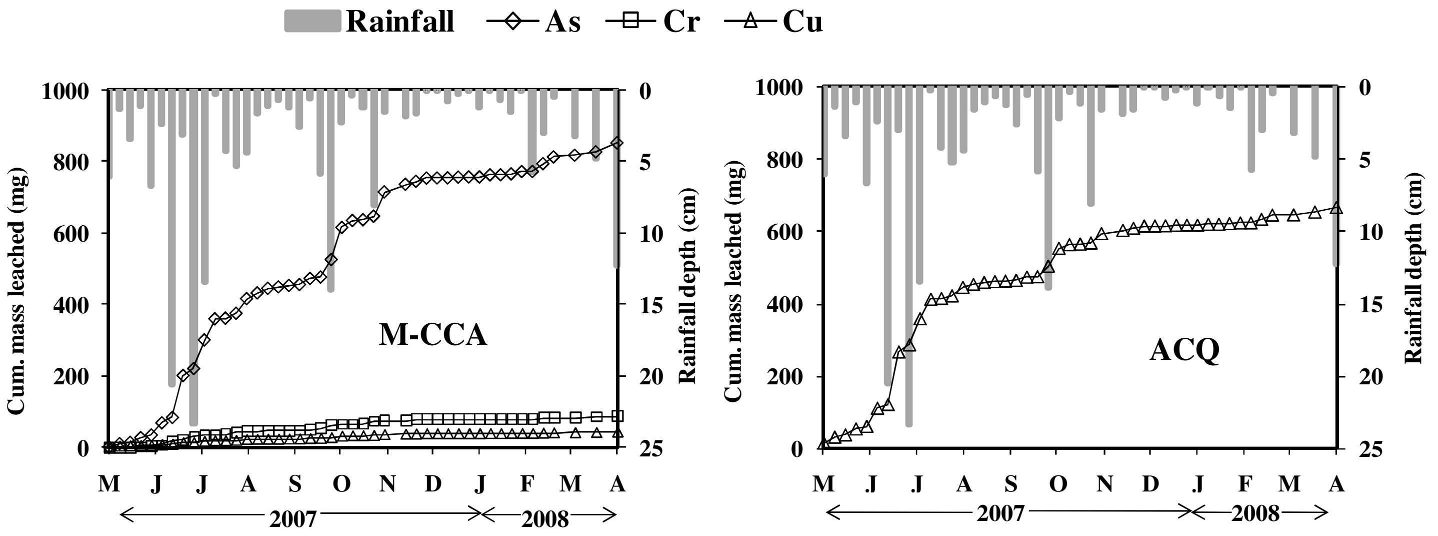


Figure 2.5 Cumulative leaching of metals from wood over the experimental period for M-CCA and ACQ.

CHAPTER 3

XRF TECHNOLOGY FOR ONLINE DETECTION OF PRESERVED WOOD WASTE

3.1 CHAPTER INTRODUCTION

Treated wood is produced by impregnating wood with chemicals. The purpose of these chemicals is to protect the wood from biological deterioration and to extend its service life. Treated wood will eventually be disposed and the most common disposal route will be through the construction and demolition (C&D) waste stream. Through 2004, the most common wood preservative observed in residential C&D waste within the U.S. was chromated copper arsenate (CCA). Wood preservatives with copper as the primary active ingredient, such as ACQ, are expected to increase in the C&D waste stream due to the shift from the production of arsenic-based treated wood such as CCA to a copper-based treatment, due to the phase out by regulatory agencies in the U.S. and other countries (U.S. EPA, 2002; Humar et al., 2006; Peek, R.-D, 2004). Since construction waste wood (representing about 2.5% of the wood produced, Cooper, 1993) is generally produced shortly after the production of the materials, the shift from arsenic-based towards copper based treated wood was sudden in this fraction of the treated wood waste stream. However the shift is much more gradual in demolition waste due to the long service life of treated wood (10-25 years in residential applications and 40 years in industrial applications). Thus disposal of arsenic-treated wood is anticipated to continue for many years into the future.

The metals found in the CCA-treated wood, arsenic, chromium and copper, are all of environmental concern. The first two are considered human carcinogens and copper is toxic to aquatic organisms (Flemming and Trevors, 1989; Stook et al., 2004; Dubey et al., 2007). The primary benefit of separating As- and Cu-based treated wood from wood waste is the production of a recycled product (such as mulch or wood fuel) that is free from wood preservative contaminants. Furthermore, separating treated pieces will facilitate the diversion of treated wood from open dumpsites and unlined landfills and so it provides protection for surface and ground waters that receive leachate from unlined landfill facilities. In many cases in the U.S., wood waste is disposed in lined landfills (Jambeck et al., 2007). Efficient sorting of the treated wood components will allow for a smaller waste volume (as it would be free from untreated wood which can be recycled) thereby decreasing the demand of lined landfills that receive waste wood products.

Detection of treated wood from the wood waste stream (Table 3.1) is mostly practiced manually at recycling facilities and depends on visually identifying the treated wood by noting the wood's original intended use (e.g. outdoor decks, fences, piling and utility poles are usually treated) (Hasan et al., 2009). Visual inspection also includes looking at end tags which identify the type of treatment and also, looking for wood that is olive green in color, which is an indication that the wood has been treated with copper, a component of CCA and ACQ, and then picking and separating the suspected pieces from the feed line. Although detection based upon visual methods is helpful to reduce the proportion of treated wood in the recycled wood waste stream, visual detection is not accurate since dirty and/or weathered wood are not easily identified based on color. Thus methods are needed to augment the identification of preservative treated wood beyond visual methods (Blassino et al. 2002; Solo-Gabriele et al., 2006; Jacobi et al., 2007b). Chemical stains and commercially available test kits, with relatively low capital costs (<US$ 200), have been found useful for augmenting the detection process for small quantities of preserved wood within C&D wood waste (Jacobi et al., 2007b). For example, PAN and Chromazurol S (CS) are chemical stains that contain active chelating agents capable to react with Cu to undergo a distinctive color change. These stains have analysis times of 5-12s and 45-60s, for PAN and CS, respectively (Blassino et al., 2002; Sawyer and Irle, 2005). Technologies for detecting arsenic specifically include the use of As-test kits, including one that is commercially available for analyzing As in drinking water (Shalat et al., 2006) and another designed for testing wood (Omae et al., 2007). Both of these methods require a 30 to 45 minute processing time per sample and are thus suitable for checking a relatively small number of wood pieces. Jacobi et al. (2007b) evaluated the fastest of these technologies, PAN stain, for detection at a full-scale wood recycling operation and concluded that the technology is suitable for detection relatively small quantities of wood waste (< 0.5 tons) but is not recommended for large quantities of commingled waste, the case mostly found in C&D recycling facilities.

When evaluating large quantities of wood at recycling facilities, faster automated sorting technologies are needed. Automated online sorting consists of three components: conveyance of wood to the detector, detection and diversion of the wood for separation. Both Laser Induced Breakdown Spectroscopy (LIBS) and X-ray flouresence (XRF) detectors can be fitted to an online system with measurement times as low as seconds to fraction of a second. LIBS technology has been shown to detect a wide range of CCA treated wood (efficiency at 92-100%) (Moskal and Hahn, 2002); however the main drawback is that the technology did not prove reliable for the detection of severely rotted and wet wood (Moskal and Hahn, 2002; Solo-Gabriele et al. 2004), and its reliance for measuring Cr which makes it difficult for the technology to distinguish between As-treated and Cu-treated wood. Commercially available handheld XRF units have been shown to detect for the As, Cr, Cu and other metals at the same time within 2-6 s and have the advantage of detecting preservative treatment, even when the wood was dirty and wet (Solo-Gabriele et al., 2004; Jacobi et al., 2007b). No studies have been conducted evaluating wood sorting efficiencies of on-line systems based upon metals masses diverted because of the limitations in analyzing each piece of wood sorted; the availability of handheld XRF analysis systems for evaluating metals in wood waste has now provided the opportunity to also evaluate sorting based upon metals masses removed. Moreover, to date, there has been no formal evaluation of full-scale on-line detection systems using XRF specifically for sorting wood. Thus there is a technical gap associated with the need to sort (handle wood, detect and divert) large quantities of wood waste using on-line automated processes. Such processes should have capabilities of distinguishing As and Cu preserved wood separately and evaluation of such systems should also include metals mass removal rates to provide a better assessment of the environmental benefits of the use of these technologies.

The primary goal of this research was to evaluate operational parameters and sorting efficiencies for the detection of inorganic-preserved treated wood using a full scale on-line XRF sorting system. Specifically, the current study focused on evaluating the effect of the thresholds for both arsenic and copper and measurement times on preserved wood sorting efficiencies as evaluated by number and weight of wood pieces and metals' mass recoveries. The discussion includes the costs of implementing the system and a comparison of these costs with other detection methods.

3.2 THEORY

XRF is based on exciting atoms in a sample with relatively high energy X-rays from a source, and detecting lower energy X-rays emitted when the atom returns to its normal state. When an X-ray tube is directed at the sample, some of the X-rays from the tube are absorbed, causing ejection of an electron from the absorbing atom. When these electrons are from an inner shell of the atom (shell K), electrons from outer shells (such as shells L and M) can move to the inner shell vacancy. The shells have different energies so the electron looses energy in this process and that energy (designated as K_α and K_β) is radiated as an X-ray photon (Figure 3.1). (Kalnicky and Singhvi, 2001; U.S. EPA, 2006). The energy difference depends on the atomic number of the atom and therefore the energy of the photon can be used to determine the element that emitted it. A detection system that can measure the energy of each photon and also build a histogram of the number of photons at each energy level is used to record a spectrum (Michette and Buckley, 1993; Lifshin, 1999).

Not all of the X-rays from the source that strike the sample cause fluorescence. A major portion is scattered by the sample. Two types of scattering are noticed: Rayleigh scattering does not change the energy of the photon and so has the characteristics of the source, and Compton scattering, the photon looses some energy to an electron in the sample and so can be used as background reference in detecting the elements in the sample (Ryon and Zahrt, 1992; Scholtz and Uhlig, 2006).

3.3 DESIGN RATIONALE

3.3.1 Background

Facilities that receive construction and demolition waste (C&D) usually have wood separation steps which can be in the form of picking lines (Jacobi et al., 2007b). Picking lines, which consist of a series of motorized belt conveyors, carry the C&D waste through a combination of automated (such as fines removal, de-stoning and metals separation) and manual sorting steps. Wood is typically manually sorted requiring that a laborer visually detect the treated wood piece and manually pick it off the conveyor and move it toward an opening which permits the wood to fall into a storage area located beneath the picking line.

3.3.2 Conveyance system

For this project, XRF sorting system was designed to be installed under a picking line of a wood recycling facility. Given the configuration of the XRF chamber on the top of the infeed conveyor, wood was limited to lengths less than or equal 150 cm, which could accommodate a vast majority of the wood pieces accepted at this facility. The system consisted of an infeed motorized belt-conveyor of 6 m length, 54.2 cm effective width and 297 cm height. In addition, an inclined conveyor (of 3 m length, 108 cm width and 165 cm highest end above the ground) was installed perpendicular to the discharge end of the infeed conveyor (Figure 3.2). The infeed conveyor (belt speed set to 0.5 m/s) was designed to receive wood fed manually by wood pickers and to convey it to the XRF detection unit, and the inclined conveyor moved the untreated wood to a separate pile for further processing.

3.3.3 Targeted metals

Preserved wood detection by the applied online XRF technology focused on the inspection of As and/or Cu presence in wood. The presence of As and Cu, indicated the presence of arsenical preservatives in the wood, most likely CCA and less likely ammonical copper arsenate (ACA) and ammonical copper zinc arsenate (ACZA). The presence of Cu only indicated the presence of copper based (non arsenical) preservatives such as alkaline copper quat (ACQ) among many others, or the recent product, micronized copper quat (MCQ) (Freeman and McIntyre, 2008).

3.3.4 Threshold and measurement time

In the X-ray spectrum of subjected wood samples, the ratio of the area under the K_α peak of the targeted metal (A_{TM}) to the area under the reference region of the X-ray tube scattering (A_R) (and for this research, the reference is Compton scattering) is named as the normalized count ratio (NCR_{TM}) (Table 3.2). The minimum NCR needed to detect wood preservative metals without the interference from other metals in the system is denoted as the operational threshold (OT_{TM}). The OT_{TM} is chosen to be higher than the NCR_{TM} normally seen on the background system. When the OT_{TM} is exceeded, the wood will be diverted (equation 3.1).

$$NCR_{TM} = \frac{A_{TM}}{A_R} > OT_{TM} \dots\dots\dots\dots\dots (3.1)$$

Higher target metal concentrations in a wood sample generally result in higher A_{TM} and lower A_R in the generated spectrum, and thus increase the likelihood of detection when compared to the set OT_{TM}.

Lowering the threshold will improve detection and diversion of weathered wood pieces, but may increase false positives due to the interference from other metals that have a spectrum overlapping or very close to the one of concern as the case of Pb with As and Zn with Cu. The time needed to count the emitted energies by the detection system is called the measurement time, and it is the time needed to develop the spectrum needed for the calculation of NCR.

3.3.5 Detection system

The XRF inspection system consisted of an X-ray tube with Rhodium anode (Varian Medical Systems, model VF-50J RH/S-1.0/S, Salt Lake City, UT) operated at 44 kV and 1 mA, mounted at 40 cm distance from the belt, emitting an X-ray beam downward when energized with 70^{o} cone angle. The beam was modified by an aluminum filter in order to reduce background from the tube's continuum radiation. The filter was mounted on the top of a lead-coated fork covered blade collimator (3 cm apart), as Pb is a good material for dampening X-rays and used here to reduce the beam angle and to focus the X-rays on the illuminated area so that small wood pieces can be detected more clearly against the background from the conveyor belt. The detector (Amptek, model XR-100CR, Bedford, MA) used in this study overcame some of the proximity problems of earlier systems (Blassino et al., 2002; Solo-Gabriele et al., 2004) and was mounted at a 45^{o} angle from the horizontal at a distance of approximately 30 cm above the wood pieces and thus allowing for inspection of the wood from the top down, instead of from the bottom up (Solo-Gabriele et al., 2004). Both the detector and X-ray tube were installed inside the closed steel chamber fitted with a thin film window to allow for the detection of X-rays. A piece of Pb covered the detector from the side facing the X-ray tube to prevent direct incidence of X-rays from the tube. The detector was connected to a digital pulse processing (DPP) unit (Amptek, DP4, Bedford, MA) which was controlled by customized software (AAI-UofM, Austin AI, Austin, TX) (Figure 3.2).

3.3.6 Diversion system

After inspection of wood samples and passage through the rest of the inspection chamber via the conveyor system, treated wood was then discharged from the end of the infeed conveyor by a slide-way diverter (a steel sheet of 81.3x81.3x0.6 cm operated pneumatically by a driving piston connected to an air compressor) which in the open position (45^{o} to the horizontal level) bypassed the inclined conveyor (Figure 3.2).

Once the targeted metal, arsenic or copper, was detected ($NCR > OT_{TM}$), the diverter was programmed to open after a set delay time and remain open for a set dwell time. The delay time is equal to the travel time of the wood piece on the moving belt from the inspection point to the discharge end of the conveyor and it is dependent on the conveyor belt-speed. For this research, the delay time was set as 1700 ms and this time was shown to properly divert small wood pieces (5 cm). The dwell time starts after the delay time and is equal to the sum of measurement times during which the target metal is consecutively detected plus a small value called pulse adjust (500 ms used in this study) to allow time for wood to transition from the belt to the diverter.

3.4 SYSTEM CALIBRATION

3.4.1 Infeed wood characteristics

Two sets of wood pieces one of 36 pieces and another of 500 pieces were used to calibrate the XRF detection system. The 36 piece set was used to calibrate the threshold and consisted of 12 of pieces As-based weathered treated wood (As concentration ranges from 100 to 10,000 ppm), 12 pieces of Cu-based weathered treated wood (Cu at 500 to 10,000 ppm), and 12 pieces of untreated wood. Furthermore, the 12 As-treated pieces within the set of 36 were also used for evaluating X-ray spectrums. The set of 500 pieces of preserved wood were used as infeed for confirming the targeted metals detection at the achieved OT and for calibration of the measurement time and evaluating the sorting efficiencies. The set of 500 pieces were collected from C&D waste wood that was permitted to enter the host facility for use by this study and thus these pieces were representative of field generated wood waste. The set consisted of 417 pieces of As-based treated wood, 66 pieces of Cu-based (non arsenical) treated wood, and 17 pieces denoted O as other than As- and Cu-based, which were extremely weathered wood samples that contained elevated levels of chromium and low or no levels of arsenic (Table 3.3). These other-treated wood samples could have been an arsenic or copper free chromated preserved wood such as chromated zinc chloride (CZC) (AWPA, 2008) or simply extremely weathered pieces of CCA that lost their As or Cu.

Each treated wood piece used in this research was given a unique identification code. This code was linked to the characteristics of that piece of wood. Thus, the total metals in the wood could be traced through the sorting system. The characteristics tracked included the wood piece dimensions, type of treatment (As, Cu or O) and the concentration of arsenic, chromium and copper in ppm measured by using a handheld XRF unit (Innov-X type alpha, Woburn, MA, USA). The measured concentration of metals in ppm (Figure 3.3) are normally a reflection of the concentrations on the wood surface that will be detected by the online XRF and are usually higher than the concentration throughout the wood piece due to the tendency of metals to migrate to the surface. So, As concentration was corrected using Block's formula (Block *et al.*, 2007). Chromium and copper measured by the handheld XRF (in ppm) were modified to the actual concentration that can be determined in the laboratory using the following formulas (See Appendix C for more details):

$$Cu_{actual} = 0.0002(Cu_{XRF})^2 \ldots\ldots\ldots (3.2)$$

$$Cr_{actual} = 0.25(Cr_{XRF}) \ \ldots\ldots\ldots\ldots\ldots (3.3)$$

The metallic content in grams of As, Cu and Cr was calculated for each piece of wood as the product of the volume and its corrected metals' concentration assuming all pieces are Southern Yellow Pine of density 511 kg/m^3.

3.4.2 Operational threshold (OT)

Thresholds of As and Cu were evaluated by inspecting the As-based and Cu-based wood pieces starting from 0.6 and 1.2 for As and Cu, respectively. Preserved wood was fed to the system and the detection of metals was monitored, followed by stepwise (0.1) reductions of the threshold values. Not all of pieces were detected at the beginning, and as thresholds were lowered, the number of detected pieces increased. Reduction of thresholds continued up to a certain value where the background concentrations of the targeted metals, or interfering metals (Pb and Zn) were detected with and without the presence of treated wood in the field view of the detector. The OT was set at a value of 0.1 higher than that certain value. The OT was confirmed by feeding untreated wood and to check for no detection of any of the targeted elements.

The OT_{As} used in this research was 0.02 and 0.05 for OT_{Cu}. Lead used in internal shielding caused a slight interference with As, giving a reading equivalent to about 100 ppm of As. The conveyor belt contained about 3500 ppm of Zn which interfered with Cu, causing a signal equivalent to about 250 ppm of Cu. Moreover, Cu was found at higher levels in the belt seam and its rivets (up to 2500 ppm). At the 0.05 limit for Cu, the sorting system was detecting Cu in the revolving belt-seam at a rate of one in three revolutions.

At the OTs, the number of energy counts at each measurement time step of the background system (with no wood) was in the range of 7-32 for As and 11-203 for Cu (Table 3.2), while with untreated wood, these values where a bit less: 4-20 and 6-70 for As and Cu, respectively, as the untreated wood shielded some of the As and Cu interferences from the belt. The shielding effect was also observed for zinc as the counts for zinc with the exposed belt was observed at the 497 to 1029 range (for K_α) whereas counts when untreated wood was added to the belt decreased to the 199 to 574 range. For treated wood the range of counts were 73-237 for Cu and 132-1088 for As, the lower counts of these ranges corresponded to extremely weathered pieces. The average spectrum for the scanned treated wood pieces (Table 3.2) showing the As peak well above all other interferences. Lead (which interferes with As) was below detection limits in the conveyor belt system and did not appear in the scanned spectral lines of the system. Cu, on the other hand, was subject to significant interferences from Zn as can be observed from the overlap between the Zn and Cu peaks for spectrum measured with treated wood on the belt. The Zn peaks were also readily observable for spectrums with untreated wood on the belt and apparently the presence of the wood itself shielded part of the zinc interference from the belt allowing for detection of Cu.

To further evaluate the threshold limits, the 500 pieces of preserved wood were fed to the detection chamber and also shown levels of counted energies for As and Cu above the background levels. For the purpose of wood diversion, it is required that the NCR will be above the set OT (equation 1) in order to be diverted as treated wood. It was found at the OTs of 0.02 and 0.05 for As and Cu, respectively, the treated wood pieces of surface concentration (measured by handheld XRF) less than 1000 ppm and 4000 ppm of As and Cu, respectively, will generate spectrums of NCR < OT, even though the range of energy counts were above the background levels.

3.4.3 Measurement time

Once the thresholds were set, measurement times of 250, 500, and 1000 ms were evaluated using the 500 pieces of preserved wood. Starting from 250 ms, the non-diverted pieces of preserved wood (that ended up in the presumed untreated pile ahead of the inclined conveyor), were fed to the system using the next highest measurement time and so on up to the 1000 ms.

Overall sorting efficiencies (Figure 3.4) were calculated as a percentage of the total number and wood weight of correctly diverted pieces (found in the presumed treated pile ahead of the sorting system) to the value of that wood type in the original feed (Table 3.2). For all treated wood pieces used in this experiment, sorting efficiencies at the 250 ms measurement time were 82±2.0% and 86.4±1.3% based on number and weight, respectively. The sorting efficiencies were slightly enhanced with increasing measurement time, but this increase in efficiency was not significant. As the measurement time doubled to 500 ms, the sorting efficiencies averaged as 84.8% and 88.3% based on number and weight, respectively. Measurement times longer than 500 ms did not result in a significant increase in sorting efficiencies, since this time will be longer than the actual time the wood piece is under the XRF beam for pieces shorter than 0.25 m.

Sorting efficiency for a subset of the infeed, the As- and Cu-preserved pieces, was higher when based on weight as opposed to number (Figures 3.5), which means that most of the incorrectly diverted pieces were lighter deteriorated pieces or smaller in size. Average sorting efficiencies at the range of applied measurement times were 95.0±1.5% and 96.7±1.3% for As-treated wood based on number and wood weight, respectively. Sorting efficiencies for Cu-based and O- pieces were low at 25.0±3.2% and 34.9±1.3% for Cu- and 26.5±4.2% and 25.9±3.5% for O- at 250 ms based on number and wood weight, respectively and increased to 33.3% and 44.1% for Cu- and 29.4% and 28.4% for O-based on number and weight, respectively for the 1000 ms measurement time. Thus for the given operational parameters increases in measurement times resulted in relatively small increases in sorting efficiencies when sorting is defined based upon bulk numbers or weight of the wood.

Metals' mass recoveries as As (%), Cu (%) and Cr (%) were calculated as the percentage ratio of the sum of each metal's content of all wood pieces that ended up in the presumed treated pile to the total metal mass in the infeed. This was possible by tracking each coded treated wood. Even though Cr was not used as a target metal for XRF inspection, Cr-content could be tracked due to the applied coding system. When evaluating metals removals (instead of bulk wood removed), the efficiencies are much higher. Between 98-99% of the As mass in wood was recovered at the applied range of measurement times, and this corresponds to 1260 g at 500 ms (Figure 3.6) relative to 19 g of As ended in the presumed untreated pile. Although about one third of Cu-based wood pieces (21 pc at 500 ms, figure 3.6) were diverted correctly, these pieces contained 78-80% of the Cu recovered from Cu-based wood (992 g relative 1089 g at 500 ms, figure 3.6). In total, the total Cu mass recovered was in the range of 90-92%, where 99% of the Cu in the As-based wood was recovered and believed to be due to As-detection. Also, between 96-97% of the Cr mass was recovered, overall 730 g of 753 g at 500 ms (Figure 3.6). Ninety-eight to 99% of Cr was recovered within the As-treated wood portion, and 42-53% within the Cu-treated wood portion. For the other treated pieces (O), less than 30% of these were diverted correctly but these correctly diverted pieces also contained a majority of the As found in the "O' samples (77%), again enhancing the sorting efficiency when evaluating sorting based upon metals recovery.

3.5 TROUBLESHOOTING

During the operation of the detection system, a problem occurred as the software would occasionally start to detect As alone or both As and Cu, even with no wood in the infeed and thus made the diverter to open and close accordingly. Repeated detection of both As and Cu was believed to be associated with overheating due to high ambient temperature during the summer in South Florida, heat production by the X-ray, coupled with poor cooling of the XRF-chamber. This problem was resolved by increasing the air flow rate into the chamber and aiming the air injection into the body of the detector. Detection of As only is believed to be due to the corrosion of the Pb sheets installed inside the XRF-chamber. Lead dust produced in the form of white powder fell in the field view of the detector and produced a thin film. As mentioned earlier, Pb has spectral lines that overlap with As, and thus the lead dust caused the continuous detection of As.

Lead corrosion was believed to occur either due to the low quality of the purge air, and/or the formation of ozone due to the high voltage field in the XRF-chamber. This issue was resolved by cleaning the XRF chamber with a vacuum and through wiping the XRF components with alcohol wipes. The production of lead dust was minimized by replacing the lead parts with polyvinyl-coated lead sheets and by painting small lead pieces with polyurethane spray paint.

Another problem was met, after heavy operations of the conveyance system; dust from the treated waste wood would remain on the belt and increase the concentration of the targeted metals in the background level. Brushing the belt with a sweeping brush was found to clean the belt to a certain acceptable level. To avoid this problem, an online cleaning brush can be equipped as part of the infeed conveyor, such a brush should be fitted to the discharge end and should be installed inside a closed replaceable bag to avoid contaminating the surroundings. For detection purposes, and as a precaution, measurement times of 250 ms will help reducing the frequent collection of the dirty belt spectrums and thus reduce the interference.

3.6. COST

The cost of implementing and operating the online XRF sorting system consists of capital cost, and operation and maintenance cost. Based on the U.S. market for 2009/2010, the capital cost of the XRF detection system including design, transportation within the U.S. and installation was estimated at US$ 85,000, while for the conveyor system was estimated at US$ 75,000. The design life of the detection, diversion, and conveyance systems was estimated at 10 years, with major overhaul of the X-ray tube and the detector after 5-years of operation at a future cost of US$10,000.

Operation and maintenance costs include power requirements over 10 hours daily for 6 days a week and at a price of 0.1$/KWH. Spare parts, estimated at US$ 3,000/year and labor cost for 2 pickers/feeders plus one part time equipment technician was estimated at US$ 50,000/year.

A present day cost of US$ 550,000 is computed by converting all the costs (both capital, yearly, and maintenance) using an 8% interest rate (continuous compounding) (Blank and Tarquin 1983). When the present day costs are annualized over a 10 year period, the yearly cost of the system corresponds to US$ 82,000.

Based on the size of the facility, assuming that 10-35 tons of wood are processed daily in 2010, the cost (including capital plus O&M) will range from US$ 10-35/ton and considering the capital cost only, will range from US$ 4-14/ton as for capital cost only (lowest costs are for the highest amount of wood processed). The estimated costs for the system described in the present study is within the same range as the estimated costs for semi-automated online systems described by Solo-Gabriele et al. (2001) who estimated on-line LIBS systems at US$ 7-26/ton for facilities processing 10-35 tons of wood per day, where the lowest cost at the highest production rate was shown to keep a reasonable benefit margin for the recycling facility.

3.7 SUMMARY AND CONCLUSION

Results of this research showed that XRF technology can be equipped for online computerized real time measurements for the detection of inorganically preserved wood such as CCA and ACQ. The high energy X-ray tubes available commercially and the advancement in X-ray detectors' technology allowed for the design of a detection compartment that can fit on a top of motorized conveyor and leaves space for wood of different shapes and sizes to be detected and passed underneath for the diversion as treated or untreated. Diversion was made possible by a slide-way diverter and operation parameters of the detection-conveyance system (measurement time, delay time, pulse adjust and thresholds) were all set. Detection limits of As and Cu can be enhanced in two ways: first, choosing the materials of the background system (conveyors' belt and seam) with almost no containment of the targeted metals or metals that has a spectral interference with them. The rubber and seam of the conveyor belt should be free of As, Cu, and Zn. In order to reduce background noise associated with the anodic source (A_R) we also recommend further optimization of the material and thickness of the X-ray tube filter.

The minimum optimum measurement time achieved at the OT was 500 ms, with sorting efficiencies at 85 and 88% based on number and weight of wood pieces. These bulk wood removals were associated with higher metals recovery due to the fact that the bulk of the wood pieces that were diverted correctly were characterized by higher metals contents (As>1000 and Cu>4000 ppm). Efficiencies as high as 98, 91, and 97% of As, Cu and Cr based upon metal mass recovered were obtained with the system configuration used in this study. For practical purposes, and to decrease the interference from the treated wood dust that may fall on the belt, a reduced measurement time as 250 ms will decrease this background interference.

In summary, the highest the concentration of targeted metals, the largest A_{TM} and the smallest A_R, yield the lowest interference from the background system; that leads to higher detection efficiencies. Also, at the low concentration end, the lower the OT_{TM} (required for minimizing the background interferences), the lower the concentration of targeted metals that can be detected, and so resulting in higher mass recoveries and sorting efficiencies.

To improve continued operation of the system, we recommend that the X-ray tube and the detector be separated in two compartments to avoid X-ray dampening by lead sheets. A thick sheet of steel can be used as the barrier between the devices. Forced purging of the compartments should be done by a filtered clean air to avoid accelerated corrosion of the metals inside the compartments especially the beryllium windows of the X-ray tube and detector.

Among all of the detection technologies described in section 1 (Table 3.1), the online detection system presented in this research appears to be the closest with respect to possible implementation for large scale facilities, since detection of the target metals was very fast (fraction of a second) and can be fully automated to detect As- and Cu- treated wood. Moreover, as shown in previous studies, XRF technologies are also suitable for wet, painted, or dirty wood, with efficiencies as high as other online systems and with costs similar to a LIBS systems.

Table 3.1 Comparison of different detection methods for waste wood containing preserved wood as reported in the literature and from this study.

Detection Technique	Description	Reference	Targeted metals	Diversion technique	Spatial distance (cm)	Measurement time	Efficiency[a]	Cost (US$)	
								Capital[c]	Per ton
Human	Visual	Blassino et al. 2002	Cu	Manual	Varied	Varied		N.I.[b]	N.I.[b]
		Jacobi et al. 2007b	Cu	Manual	Varied	Varied	60-100%	N.I.[b]	21-96
Stains	PAN indicator	Blassino et al. 2002	Cu	Manual	Surface application	12 s	40-97%	N.I.[b]	N.I.[b]
		Jacobi et al. 2007b	Cu	Manual	Surface application	12 s	~50-96%	N.I.[b]	N.I.[b]
		Sawyer and Irle 2005	Cu	Manual	Surface application	5 s	N.I.[b]	N.I.[b]	N.I.[b]
	Chromazurol S	Blassino et al. 2002	Cu	Manual	Surface application	63 s	N.I.[b]	N.I.[b]	N.I.[b]
		Sawyer and Irle 2005	Cu	Manual	Surface application	45 s	N.I.[b]	N.I.[b]	N.I.[b]
	Stannous chloride	Omae et al. 2007	As	Manual	Surface application	> 5 min	N.I.[b]	30	N.I.[b]
Test Kits	EM Science, 17926	Solo-Gabriele et al. 2006	As	Manual	Mixing with reagents	45 min	~100%	195	N.I.[b]
		Shalat et al. 2006	As	Manual	Mixing with reagents	30 min	~100%	195	N.I.[b]
	Stannous chloride	Omae et al. 2007	As	Manual	Mixing with reagents	> 5 min	~100%	15-35	N.I.[b]
		Arsenichometest.com	As	Manual	Mixing with reagents	55 min	~100%	30	N.I.[b]
Handheld XRF	ASOMA, Model 400	Blassino et al. 2002	As, Cu, Cr	Manual	2.5	< 2 s	~100%	120K	N.I.[b]
		Solo-Gabriele et al. 2004	As, Cu, Cr	Manual	1.9, 2.5	3 s	~100%	120K	N.I.[b]
	OURSTEX 100FA	Yasuda et al. 2006	As, Cu, Cr	Manual	Surface application	N.I.*	~100%	N.I.[b]	N.I.[b]
	Innovx,I-3000C	Jacobi et al. 2007b	As, Cu, Cr	Manual	Surface application	6 s	~100%	20-35K	113
	Innovx, α-2000S	Block et al. 2007	As, Cu, Cr	Manual	Surface application	6 s	~100%	20-35K	N.I.[b]
Online LIBS	Q-switched Nd: YAG	Moskal and Hahn 2002	Cr	Semi automatic	20	3-5 s	92-100%	105K	7-26[d]
	Q-switched Nd: YAG	Solo-Gabriele et al. 2004	Cr	Semi automatic	20	3-5 s	98-100%	105K	7-26[d]
Online XRF	Section 3of this paper	This research	As, Cu	Automatic	30	0.25,0.5 s	85-100%	160K	10-35

[a] Efficiences are for detection except for the results of this research where the efficiency is for both detection and seperation.

[b] Not included.

[c] Minimum cost for at least one test, K corresponds to 1000.

[d] Cost was reported in Solo-Gabriele et al. (2001).

Table 3.2 Range of counts and sample spectrums of targeted (As and Cu), interfering (Zn), and anodic (Compton and Rayleigh) source metals for the scanned belt, 12 pcs of untreated wood and 12 pcs of As-treated wood. Minimum values were averaged among all collected spectrums to avoid the minimum of zero at the completely scattered x-rays situations.

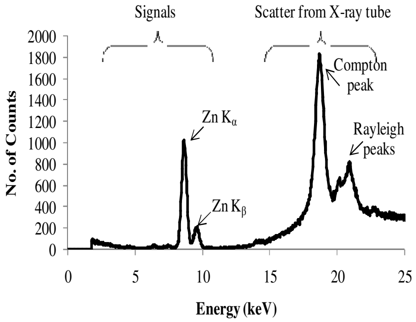
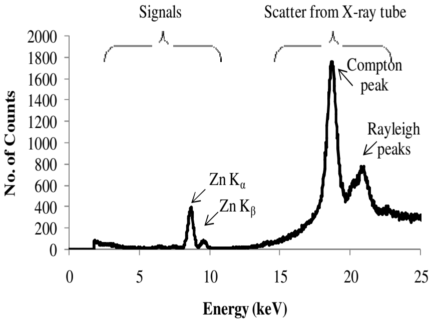
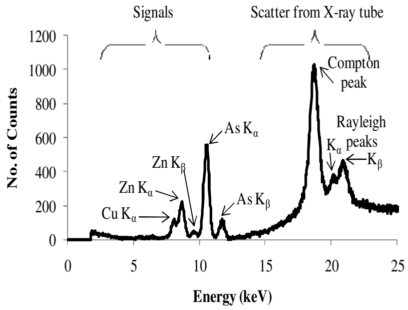
Targeted elements	Energy range (keV)	Range of Energy-Counts		
		Background system (conveyor belt)	Untreated wood	Treated wood
Cu Kα	7.85-8.24	11-203	6-70	73-237
Zn Kα	8.43-8.86	497-1029	199-574	118-424
As Kα	10.16-10.79	7-32	4-20	132-1088
Compton (reference)	18.04-19.53	500-2956	512-2586	291-2002
Rayleigh Kα	19.85-20.65	518-1122	503-1042	300-805
Rayleigh Kβ	20.67-21.49	475-1311	464-1134	269-896
Average Spectrum				

Table 3.3 Treated wood chemical-characteristics for the 500 piece infeed used for confirming target metals detection, calibration of the measurement time, and evaluating sorting efficiencies.

	No. of Pieces	**Weight of pieces (kg)**	**As content (g)**	**Cu content (g)**	**Cr content (g)**
As- treated	417	424	1252	682	736
Cu- treated	66	67	2.9	403	11.6
Others (O)	17	9.4	0.74	3.74	4.72
Total	500	501	1,256	1,089	752

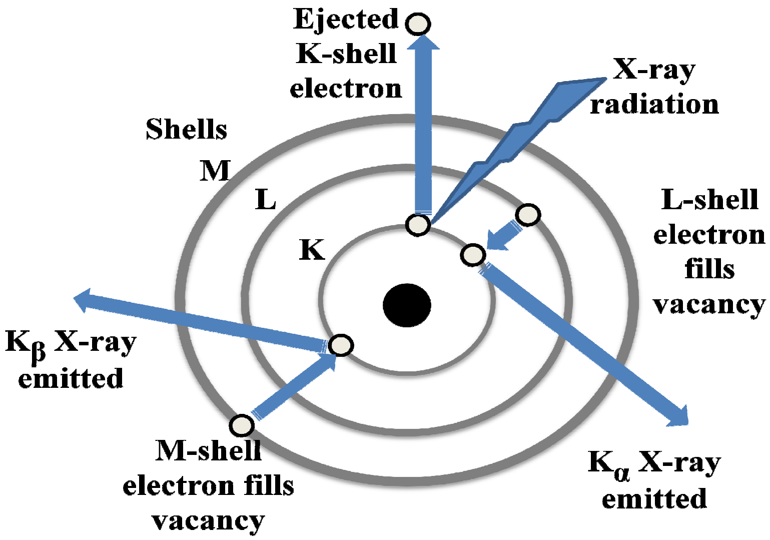


Figure 3.1 X-ray process (U.S. EPA, 2006).

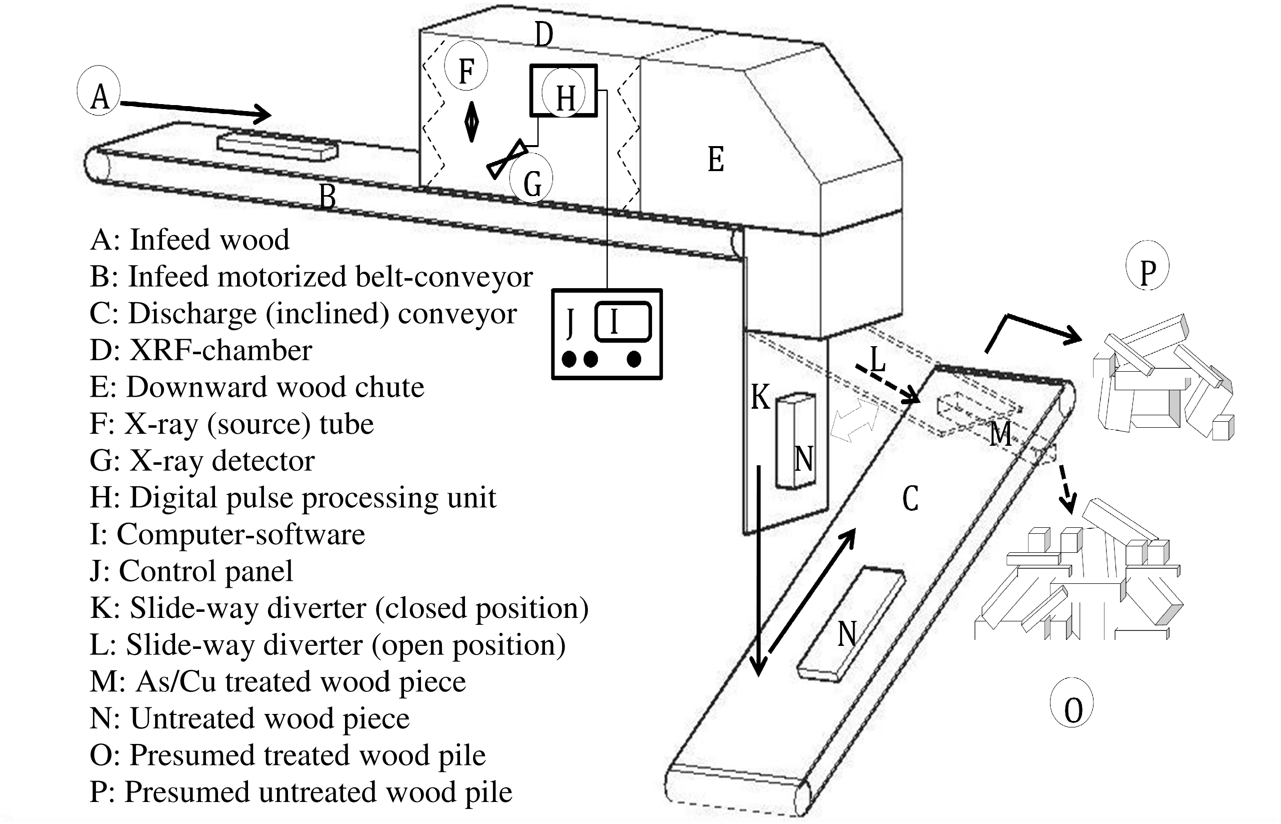


Figure 3.2 Schematic diagram of the sorting system

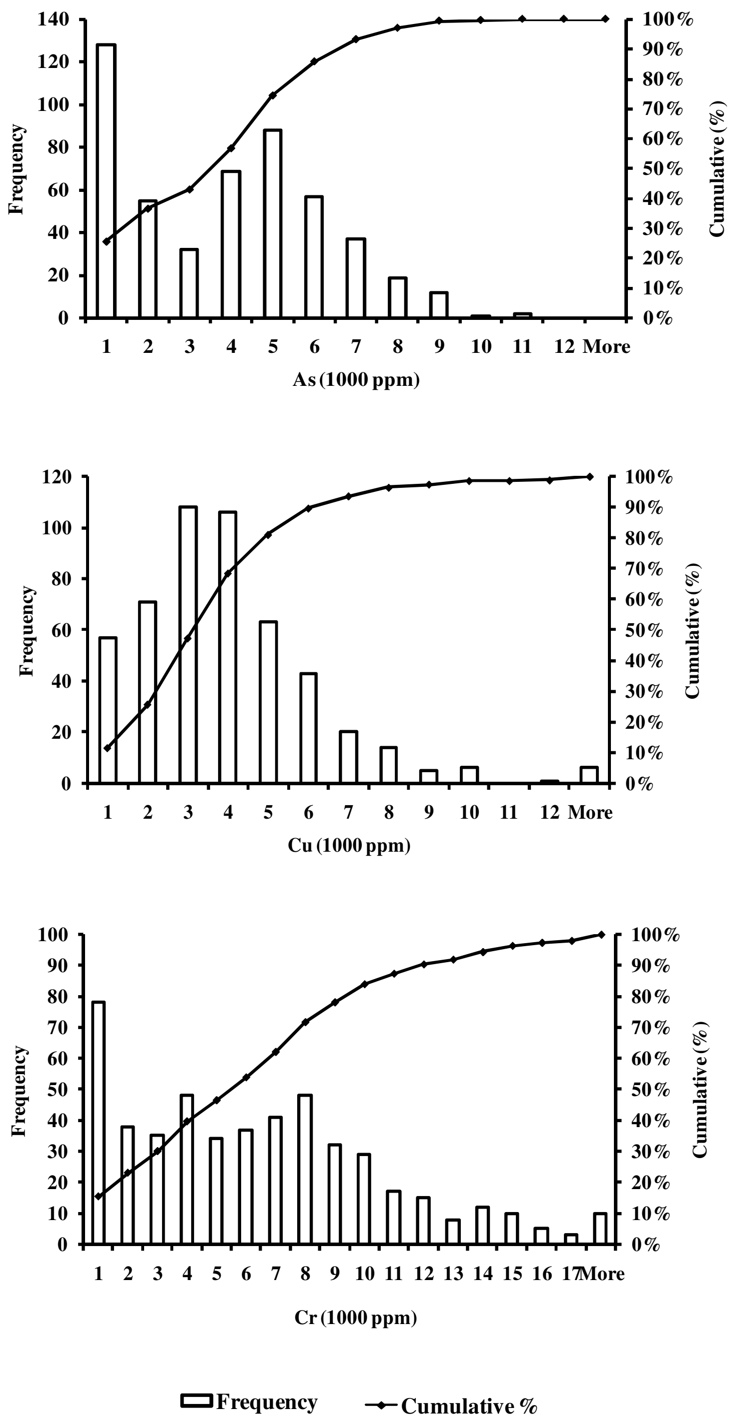


Figure 3.3 As, Cu and Cr distribution in the 500 preserved wood pieces. The x-axis label corresponds to the upper limit of the bin. Values of concentrations correspond to the raw XRF readings.

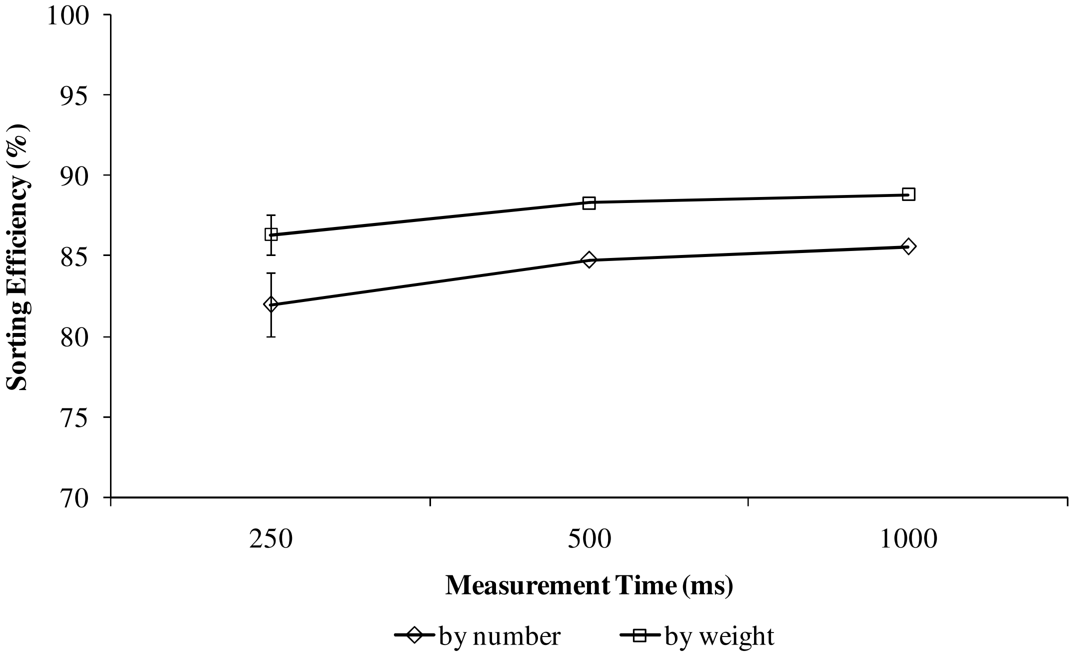


Figure 3.4 Sorting efficiency of 500 wood piece sorts, based on total number of pieces and weight, at the different applied measurement times.

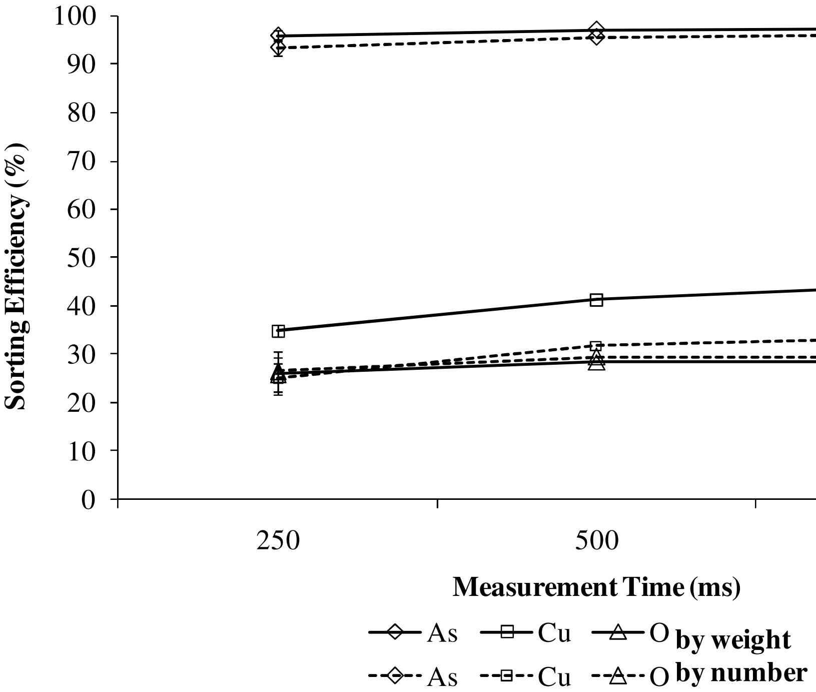


Figure 3.5 Sorting efficiencies of sub-groups of the 500 pieces set. The subgroups included the As-based treated wood fraction (n=417 pcs), the Cu-based treated wood fraction (n=55 pcs) and the other-treated wood fraction (n= 17 pcs). Results are reported by number of pieces and by weight based on wood category at the different applied measurement times.

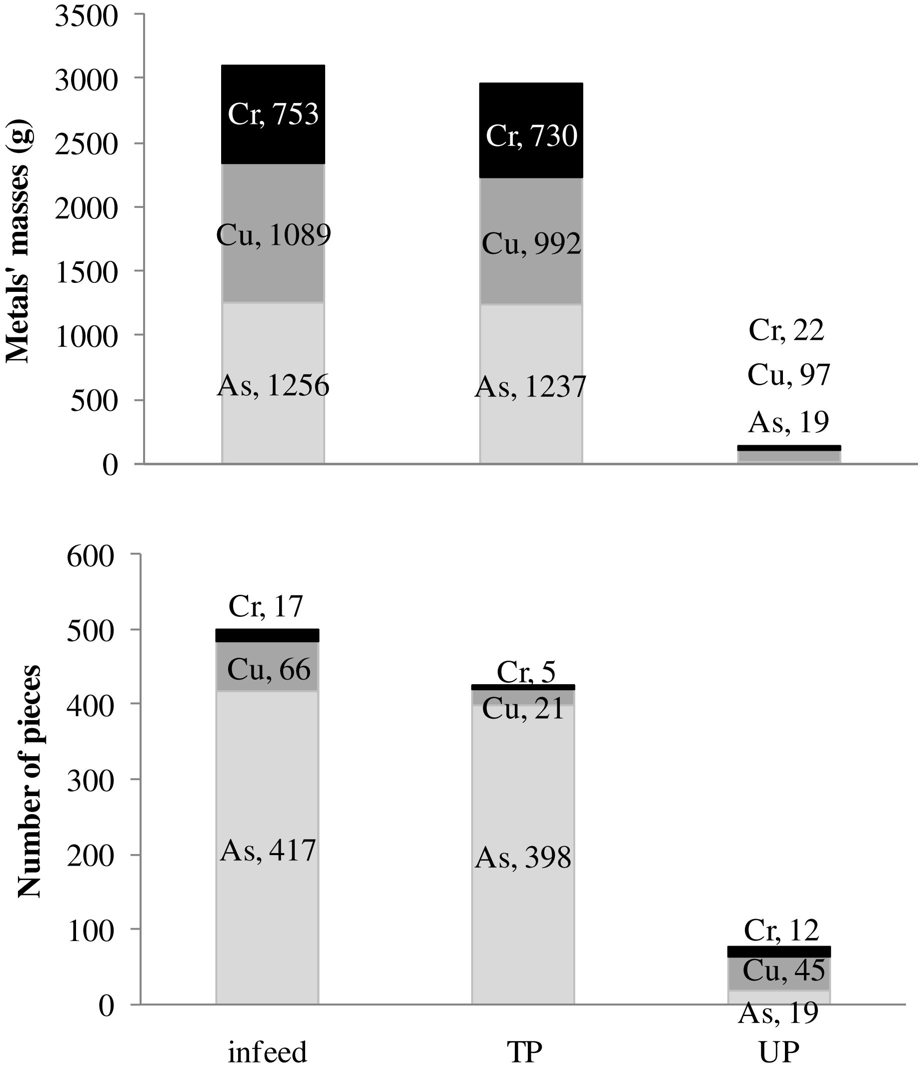


Figure 3.6 Infeed wood distribution between the presumed treated pile (TP) and presumed untreated pile (UP) after online detection and diversion using a measurement time of 500 ms.

CHAPTER 4

SORTING OF RECOVERED WOOD WASTE BY AUTOMATED XRF TECHNOLOGY

4.1 CHAPTER INTRODUCTION

Waste wood commonly contains two basic types of wood: vegetative debris and construction/demolition (C&D) (Jacobi et al., 2007a). Vegetative debris, such as tree branches, is considered ready to be recycled since it is mostly uncontaminated with chemicals. On the other hand, C&D wood waste includes sawn wood products (lumber, timber, plywood, posts, etc...) that can be either untreated or treated with chemical preservatives. Historically, the most common preservative utilized has been an arsenic-based preservative known as chromated copper arsenate (CCA). Arsenic, chromium and copper from the treated wood can be released to the environment or routed to humans by many different mechanisms (Stilwell and Gorny, 1997; Stilwell and Graetz, 2001; Khan et al., 2006, Ochoa-Acuna and Roberts, 2006; Shibata et al., 2007; Hu et al., in review; Chapter 2 of this dissertation). Each of these three elements has negative impacts on the environment and human health when their concentration is elevated (Adler-Ivanbrook and Breslin, 1998; Stook et al., 2004 and 2005; Shalat et al., 2006, Dubey et al., 2007). Due to increased awareness of the negative potential impacts, this chemical as of 2004 was voluntarily phased-out by the wood treatment industry from most residential applications in the U.S. Due to this phase out of arsenic-based preservatives, Cu-based preservatives such as alkaline copper quat (ACQ) and micronized copper quat (MCQ) are expected to dominate the residential treated wood market (Dubey et al. 2005; Freeman and McIntyre, 2008). Even with the phase out, the amount of disposed CCA is significant and will increase in the waste stream, to peak to 6-10 million m^3 in the U.S. in 2030 (Jambeck et al., 2007), and peak at 0.8 million m^3 in Canada in 2010 (Cooper, 1994). Up to the year 2000, treated wood waste was found to represent a significant fraction of wood waste (5-30%) received at recycling facilities (Tolaymat et al., 2000; Blassino et al., 2000). This percentage can be larger in some cases where facilities receive complete structures of treated wood as part of their infeed. In order to recycle C&D as fuel (and ultimately dispose the ash in a lined landfill), levels should be less than 5% CCA (Solo-Gabriele et al., 2002), and for recycle as mulch, levels should be less than 0.05% CCA-treated wood. However, it can contain up to 2% ACQ-treated (Jacobi et al., 2007b). Thus, efforts are needed to identify and separate treated wood from wood waste, so the untreated fraction can be recycled without the added burden from wood preservative chemicals (Solo-Gabriele et al., 2002; Townsend et al., 2003; Shibata et al. 2006; Jacobi et al. 2007b).

XRF technology is one technology that is suitable for more accurate assessment of preserved wood that is difficult to identify. XRF technology is a multi-elemental non-destructive technique of metals' inspection (Hou et al., 2004), requiring no prior sample preparation (Solo-Gabriele et al., 2004). The technology is very fast (Wheeler, 1993; Kalnicky and Singhvi, 2001), requiring only milliseconds, which makes it suitable for online applications. XRF is based upon the use of high energy X-rays which knock electrons out of the innermost orbital of atoms in the treated wood changing the atoms into unstable ions. A more energetic electron from outer orbital will move into the newly vacant space in the inner orbital in order to reach the lowest stable energy state and so releasing the extra energy possessed before. The emitted energy is equal to the difference in energies between the innermost orbital and the outer one; thus it is a characteristic of the element fluorescing. Emitted energy as photons can be detected by an X-ray detector and so the count of emitted energies is proportional to the concentration of the metal in wood pieces and is simulated by a spectrum representing the number of counts versus energy (KeV). The time to count the emitted energies is called the measurement time. The ratio of area under the measured counts-curve of the targeted metal to a reference spectral background area that is related to the radiation source of the X-ray is called the threshold.

Sorting is defined in this document as a three step process: handling of wood, identification, and separation. Specially, for automated sorting by an online XRF-system, the analogous terms are conveyance, detection and diversion. Chapter 2 focused on the second step: detection. The earlier work established the optimum thresholds and measurement times for online for real-time detection of preserved wood. The next steps that are to be evaluated include conveyance and diversion which routes the wood to the XRF detector and routes the detected pieces to the appropriate location.

The over arching goal of the current study was to evaluate conveyor operational conditions on sorting as a whole, (conveyance, detection and diversion) for a full scale online XRF system. A factorial randomized block design was used to evaluate the effects of belt speed and wood feeding rates on the system. This is the first study to evaluate the conveyance and diversion component of sorting wood, which represents a particular challenge due to the wide range of sizes of this particular waste. Results of this study are discussed in the context of recycling wood as mulch.

4.2 METHODS

4.2.1 Conveyance, detection and diversion systems

The conveyance, detection and diversion system used in this study was described in chapter 2. In summary, the conveyance equipment consisted of an infeed motorized belt-conveyor and an inclined conveyor installed perpendicular to the discharge end of the infeed conveyor. The infeed conveyor was designed to convey wood to the XRF detection unit, and the inclined conveyor to move the untreated wood to a separate pile for further processing. The XRF detection system was installed on the top of the infeed conveyor. After inspection, treated wood was then discharged from the end of the infeed conveyor by a slide-way diverter bypassing the inclined conveyor (Figure 4.1) via a stationary slide-way connector. Steel shields were installed on the inclined conveyor to minimize the effects of bouncing and rolling of wood pieces once diverted. The time required to move the slide-way diverter was set equal to the delay time, the time for the wood piece to move from the inspection point to the discharge end of the conveyor. The delay time is a function of the belt speed and the distance from the XRF inspection point on the belt to the discharge end of the infeed conveyor.

Identification of preserved wood by XRF focused on the detection of As and/or Cu presence in wood. The detection of As and Cu, indicated the presence of arsenical preservatives in the wood, most likely CCA. The presence of Cu only indicated the presence of copper based preservatives such as alkaline copper quat (ACQ), among other copper-based preservatives (AWPA, 2008).

Based on chapter 2, the operational thresholds for As and Cu detection were chosen as 0.02 and 0.05, respectively, and the measurement time of the XRF system was chosen as 250 ms.

4.2.2 Infeed wood characteristics

Two sets of wood were used as infeed and consisted of a 1000 pieces of wood and differ from each other by the proportion of untreated wood versus treated wood, as defined by the number of pieces in each category. One set was characterized by 50% untreated wood and 50% treated wood (50:50) and the other set was characterized by 95% untreated wood and 5% treated wood (95:05). The group of 500 pieces of treated wood used in the 50:50 set was the same as used in chapter 2. Thus, this infeed differed from the infeed used in chapter 2 by the addition of 500 untreated wood pieces which were randomly mixed with the treated pieces. The 50:50 set was chosen as a balance point to evaluate treated versus untreated wood sorting when the proportions were equal, thus removing the effect of treated wood fraction in discriminating between treated wood versus untreated wood sorting efficiencies. The 95:05 set was chosen because this was the proportion observed at wood recycling facilities which practice visual sorting (Jacobi et al., 2007b). Treated wood included As-based treated wood, Cu-based (non arsenical) treated wood, and other-treated wood which were extremely weathered wood samples that contained elevated levels of chromium and low or undetectable levels of arsenic. The three groups of treated wood were denoted as As-, Cu- and O-treated (Table 4.1).

The configuration of the XRF chamber on the top of the infeed conveyor permitted for sorting wood of lengths less than or equal 150 cm. Given this constraint, 500 pieces of untreated wood were randomly collected at recycling facility located in South Florida, USA, thus reflecting the distribution which would be observed at full scale facility. In order to minimize the effects from the different sizes of wood pieces, each portion of the wood infeed used had (treated and untreated) the same length distribution, since the length was an important factor to affect proper sorting. The length distribution of the 500 treated pieces used in the treated portion of the 50:50 set (Figure 4.2), the other 500 untreated pieces of the 50:50, the 950 untreated pieces and the 50 treated pieces of the 95:05 set, all had a bell-like shape resembling the normal distribution shifted towards positive range.

Each treated wood piece used in this research was given a unique identification code. This code was linked to the characteristics of that piece of wood. The characteristics tracked included the wood piece dimensions, type of treatment (As-, Cu- or O-) and the concentration of As, Cr and Cu in ppm. The metallic content in grams of As, Cu and Cr was calculated for each piece of wood from the volume of each piece and its metals' concentration assuming all pieces were Southern Yellow Pine of density 511 kg/m^3. Concentrations of As, Cr and Cu measured by handheld XRF unit were corrected according to the method described in chapter 2 and appendix C. Thus, the total metals in the wood (Table 4.1) could be traced through the sorting system.

4.2.3 Experimental design

Experiments were completed using a randomized factorial block design without replication (Hicks and Turner, 1999) in an effort to evaluate the wood sorting efficiency, metal recovery, and the composition of each sorted pile (Figure 4.3). A combination of two different factors was chosen randomly at each experimental run. These factors included wood feeding rate, FR of 20, 40 and 60 pc/min (simulating one, two and three persons on a picking line, assuming that it would take an average of 3 seconds to pick a piece of wood and transfer it to the system) and belt speed of the infeed conveyor, BS of 0.25, 0.375 and 0.5 m/s (to simulate the speeds of readily available commercial conveyors). Delay times (1.7, 1.95 and 2.2 s) were changed accordingly with the belt speed.

Nine experiments were conducted by sorting 1000 pieces of wood of the 50:50 infeed set and four experiments of the 95:05 infeed set. After each experimental run, wood-pieces in the two piles (presumed treated and presumed untreated) were manually sorted to confirm actual treatment, counted for number of pieces, and weighed using an industrial platform scale with a resolution of plus or minus 0.5 kg. Within each "presumed" pile from the XRF system, wood was identified as either truly treated or truly untreated. Treated wood in both sorted piles were further separated into various categories including As-, Cu-, and O- treated wood. Manual sorting of the presumed treated and presumed untreated wood was based upon the identification code established for each wood piece thus allowing the researchers to track each individual piece of wood within the set of 1000.

4.2.4 Data analysis

4.2.4.1 Sorting efficiencies

Wood sorting efficiencies were calculated for treated wood (TW) and untreated wood (UW) pieces at each experimental run based on the number and weight (SEN and SEW)

(Figure 4.3). Sorting efficiency was calculated as ratio between the number and weight of correctly diverted pieces in each pile to the total in the infeed pile on a percent basis. This principle was extended for the As-, Cu- and O-treated wood.

4.2.4.2 Mass recovery

Metals' mass recovery (R) is an indication of the rate of mass diverted from the wood recycling stream, diverted away from the presumed untreated pile (Figure 4.3). These percentages were calculated for As, Cu, and Cr by tracking each coded treated wood piece and summing up the metals content in the presumed treated pile and dividing by the total mass in the corresponding infeed (Table 4.1). R values (%) were computed for As, Cu and Cr, even though Cr was not used as a target metal for XRF inspection. The Cr-content was tracked because the Cr mass for each wood piece was included in the applied coding system.

4.2.4.3 Sorted piles' composition

Each presumed sorted pile was analyzed for its composition based on number of pieces and weight (CN and CW) (Figure 4.3). Sorted pile composition was calculated based on the percentage of each wood category (number or weight) that ended up in the pile to the total number of pieces in the pile. Composition was also evaluated based on metallic content (CM) (g/kg) for the presumed untreated pile as an indication of the metals content in the recycled wood. CM is defined as the ratio between the total of each metal mass to the total wood weight of the presumed untreated pile.

4.2.4.4 Statistical inferences

The randomized factorial block designs for the 50:50 and 95:05 experiments were analyzed by the generalized linear model of the analysis of variances (Two way ANOVA) by SigmaStat program (SigmaStat for windows version 3.5, © Systat Software Inc., Richmond, CA, USA) as 3^2 factorial experiments for the 50:50 set and as 2^2 for the 95:05 set. Two variable factors, belt speed (BS) and feeding rate (FR), were evaluated for their effects on the system response. The operational thresholds and measurement time of the XRF system were kept as fixed factors, and the different types of wood pieces in the infeed pile were randomly mixed before each experimental run and randomly fed to the sorting system. The sensitivity of the tests were carried at $\alpha = 0.05$. The response data was checked for its normality (using the Kolmogorov-Smirnov test) and equality of variances assumptions, both at p values greater than 0.05. All the reported values in the results section were verified to pass these two tests. Significant differences at different treatment levels were furthered evaluated by a Tukey test as a multiple comparison procedure with p value less than 0.05.

4.3 RESULTS

4.**3.1 Sorting efficiency**

4.3.1.1 UW sorting efficiency

The untreated wood sorting efficiency for the 50:50 set decreased significantly by number of pieces (p <0.01), and by weight (p <0.001) as feeding rate increased, with a more significant change as FR increased from 20 to 40 (pc/min) than from 40 to 60 (pc/min) (p <0.016). Based on number, sorting efficiencies of untreated wood measured at 95.9±1.2%, 79.1±5.6% and 73.6±8.3% for the 50:50 infeed. Based on weight, the corresponding sorting efficiencies were 93.2±2.8%, 79.3±5.6% and 72.4±7.2% (Figure 4). For the 95:05 infeed, the measured sorting efficiencies by number of untreated wood decreased significantly (p <0.05) as feeding rate increased, and measured at 96.1±1.3% and 93.2±1.6% for FR of 20 and 60 (pc/min), respectively. The measured sorting efficiencies by weight also decreased with increasing FR as 94.1±0.9% and 91.1±1.5%t, respectively, but this decrease was not significant.

When evaluating the effects of belt speed, the untreated wood sorting efficiency for the 50:50 infeed decreased slightly (from 80.1±12.5% to 77.4±11.6%) as BS increased from 0.25 to 0.375 m/s, but increased significantly (to 87.3±7.8%, p <0.021) as BS increased to 0.5 m/s. Similar trends were observed for changes in belt speed for the 95:05 set, but these changes were not significant.

4.3.1.2 TW sorting efficiency

Sorting efficiencies for treated wood based on numbers and weights showed no significant change at the different applied levels of FR and BS (Table 4.2). The measured sorting efficiency for treated wood for all 9 experimental runs of the 50:50 set was 83.9±3.0% based on number and was 88.6±3.5% based on weight (Figure 4.4). For the 95:05 set, the sorting efficiency for treated wood for all 4 experimental runs was 80.5±7.2% based on number and was 83.7±6.3% based on weight.

When evaluating sub-sets of the treated wood infeed, the measured sorting efficiency for As-based wood for the 50:50 set was above 90% (93.4±2.9% based on number and was 95.8±3.0% based on weight). For the 95:05 set, the measured efficiency of As-treated wood was near 90% (88.1±7.3% based on number and was 91.9±5.5% based on weight). On the contrary, sorting efficiency for Cu-based pieces were lower (35.9±12.5% based on number and 43.1±12.1% based on weight for the 50:50 set and 30±12.0% based on number and 30.7±15.1% based on weight for the 95:05 set). The measured sorting efficiencies for O-treated pieces were also relatively low (38.6±9.4% based on number and 29.1±8.5% based on weight for the 50:50 set).

4.3.2 Mass recovery

4.3.2.1 Arsenic recovery

The above sorting efficiencies achieved a recovery of arsenic as 96.7±2.1%, for the 50:50 set and as 93.3±8.5% for the 95:05 set, with no significant differences among the applied belt speeds and feeding rates. Arsenic was mostly recovered due to correctly sorting the As-based pieces (96.8±2.1% and 93.3±8.6%, for the 50:50 and 95:05 respectively). For the Cu- and O-treated pieces a lower fraction of arsenic was recovered (49.2±13.2% and 59.6±32.3% for the 50:50 experiments).

4.3.2.2 Copper recovery

Even though the sorting efficiency of Cu-based pieces was low, the recovery of Cu metal mass was high (83.4±6.9% recovery for the 50:50 set and 87.7±8.6% recovery for the 95:05 set). The majority of the Cu was removed as a result of the arsenic detection within the As-based pieces due to the predominance of the CCA preservative which contains both As and Cu. The amount of Cu that was recovered within As-based pieces was higher (97.8±1.4%, 94.4±6.3% for the 50:50 and 95:05 sets, respectively) than that within the Cu-based ones (59.6±17.5% and 40.9±36.1% for the 50:50 and 95:05 sets, respectively).

4.3.2.3 Chromium recovery

Chromium was recovered from the infeed mostly within the As-based pieces. The recovery for Cr within the As-based pieces was 96.3±2.3% and 93.1±7.4% for the 50:50 and 95:05 sets, respectively. The recovery for Cr within the Cu-based pieces was lower at 50.3±12.8% and 17.3±7.7% for the 50:50 and 95:05 sets, respectively. In total Cr was recovered at 95.2±2.3% and 92.6±7.4% from the infeed for the 50:50 and 95:05 sets, respectively.

4.3.3 Sorted piles' composition

4.3.3.1 UP composition

No significant difference in the composition of the presumed untreated pile was observed at the different applied FR and BS for the 50:50 and 95:05 sets. The presumed untreated pile was dominated by untreated wood and the untreated wood fraction was higher for the 95:05 set than the 50:50 set due to the large difference in the number of treated wood pieces in the infeed. For the 50:50 set the composition of the untreated wood pieces in the presumed untreated pile was 83.7±3.3% based on number and was 83.7±3.5% based on weight. For the 95:05 set, composition of the untreated wood pieces in the presumed untreated pile higher at 98.9±0.4% based on number and 98.8±0.6%

based on weight (Table 4.2). The composition of treated wood in the presumed untreated pile was the complement of 100%.

4.3.3.2 TP composition

The composition of the presumed treated pile for the 50:50 set, by number, decreased significantly (*p* <0.001) for treated wood (and increased for untreated wood) as the different levels of the applied feeding rates were increased (95.4±1.3%, 80.0±3.5% and 76.8±5.7% for FR of 20, 40 and 60 pc/min), with more significant changes as FR increased from 20 to 40 (pc/min) than 40 to 60 (pc/min) (*p* <0.003). The same trends were observed for the TP composition based on weight (*p* <0.001) (94.9±1.9%, 85.9±2.5% and 82.4±3.5% for FR of 20, 40 and 60 pc/min), with a more significant change from 20 to 40 (pc/min) (*p* <0.001). When evaluating the effects of BS, the composition of the presumed treated pile as treated wood for the 50:50 set by weight, decreased slightly (from 87.3±7.3% to 85.4±6.7%) as belt speed increased from 0.25 to 0.375 m/s, but increased significantly (to 90.5±5.4%, *p* <0.012) as belt speed increased to 0.5 m/s. Similar trends, but insignificant, were observed for composition by number (87.3±7.3% to 85.4±6.7% to 90.5±5.4%). The untreated wood composition changed accordingly as complement of 100.

For the 95:05 set, similar trends were observed with a significant (*p* <0.029) decrease in composition for treated wood by number (51.7±7.1% for FR of 20 pc/min and 37.5±8.0% for FR of 60 pc/min) and weight (51.2±1.6% for FR of 20 pc/min and 36.8±1.9% for FR of 60 pc.min) as the FR increased (Figure 4.5).

When evaluating the effects of belt speed, the composition of the presumed treated pile as treated wood, increased significantly by number (from 39.3±10.6% to 50±9.6%, p <0.039), and insignificantly by weight (from 42.5±10.6% to 45±10.0%, p <0.098) as belt speed increased from 0.375 to 0.5 m/s. The untreated wood composition changed accordingly as complement of 100.

These observations were strongly affected by the composition of As-based portion of treated wood (p<0.004 for 50:50 and p<0.05 for 95:05, by number and weight respectively) since As-based pieces represented the bulk of the treated wood in the infeed (83.4%, for the 50:50, and 88% for the 95:05 experiments).

4.4 DISCUSSION

4.4.1 Sorting efficiency

Sorting efficiencies of both untreated and treated wood based on numbers and weights were generally above 67% for the 50:50 set and above 70% for the 95:05 set, although efficiencies increased for specific FR and BS settings.

4.4.1.1 UW sorting efficiency

Observations showed that incorrect diversion of UW was due, in large part, to overlapping of wood on the conveyor belt or wood bouncing from the inclined conveyor (which carries UW to the UP) to the TP. FR predominantly impacted overlapping of wood (observed for wood pieces that were generally less than 80 cm in length) whereas BS predominantly impacted the bouncing of wood (observed for wood pieces that were generally longer than 80 cm in length). UW sorting efficiency decreased more significantly as FR doubled from 20 to 40 pc/min and less significant from 40 to 60 pc/min, due to the smaller proportional increase in FR. As FR increased, the amount of wood overlapped with TW on the conveyor belt became frequent. The sorting system was designed to sort towards the presumed treated pile, so untreated wood which overlapped the treated wood on the infeed conveyor was diverted to the treated wood pile and counted as incorrectly diverted. For UW pieces of length less than 80 cm, the fraction of incorrectly diverted pieces by number (as % of the original UW in the infeed) changed significantly for both experimental sets as FR was increased (1.7±0.6%, 17.2%±6.0%, and 21.5±8.6 at FR of 20, 40 and 60 pc/min for the 50:50 set ($p<0.015$) and 1.3±0.5% and 4.0±0.7% at 20 and 60 pc/min for the 95:05 set ($p<0.037$)). These pieces are believed to be incorrectly diverted due to overlapping with TW because of the increased probability for UW to overlap TW as FS increases.

For BS, increases in BS resulted in two complementary phenomena which improved sorting efficiencies. The first and most significant was less bouncing of TW towards the UP and secondly an increase in BS also resulted in a decrease in wood overlapping. The observed increase in efficiency as BS increased was relatively small when BS varied from 0.25 to 0.375 m/s, and a major enhancement was observed as BS increased 0.375 to 0.5 m/s. With respect to bouncing of wood, when BS was high, long UW pieces were dropped on the inclined conveyor and hit the shielding at the farthest end of the conveyor or the stationary slide-way connector, where they lost their momentum and fell on the conveyor and moved correctly toward the UP. At the lower BS, wood dropped straight down on its smallest edge hitting the conveyor and this would then bounce above the shielding toward the TP. So here the key was that the increased forward momentum of the wood at higher belt speeds resulted in longer pieces of wood hitting the shielding of the inclined conveyor in such a way so that it would fall back towards the inclined conveyor thus promoting correct sorting toward the UP. For UW pieces of length longer than 80 cm, the fraction incorrectly diverted by number (as % of the original UW in the infeed) averaged at 3.6±1.5% for the 50:50 set and 2.9±0.6% for the 95:05 set. These fractions decreased as BS increased (4.5±2.0% to 3.5±0.5% to 2.9±1.6% for the 50:50 set and 3.4±0.1% to 2.3±0.1% for the 95:05 set ($p<0.03$) thereby indicating that sorting of longer pieces of treated wood was impacted by BS.

4.4.1.2 TW sorting efficiency

Treated wood detection and sorting will depend on many factors, 1) dimension of wood plays a major role in the number of times a piece will be detected (multiples of 250 ms), 2) its surface condition (painted, coated or covered with soil,…etc.) and 3) metallic contents (depends on original retention of metals and age). High As and Cu concentration pieces (As>1000 and Cu>4000 ppm, chapter 2) were correctly diverted all the time. Correct diversion of very low As and Cu concentration-treated wood pieces or As and Cu free preserved wood (as may found among the O-pieces), is believed to occur due to overlapping and bouncing effects as untreated wood, rather than to correct detection. On the contrary, some small treated pieces (<10 cm in length) were found to be diverted correctly by the diverter, but bounce from the diverter and fly to rest on the inclined conveyor and so diverted to the untreated pile and counted as incorrectly diverted; such pieces will not have a major effect on the sorting efficiency based on weight or metallic contents, but has an equal effect as any wood piece on the sorting efficiency based on the number. Overall, because of all of these competing phenomena, TW sorting efficiencies did not change significantly with FR or BS.

4.4.2 Mass recovery

In summary, total As, Cu and Cr mass recovery from all treated wood were 96.8±2.1%, 83.3±6.9% and 95.2±2.3%, respectively for the 50:50 set. For the 95:05 set, the respective As, Cu and Cr recoveries were 93.3±8.5%, 87.7±8.6% and 92.6±7.4%.

Within the treated wood portion, the highest sorting efficiencies among all types of preserved wood used in this experiment was observed within As-treated wood, and thus As had the highest mass recovery. The reason behind this is twofold. The first reason was operational as the detection system was sensitive to As as evidenced by the low operational threshold for As which was 150% less than that of Cu. The second reason is due to the composition of the majority of the wood as CCA; most of the As-based pieces contained both As and Cu, and so each CCA piece has a chance to detected based on the content of one or two of these metals.

In addition to the sort based on As, which recovers a considerable amount of Cu and Cr, additional recoveries were facilitated by the detection of Cu treated wood, especially the Cu-based pieces with high concentrations of Cu.

4.4.3 Sorted piles' composition

The analysis of the composition of each presumed treated and untreated pile provides additional evidence for the success of recovered wood sorting by XRF technology. The concern after the sorting process, is the amount (or percentage) of the targeted metals that goes to the recycling stream of the untreated pile, and the amount of the untreated wood that will be diverted into environmentally safe landfills or wood-monofills and hence occupying a space that can be designated for treated wood.

4.4.3.1 TP composition

The major component of the presumed treated pile in the 50:50 experiments was As-treated wood, and for the 95:05 experiments was UW. The reason for this observation is because of the large differences in the infeed composition. Fifty percent of the wood infeed for the 50:50 set was composed of treated wood and thus the probability of getting untreated wood within the treated wood pile was much smaller than for the 95:05 set which had only 5% treated wood and 95% untreated wood. Specifically, for the 95:05 experiments, the presumed treated pile was composed of 44% untreated wood based upon number (Figure 4.6 is an example for one of the experimental runs of the 95:05 set). Because of the overwhelming number of untreated wood pieces in the 95:05 infeed, a sacrifice is generally made to incorrectly divert at least one untreated piece for every piece of treated wood in the infeed. This loss of untreated wood to the presumed treated pile represents a relatively small fraction (about 2.5% of UW in the infeed) of all wood diverted; the majority of the wood was diverted correctly.

The composition of TP was most strongly affected by the UW sorting efficiencies.

4.4.3.1 UP composition

The presumed untreated pile is the most important pile for wood recycling facilities since it represents their infeed for recycling. For the 50:50 experiments, 78-86% and 76-88% of the piles were UW, by number and weight respectively. Almost, another 10% by number and weight are Cu- and O-treated pieces. As-based pieces formed 4-11% and 2-13% based on number and weight. In the 95:05 experiments, the presumed untreated pile composed of 98-99% of UW by number and weight (Figure 4.6). So, as the treated wood fraction increased (5% to 50%) in the infeed, the fraction of treated wood will increase in the wood recycle stream. Thus, maintaining a wood infeed of high quality is critical for assuring an optimal recycled product as observed through the composition of the UP.

4.5 ENVIRONMENTAL IMPACT

In order to evaluate the significance of the results of this project, a case of recycling the recovered wood waste as mulch was considered. In Florida, USA, land applied materials should meet the soil clean-up target levels (SCTL), and these are generally lower for the arsenic by roughly a factor of 100 relative to copper and chromium, and thus arsenic is the most stringent criteria that will typically govern the design of a particular wood sorting system. The specific arsenic guideline level for land application of materials in residential areas is 2.1 mg of arsenic per kg of the applied material, and 12 mg/kg for commercial and industrial applications (FDEP, 2005). The 95:05 infeed used in this study had 164 mg As per kg of wood. With the XRF sorting system used in the current study, the presumed untreated pile reduced the arsenic levels to 1.75 mg/kg (for

BS= 0.5 m/s, and FR= 20 pc/min), which is within the residential SCTLs, in addition to 4.34 mg/kg (for BS= 0.375 m/s, and FR= 20 pc/min), and 8.30 mg/kg (for BS= 0.5 m/s, and FR= 60 pc/min) which are within the commercial SCTLs. Chromium and Cu criteria, which are less strict than As, were met, in all four experiments of the 95:05 infeed set. Thus, the technology achieved considerable improvements in the quality of the wood that could ultimately be used for recycling purposes; however, additional improvements are needed to the system to make sure that the strict 2.1 mg/kg level needed for residential applications is achievable all times during the operation of the system. Improvements can be achieved through the redesign of the wood conveyance system which will minimize the tendency for wood to bounce when sorted into treated versus untreated wood piles, as the majority of the inaccuracies associated with sorting were due to mechanical conveyance issues and not the detection of As by the XRF.

4.6 CONCLUSIONS

The main purpose of sorting at wood recycling facilities is to decrease the contamination in the recycling stream (the recycled stream as represented by the presumed untreated pile in this research), and to divert the contaminated pieces in the presumed treated pile into more acceptable disposal options such as lined landfills. This can be accomplished by enhancing both the TW and the UW sorting efficiencies. Enhancing the overall sorting efficiency required decreasing the overlapping and bouncing events. The optimum results were obtained at the lowest feeding rate of 20 pc/min and the highest BS of 0.5 m/s with feeding rate playing a larger role in the performance of the system. The lowest feeding rate decreased the overlapping events and the highest BS decreased both the overlapping and bouncing. Overlapping of untreated wood with treated wood can be decreased by training the wood pickers and feeders ahead of the system to practice visual sorting and to feed only the suspected pieces to the system. This will decrease both the number of treated pieces fed to the system and the feeding rate. Bouncing of wood can be decreased by replacing the inclined conveyor with low height horizontal roller conveyor, and increasing the height of the shielding between the two presumed piles, in addition to operating the system at the highest belt speed. Another alternative that can be considered to minimize bouncing effects is homogenizing the size of the wood infeed by using a size reduction process ahead of the XRF system. Sorting of uniform pieces of wood will minimize the conveyance and diversion problems associated with handling such large differences in wood size; however, this improvement in uniformity of the infeed will require very rapid detection due to the larger number of smaller pieces of wood that would need to be sorted. One recommendation for future work is to evaluate whether size reduction of the wood infeed will enhance overall sorting efficiencies. This is especially relevant for large wood cogeneration facilities which receive size reduced wood as their infeed. If the efficiencies are good, sorting of size reduced wood may represent one additional for wood cogeneration facilities to assure that their wood infeed is free of metal contaminants.

Overall, online sorting of recovered wood waste by automated XRF for the diversion of wood preservatives from wood recycling streams is a promising process. Observations of the system indicated that the majority of the incorrect diversion was not associated with the ability of the XRF system to detect the target metals in the wood. Improved efficiencies can be obtained by correcting mechanical problems associated with the movement of the wood.

Table 4.1 Treated wood chemical-characteristics for wood infeeds used in this study. Number of untreated pieces in the 50:50 infeed was 500 and the number of untreated pieces in the 95:05 infeed was 950.

	No. of treated pieces		**Arsenic content (g)**		**Copper content (g)**		**Chromium content (g)**	
Infeed type	50:50	95:05	50:50	95:05	50:50	95:05	50:50	95:05
As- treated	417	44	1252	137	682	50	736	71
Cu- treated[a]	66	5	2.9	0.1	403	7	11.6	0.3
O-treated[b]	17	1	0.74	0.01	3.74	0.00	4.72	0.13
Total	500	50	1,256	137	1,089	57	752	71

[a] Wood containing Cu and not As.

[b] Extremely weathered pieces containing elevated levels of Cr and not identified as As- or Cu-treated pieces.

Table 4.2 Results of experimentation of the 50:50 infeed and the 95:05 infeed. Statistics in the table correspond to 9 exp for the 50:50 set and 4 experiments for the 95:05 set.

		50:50 experiment					**95:05 experiment**				
Property	**Unit**	**Mean**	**St. dev.**	**Range**	**(p<)**^{a} FR	**(p<)**^{a} BS	**Mean**	**St. dev.**	**Range**	**(p<)**^{a} FR	**(p<)**^{a} BS
$\mathbf{SEN_{UW}}$	%(pc/pc)	82.9	11.3	66.6-97.0	0.01	0.104	94.5	1.9	92.1-96.6	0.05	0.067
$\mathbf{SEN_{TW}}$	%(pc/pc)	83.9	3.0	77.0-87.2	0.39	0.159	80.5	7.2	70-86	0.42	0.605
$\mathbf{SEN_{As-}}$	%(pc/pc)	93.4	2.9	86.1-95.4	0.77	0.431	88.1	7.28	77.3-93.2	0.50	0.605
$\mathbf{SEN_{Cu-}}$	%(pc/pc)	35.9	12.5	21.2-63.6	0.09	0.175	30	12	20-40	-	-
$\mathbf{SEN_{O-}}$	%(pc/pc)	38.6	9.4	23.5-52.9	0.82	0.655	-	-	-	-	-
$\mathbf{SEW_{UW}}$	%(kg/kg)	81.6	10.4	67.7-95.9	0.001	0.021	92.6	2.0	90.0-94.7	0.10	0.174
$\mathbf{SEW_{TW}}$	%(kg/kg)	88.6	3.5	80.5-91.6	0.56	0.129	83.7	6.3	74.6-88.2	0.31	0.467
$\mathbf{SEW_{As-}}$	%(kg/kg)	95.8	3.0	88.3-98.2	0.75	0.336	91.5	5.5	84.0-95.7	0.33	0.514
$\mathbf{SEW_{Cu-}}$	%(kg/kg)	43.1	12.1	31.9-69.2	0.31	0.144	30.7	15.1	14.3-50.0	-	-
$\mathbf{SEW_{O-}}$	%(kg/kg)	29.1	8.5	20.0-42.9	0.66	0.759	-	-	-	-	-
$\mathbf{R_{As/TW/TP}}$	%(g/g)	96.7	2.1	91.7-98.8	0.75	0.244	93.3	8.5	80.6-99.1	0.37	0.443
$\mathbf{R_{Cu/TW/TP}}$	%(g/g)	83.4	6.9	75.0-92.0	0.68	0.19	87.7	8.6	75.4-95.4	0.55	0.746
$\mathbf{R_{Cr/TW/TP}}$	%(g/g)	95.2	2.3	89.8-97.4	0.65	0.166	92.6	7.4	82.5-98.5	0.23	0.431
$\mathbf{R_{As/As-/TP}}$	%(g/g)	96.8	2.1	91.2-98.9	0.74	0.25	93.3	8.6	80.7-99.1	0.38	0.443
$\mathbf{R_{As/Cu-/TP}}$	%(g/g)	49.2	13.2	35.1-76.5	0.71	0.134	15.0	12.3	1.7-28.3	0.81	1
$\mathbf{R_{As/O-/TP}}$	%(g/g)	59.6	32.3	8.9-83.0	0.44	0.99	-	-	-	-	-
$\mathbf{R_{Cu/As-/TP}}$	%(g/g)	97.8	1.4	94.9-99.3	0.61	0.105	94.4	6.31	85.6-99.7	0.24	0.375
$\mathbf{R_{Cu/Cu-/TP}}$	%(g/g)	59.6	17.5	38.3-83.7	0.64	0.244	40.9	36.1	4.5-77.3	0.88	1
$\mathbf{R_{Cu/O-/TP}}$	%(g/g)	16.5	27.3	0.35-86.2	0.51	0.501	-	-	-	-	-
$\mathbf{R_{Cr/As-/TP}}$	%(g/g)	96.3	2.3	91.1-98.7	0.59	0.175	93.1	7.4	82.9-99.0	0.23	0.434
$\mathbf{R_{Cr/Cu-/TP}}$	%(g/g)	50.3	12.8	37.2-74.7	0.81	0.259	17.3	7.7	8.1-26.6	0.39	1
$\mathbf{R_{Cr/O-/TP}}$	%(g/g)	25.6	11.1	11.6-46.0	0.29	0.864	-	-	-	-	-
$\mathbf{CN_{TP/UW}}$	%(pc/pc)	16.0	9.3	3.6-27.7	0.003	0.115	55.4	10.3	43.2-68.2	0.029	0.039
$\mathbf{CN_{TP/TW}}$	%(pc/pc)	84.0	9.3	72.3-96.5	0.003	0.115	44.6	10.3	31.8-56.8	0.029	0.039
$\mathbf{CN_{TP/As-}}$	%(pc/pc)	78.1	9.9	64.0-91.7	0.004	0.109	42.9	9.5	30.9-54.1	0.042	0.052
$\mathbf{CN_{TP/Cu-}}$	%(pc/pc)	4.6	1.1	3.3-7.0	0.23	0.313	1.7	0.9	0.91-2.70	0.08	0.331
$\mathbf{CN_{TP/O-}}$	%(pc/pc)	1.3	0.3	0.7-1.8	0.93	0.578	-	-	-	-	-
$\mathbf{CN_{UP/UW}}$	%(pc/pc)	83.7	2.3	78.3-86.2	0.36	0.473	98.9	0.4	98.0-99.0	0.41	0.585
$\mathbf{CN_{UP/TW}}$	%(pc/pc)	16.3	2.3	13.8-21.7	0.36	0.473	1.2	0.6	0.82-2.04	0.41	0.585
$\mathbf{CN_{UP/As-}}$	%(pc/pc)	5.6	2.4	3.6-11.0	0.60	0.617	0.6	0.4	0.33-1.12	0.49	0.594
$\mathbf{CN_{UP/Cu-}}$	%(pc/pc)	8.5	1.0	6.0-9.7	0.43	0.558	0.4	0.1	0.32-0.45	0.003	0.047
$\mathbf{CN_{UP/O-}}$	%(pc/pc)	2.1	0.4	1.6-3.0	0.63	0.434	0.1	0.0	0.1-0.11	0.04	0.044
$\mathbf{CW_{TP/UW}}$	%(kg/kg)	12.3	6.2	3.4-20.2	<.001	0.012	56.1	8.6	47.7-65.0	0.02	0.098
$\mathbf{CW_{TP/TW}}$	%(kg/kg)	87.7	6.2	79.8-96.6	<.001	0.012	43.9	8.6	35.0-52.3	0.02	0.098
$\mathbf{CW_{TP/As-}}$	%(kg/kg)	82.3	6.6	72.4-91.3	0.002	0.029	41.6	7.3	34.1-50.0	0.05	0.159
$\mathbf{CW_{TP/Cu-}}$	%(kg/kg)	5.0	1.0	3.9-7.1	0.73	0.237	1.3	0.7	0.81-2.33	0.41	0.396
$\mathbf{CW_{TP/O-}}$	%(kg/kg)	0.4	0.1	0.2-0.6	0.50	0.482	-	-	-	-	-
$\mathbf{CW_{UP/UW}}$	%(kg/kg)	83.7	3.5	75.2-87.7	0.49	0.337	98.8	0.6	98.0-99.2	0.40	0.409
$\mathbf{CW_{UP/TW}}$	%(kg/kg)	16.3	3.5	12.3-24.8	0.49	0.337	1.2	0.6	0.82-2.04	0.40	0.409
$\mathbf{CW_{UP/As-}}$	%(kg/kg)	5.2	3.2	2.4-12.8	0.71	0.499	0.5	0.4	0.27-1.08	0.38	0.496
$\mathbf{CW_{UP/Cu-}}$	%(kg/kg)	9.8	1.4	6.4-10.9	0.78	0.702	0.4	0.3	0.27-0.82	0.49	0.334
$\mathbf{CW_{UP/O-}}$	%(kg/kg)	1.3	0.3	0.9-1.9	0.23	0.615	0.2	0.1	0.14-0.28	0.54	0.52
$\mathbf{CM_{UP/As}}$	g/kg	0.11	0.06	0.04-0.23	0.61	0.352	0.01	0.02	0.01-0.04	0.22	0.426
$\mathbf{CM_{UP/Cu}}$	g/kg	0.47	0.17	0.26-0.69	0.57	0.468	0.01	0.01	0.00-0.01	0.53	0.748
$\mathbf{CM_{UP/Cr}}$	g/kg	0.1	0.04	0.05-0.17	0.33	0.301	0.01	0.01	0.00-0.02	0.37	0.441

^{a}Significant when $p<0.05$.

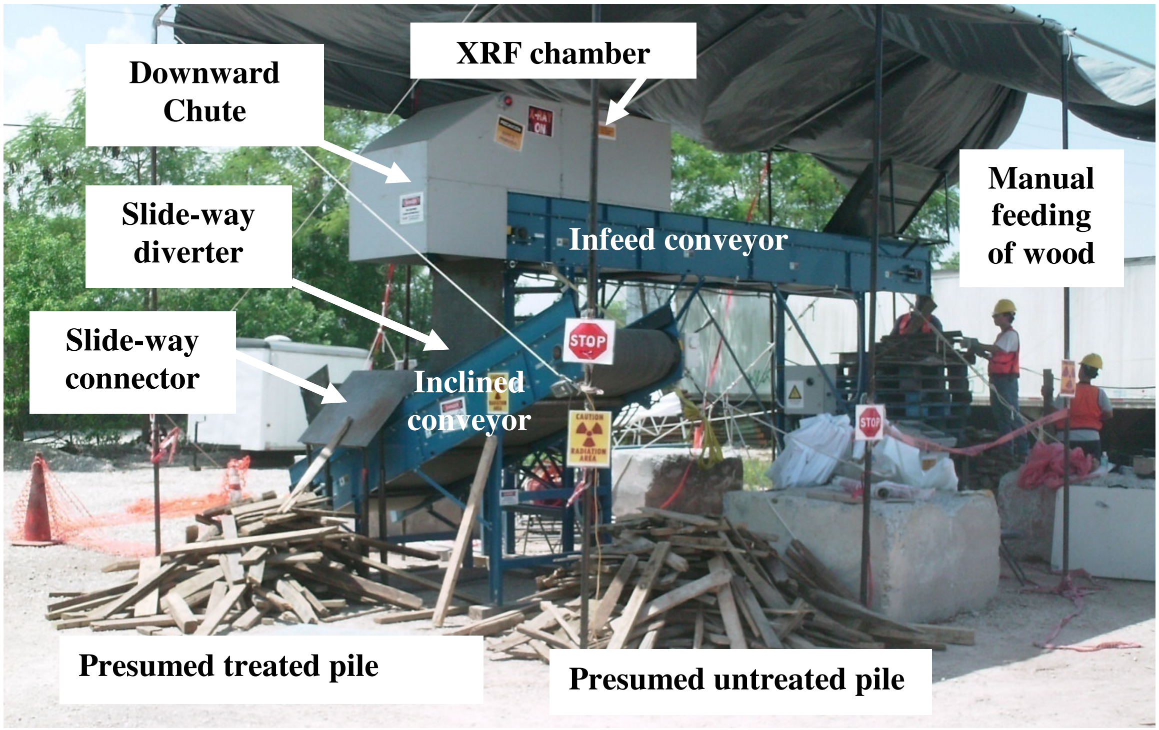


Figure 4.1 The XRF detection and sorting system. The dimensions of the motorized infeed belt-conveyor are: 6 m length, 54.2 cm width and 297 cm height, and for the inclined conveyor: 3 m length, 108 cm width and 165 cm highest end above the ground. The slide-way diverter is made of a steel sheet with dimensions as 81.3x81.3x0.6 cm.

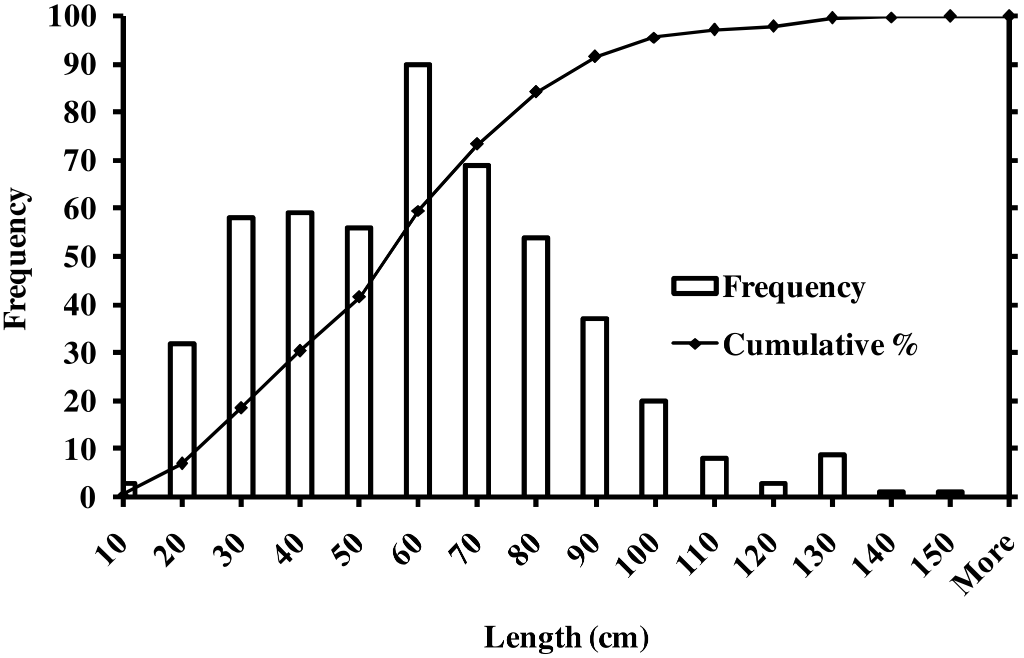
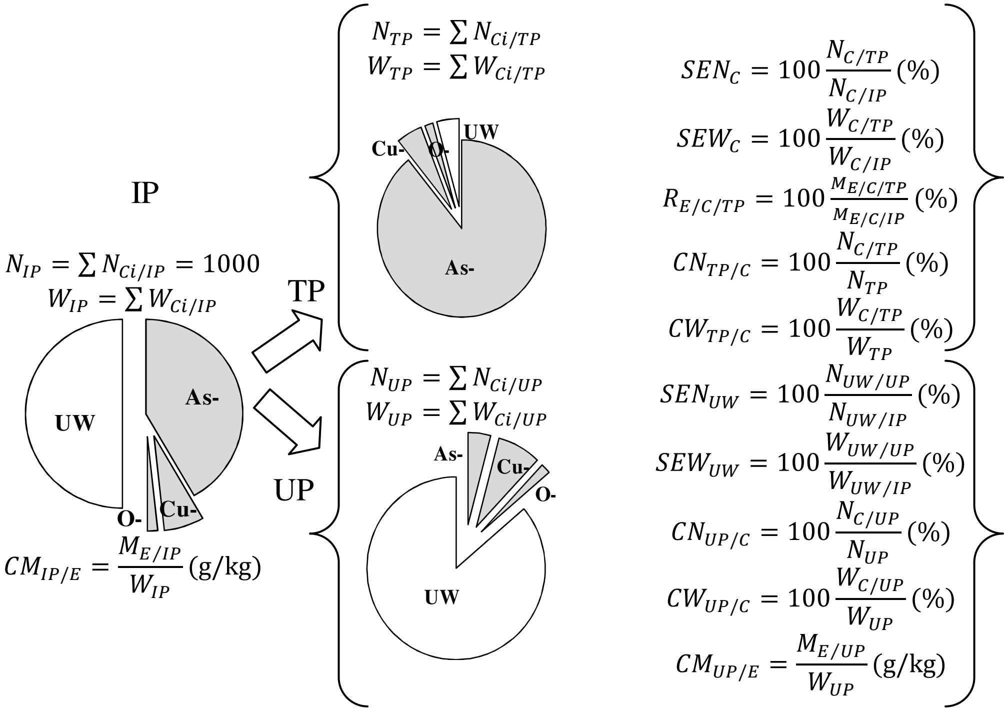


Figure 4.2 Wood distribution based on number of pieces according to their length for the 500 treated wood pieces. The x-axis label corresponds to the upper limit of the bin.

Legend:

P: wood pile
IP: infeed pile.
TP: presumed treated-wood pile.
UP: presumed untreated-wood pile.
TW: treated wood.
UW: untreated wood.
C: wood category (UW and TW which includes: As-, Cu-, and O-treated wood).
M: mass (g).
E: element (As, Cu or Cr).
pc: piece of wood.
$N_{C/P}$: number of pieces for a wood category.
$W_{C/P}$: weight of pieces for a wood category (kg).
$M_{E/P:}$ mass of a metal in one of the three piles (g).
SEN_C: sorting efficiency based on number for a wood category (%).
SEW_C: sorting efficiency based on weight for a wood category (%).
$R_{E/C/TP}$: mass recovery of a metal in a pile for a wood category in the TP (%).
$CN_{P/C}$: composition based on number for a pile based on a wood category (%).
$CW_{P/C}$: composition based on weight for a pile based on a wood category (%).
$CM_{P/E}$: composition of a pile based on metallic content (g of metal/Kg of wood).



$$N_{IP} = \sum N_{Ci/IP} = 1000$$
$$W_{IP} = \sum W_{Ci/IP}$$
$$CM_{IP/E} = \frac{M_{E/IP}}{W_{IP}} \text{ (g/kg)}$$

$$N_{TP} = \sum N_{Ci/TP}$$
$$W_{TP} = \sum W_{Ci/TP}$$

$$SEN_C = 100 \frac{N_{C/TP}}{N_{C/IP}} (\%)$$
$$SEW_C = 100 \frac{W_{C/TP}}{W_{C/IP}} (\%)$$
$$R_{E/C/TP} = 100 \frac{M_{E/C/TP}}{M_{E/C/IP}} (\%)$$
$$CN_{TP/C} = 100 \frac{N_{C/TP}}{N_{TP}} (\%)$$
$$CW_{TP/C} = 100 \frac{W_{C/TP}}{W_{TP}} (\%)$$

$$N_{UP} = \sum N_{Ci/UP}$$
$$W_{UP} = \sum W_{Ci/UP}$$

$$SEN_{UW} = 100 \frac{N_{UW/UP}}{N_{UW/IP}} (\%)$$
$$SEW_{UW} = 100 \frac{W_{UW/UP}}{W_{UW/IP}} (\%)$$
$$CN_{UP/C} = 100 \frac{N_{C/UP}}{N_{UP}} (\%)$$
$$CW_{UP/C} = 100 \frac{W_{C/UP}}{W_{UP}} (\%)$$
$$CM_{UP/E} = \frac{M_{E/UP}}{W_{UP}} \text{ (g/kg)}$$

Figure 4.3 Calculation formulas for sorting efficiencies (SEN and SEW), metals mass recovery (R), and sorted piles' composition (CN, CW and CM).

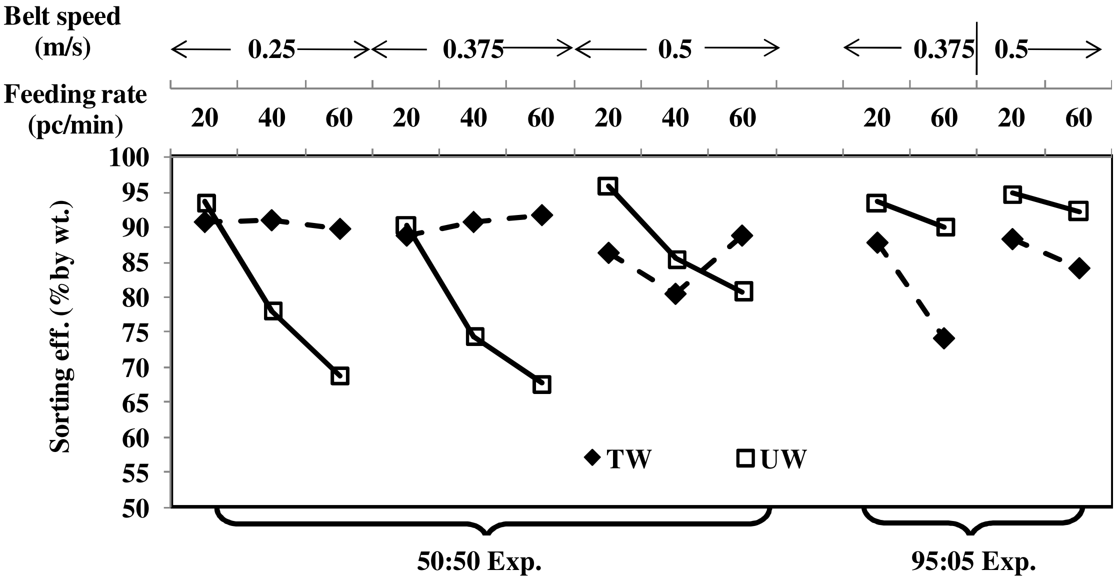


Figure 4.4 Treated and untreated wood sorting efficiencies based on wood weight.

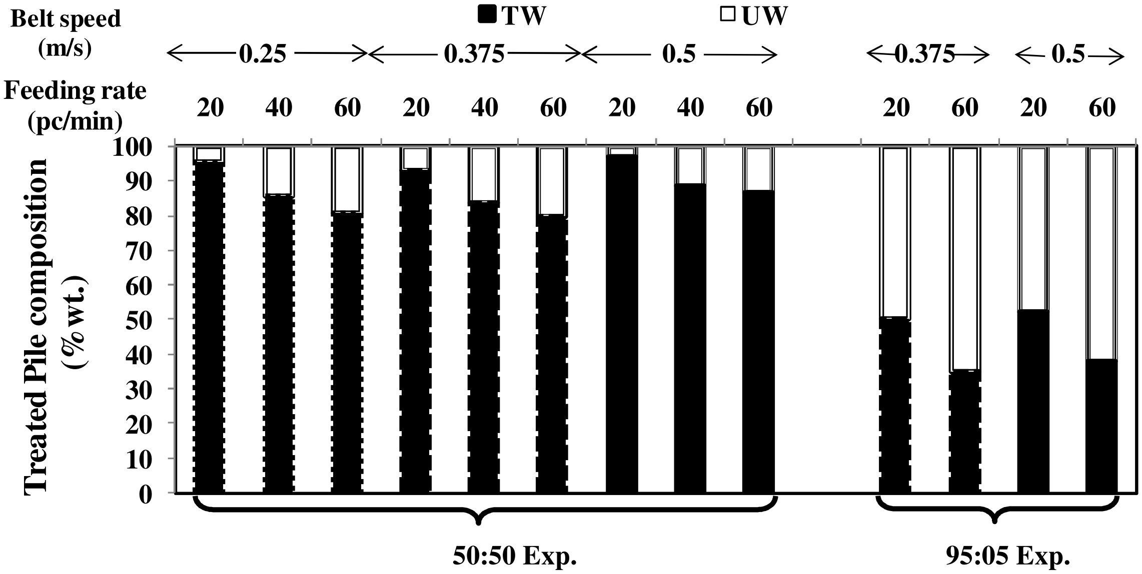
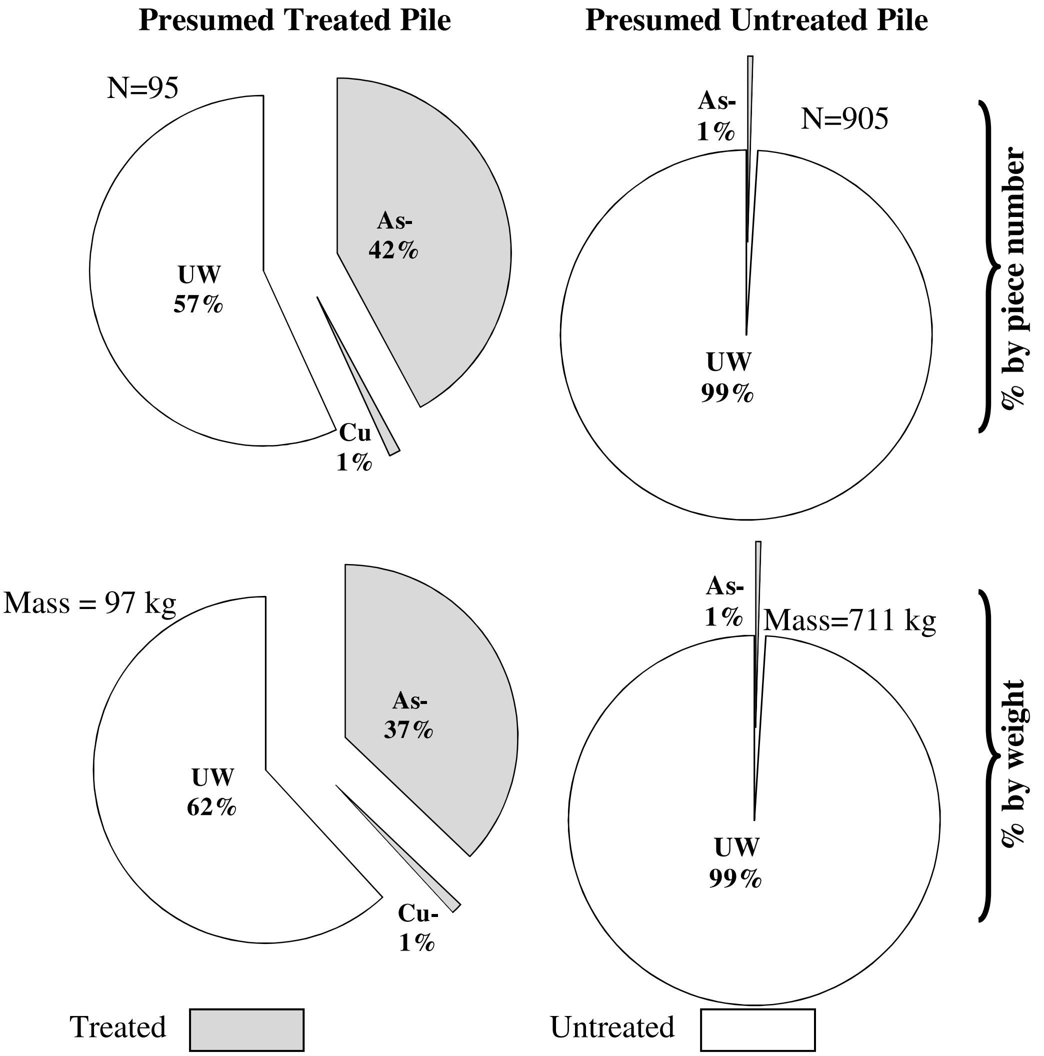


Figure 4.5 Composition of presumed treated pile based on wood weight.



Treated (As-: As-based, Cu-: Cu-based, O-: other-treated) and UW: untreated.

Figure 4.6 Wood distributions in presumed treated and presumed untreated piles after an experiment conducted using a 95:05 wood infeed. Experimental parameters included a belt speed of 0.5 m/s and a feeding rate of 60 pieces per minute. Wood distribution is based on number of pieces (above) and weight (below).

CHAPTER 5

SUMMARY, CONCLUSION AND RECOMENDATION

5.1 CHAPTER INTRODUCTION

Chromated copper arsenate (CCA) was the most widely used preservative for wood treatment up to 2004. Effective on December 31, 2003, CCA-treated wood was banned from most residential application in the U.S. Copper based treated wood is expected to dominate the market for residential applications of treated wood. Even though CCA was phased out, CCA-treated wood structures are expected to remain in service for at least another 15 years. As these structures weather, leaching of preservative metals are expected to continue, imposing threats on the surrounding environment and human beings. Leaching of preservative chemicals from weathered treated wood and the new Cu-based treated wood (known as ACQ) were poorly covered in the literature. Almost no documentation of leaching rates was found.

At the end of wood service life, both treated and untreated wood are collectively gathered at C&D facilities for sorting out treated wood and recycling of untreated wood. As most of the C&D wood is weathered-wood, visual sorting based on the distinctive olive-green color of all Cu-based treated wood (including CCA), has many disadvantages. Wood might be weathered to a level that the green color is totally faded, yet wood might be covered with dust and mud, and the end tags were removed due to fabrication. Visual sorting and other manual methods such as stains, test kits and held XRF are laborious, time consuming and proved not to be valid for medium sized facilities and larger. LIBS technology is promising, but with some drawbacks with the technology developed until this current time. LIBS is targeting Cr in wood pieces, a metal used in CCA, but not in Cu-based preservatives. Also, LIBS was not efficient at identifying severely rotted and dirty pieces. Online detection and sorting by XRF-technology was proposed in the literature.

This dissertation covered the above mentioned two main aspects in concern for environmental impacts of weathered waterborne preserved wood; leaching of metals during service (chapter 2) and metals' based detection (chapter 3) and sorting (chapter 4) from recovered wood waste upon recycle. The two main subjects will be handled separately in the rest of this chapter.

5.2 LEACHING OF METALS FROM WEATHERED TREATED WOOD

5.2.1 Summary

Weekly rainfall leachates were collected over one year after impacting low (in duplicate), medium and high retention weathered CCA wood samples, in addition to new ACQ and untreated wood. Leachates were analyzed for pH and total metals concentration of As, Cr and Cu.

pH of the leached water was found as higher than that of the background levels of rain and found as inversely proportional to the volume of leachated water,

Metals concentrations in the rainfall leachates of the duplicated low retention CCA wood samples, showed no significant differences between these replicates with coefficients of variation of less than 21% for As, Cr and Cu. Metals' concentrations in the rainfall leachates were proportional in magnitude with retention levels of CCA samples. New ACQ sample showed a wash off phase at the first three months of the experimentation, and leached Cu the highest among all wood samples though the medium and high retention CCA samples contained much more Cu than the ACQ sample. Results showed no strong relationship between weekly rainfall depth and measured metal concentrations in the leachates. However, when data were combined into seasonal categories (wet versus dry seasons) distinct differences were observed.

Mass of metals leached from CCA samples was found as significantly dependent on the original retention levels of wood ($p<0.001$) and primarily dependent on rainfall volume ($p<0.001$) and secondarily on concentration of metals in the leachate ($p<0.0014$), with a higher correlation between rainfall and metals' mass leached at the higher CCA-retention. Also, Cu mass leached from the ACQ sample was primarily dependent on the rainfall volume ($p<0.001$) and secondarily on the Cu concentration observed in the leachate ($p<0.033$).

Leaching of As and Cu was significantly correlated ($p<0.001$) with the amount of Cr leached (the fixing agent) for all CCA-treated wood samples. For all CCA samples, the As to Cr mass ratios was always higher than 1, while the Cu to Cr mass ratios oscillated around 1.

Cumulative leached masses showed that As leached the highest when compared to Cr and Cu. The cumulative masses of leached metals from all samples evaluated was highly correlated ($p<0.001$) to the cumulative rainfall. Initial mass leaching was low for the first month of the experiment (except for ACQ) and followed by several sudden increases that occurred during weeks of low to moderate rainfall depths that followed major rainfall peaks.

5.2.2 Conclusion

This study supports that wood buffers the pH of the rainwater, and as the volume of collected rainfall leachate increases, pH decreases. Also, this study emphasized that leaching of metals from treated wood is driven by rainfall. The higher leaching of metal masses from wood were associated with larger collected volumes of rainfall leachate, and may have also been facilitated by a slight shift of the leachate pH towards the acidic range as volume of rainfall leachate increased. Although metal leached was reduced with increasing pH value, the correlation between the pH and metals' mass leached was found as not significant, and this may happened due to the changes in the background levels of the rainfall's pH over the year of study.

Also, concentration and mass data of the rainfall leachate from the duplicate of low retention CCA sample support the similar behavior of metals leaching among wood pieces of same original retention, age, and use.

Chromium acts as a fixing agent for As and Cu in CCA preserved wood. Loss of Cr from the wood may have led to higher loss of As and moderate loss of Cu. Absence of fixation in ACQ samples may led to the massive loss of its Cu in comparison to Cu lost from CCA samples.

Also, as a support for other literature, this study suggest that the mechanism of leaching is associated with the transport of metals from the interior portions of the wood towards the surface where sudden increases of metals lost were observed at a one week delay from maximum rainfall amounts. Furthermore, at low retention levels, the metal concentrations were diluted presumably due to a limitation in the amount of metal transported to the surface whereas for high retention levels increases in metal concentrations were observed during the wet season.

The seasonal variation from wet summer (end of April to end of October) to dry winter in south Florida, resulted in a 240% decrease in rainfall depth. This decrease in rainfall led to a significant decrease in masses of As, Cr and Cu leached during the two seasons,

This study in comparison with other literature concluded that weathering can increase percentage leaching rates of As; however, because the retention of metals in the wood decreases over time, the mass of metals leached would decrease. In spite of the decrease in total mass leached, metals leaching from treated wood are expected to continue over the service life of wood, and the leaching mechanism is expected to change as wood weathers due to loss of Cr fixation, cracking of wood, and deterioration of the wood fiber.

5.2.3 Recommendation

This study recommends that environmental leaching research of rainfall-impacted treated wood should take into consideration two important issues:

1. To be conducted over a yearly basis, to avoid the effect of seasonal variations that might led to overestimating leaching rates of metals, if experiments were to be conducted in the wet season, and vice versa for the dry season.
2. Not to quantify the loss of metals from the subjected wood only based on their concentration in the collected leachate, and not to correlate the concentration with rainfall. The reason behind this is the dilution effect that was noticed in this research, especially for the low retention CCA-treated wood.

ACQ treated wood might not be the ideal replacement of CCA-treated wood due to the large loss of its active ingredient (Cu) over a short period. This loss is expected to shorten the service life of this Cu-based treated wood, and hence, will increase the demand on forests wood, and negatively impact the global climate.

A solution for the above mentioned issue includes the new Cu-based formulation of micronized copper quat (MCQ), produced by the wood treatment industry since 2006. This new product is believed to leach Cu at a slower rate relative to the early ACQ formulations. Of interest for future research is to evaluate new and weathered micronized Cu treated wood under natural field conditions to evaluate Cu leaching rates and to provide a comparison with values published in the literature for other wood preservative formulations.

5.3 DETECTION AND SORTING OF PRESERVED WOOD

5.3.1 Summary

A full scale unit of conveyance, detection and diversion for a medium sized wood-recycling facility was used. The conveyance equipment consisted of an infeed motorized belt-conveyor and an inclined conveyor installed perpendicular to the discharge end of the infeed conveyor. The infeed conveyor was designed to convey wood to the XRF detection unit, and the inclined conveyor to move the untreated wood to a separate pile for further processing. The XRF detection system was installed on the top of the infeed conveyor, and included an X-ray source, X-ray detector and digital pulse processing unit, controlled by customized software. Identification of preserved wood by XRF focused on the detection of As and/or Cu presence in wood. The detection of As and Cu, indicated the presence of arsenical preservatives in the wood, most likely CCA. The presence of Cu only indicated the presence of copper based preservatives such as alkaline copper quat (ACQ), among other copper-based preservatives.

After wood inspection within the detection chamber, treated wood was then discharged from the end of the infeed conveyor by a slide-way diverter bypassing the inclined conveyor. The time required to move the slide-way diverter was set equal to the delay time, the time for the wood piece to move from the inspection point to the discharge end of the conveyor. Thus, wood would accumulate in two separate piles, a presumed as untreated and presumed treated wood pile.

Four main parameters were evaluated to optimize detection and sorting efficiencies. The first two parameters are related to the XRF-detection system; operational threshold (OT) and measurement time, and were evaluated using an infeed of purely treated wood, and analyzing the spectrums generated in the field view of the detector. The other two parameters were related to the operational conveyance system, conveyor belt speed and wood feeding rate, and were studied based on a randomized block design for two different wood infeeds each of 1000 piece: 50:50 and 95:05 of untreated to treated wood.

Optimized OT of targeted metals, As and Cu, were lower for As than for Cu, resulting in a system that was more sensitive to As. The optimum minimum measurement times (250-500 ms) resulted in mass recoveries of 98, 91 and 97% for As, Cu and Cr, respectively. At the different applied feeding rates (20-60 piece/min) and belt speeds (0.25-0.5 m/s), online sorting efficiencies of waste wood by XRF technology were high based on number and weight of pieces (70-87% and 74-92% for treated wood and 82-

97% and 69-96% for untreated wood, respectively). These sorting efficiencies achieved mass recovery for metals of 81-99% for As, 72-92% for Cu and 80-97% of Cr. The optimum results were obtained at the lowest feeding rate as 20 pc/min and the highest BS as 0.5 m/s with more predominant impact by the feeding rate on the performance of the system.

5.3.2 Conclusion

Results showed that XRF technology can be equipped for online computerized real time measurements for the detection of inorganically preserved wood such as CCA and ACQ. The high energy X-ray tubes available commercially and the advancement in X-ray detectors' technology allowed for the design of a detection compartment that can fit on a top of motorized conveyor and leaves space for wood of different shapes and sizes to be detected and passed underneath for the diversion as treated or untreated. Diversion was made possible by a slide-way diverter and operational parameters of the detection-conveyance system

The higher the concentration of targeted metals in the treated wood pieces, the lower the interference from the background system; leading to higher detection efficiencies. Also, at the low concentration end, the lower the OT_{TM} (required for minimizing the background interferences), the lower the concentration of targeted metals that can be detected, and so resulting in higher mass recoveries and sorting efficiencies.

The incorrectly diverted pieces of wood were attributed to deficiencies in the wood conveyance systems and not to deficiencies in the XRF-based detection. Even with the deficiencies in the conveyance systems, online sorting was shown to sort wood which would meet both the residential and commercial/industrial soil cleanup target levels in Florida when an infeed is composed of 5% of treated wood. Comparisons with other sorting methods show that XRF technology appears to be the closest with respect to possible implementation and can potentially fulfil the need for cost-effective processing at large facilities (> 30 tons per day).

5.3.3 Recommendation

Treated and untreated wood efficiencies can be enhanced to divert more contaminates from the recycle stream and isolate contaminants in a safe destination. Treated wood sorting efficiency can be enhanced by:

1. Choosing a conveyor belt free of targeted or their interfering metals that will allow for a lower operational threshold.
2. The X-ray tube and the detector separated in two compartments to avoid X-ray dampening by lead sheets, that interfered with the detection of As. Forced purging of the compartments should be done by filtered clean air to avoid accelerated corrosion of the metals inside the compartments, and so the lower operational threshold can be maintained.
3. To decrease the interference from the treated wood dust that may fall on the belt, an online cleaning brush should be equipped as part of the infeed conveyor. So, a higher measurement time as 500 ms can be set, that will lead to an increase in the treated wood sorting efficiency.

Untreated wood sorting efficiency can be enhanced by:

1. Decreasing treated and untreated wood overlapping over the conveyor belt. Lowering the feeding rate and increasing the belt speed will decrease the overlapping events. Feeding rate can be decreased by training the wood pickers and feeders ahead of the system to practice visual sorting and to feed only the suspected pieces to the system, this will also decrease the number of treated pieces fed to the system as such.
2. Decreasing wood bouncing from the system, and this can be done by replacing the inclined conveyor with low height horizontal roller conveyor, and increasing the height of the shielding between the two presumed piles, in addition, to operating the system at the highest belt speed.
3. Another alternative that can be considered to minimize bouncing effects is homogenizing the size of the wood infeed by using a size reduction process ahead of the XRF system. Sorting of uniform pieces of wood will minimize the conveyance and diversion problems associated with handling such large differences in wood size; however, this improvement in uniformity of the infeed will require very rapid detection due to the larger number of smaller pieces of wood that would need to be sorted.

One recommendation for future work is to evaluate whether size reduction of the wood infeed will enhance overall sorting efficiencies. This is especially relevant for large wood cogeneration facilities which receive size reduced wood as their infeed. If the efficiencies are good, sorting of size reduced wood may represent one additional for wood cogeneration facilities to assure that their wood infeed is free of metal contaminants.

APPENDICES

APPENDIX A: Supplementary information for chapter 2.

Table A.1 Characteristics of wood samples including number of pieces, dimensions, surface area, and wood volume.

Label	No. of Pieces/shape	Dimension of each piece (cm)	Total area impacted by rainfall (cm^2)	Total wood volume (cm^3)
UW	2, rectangular	57 x 17.8 x 3.8	2029	7711
ACQ	3, rectangular	49.5 x 13.8 x 3.8	2049	7787
La-CCA	3, rectangular	49.5 x 14.1 x 1.8	2094	3769
Lb-CCA	3, rectangular	49.5 x 14.1 x 1.8	2094	3769
M-CCA	4, rectangular	8.8 x 58.5 x 8.8	2059	18121
H-CCA	1, cylindrical	L = 74, D = 28.5	2109	47227

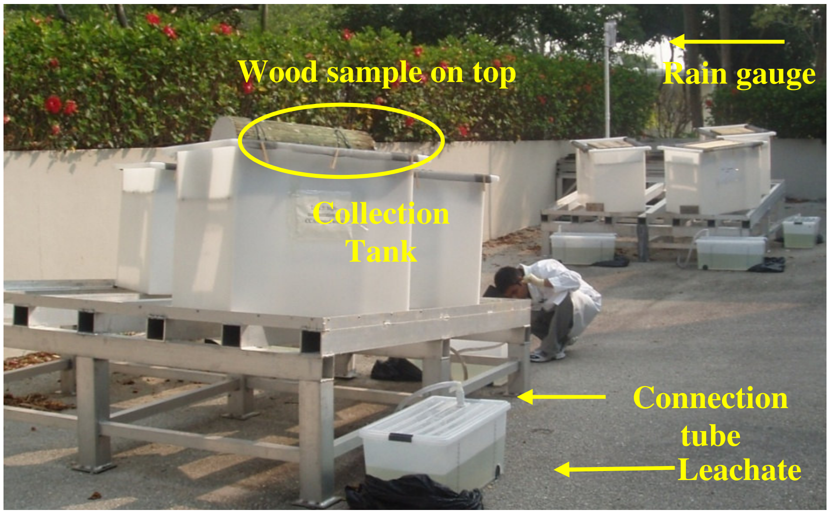


Figure A.1 The experimental leachate-collection systems.

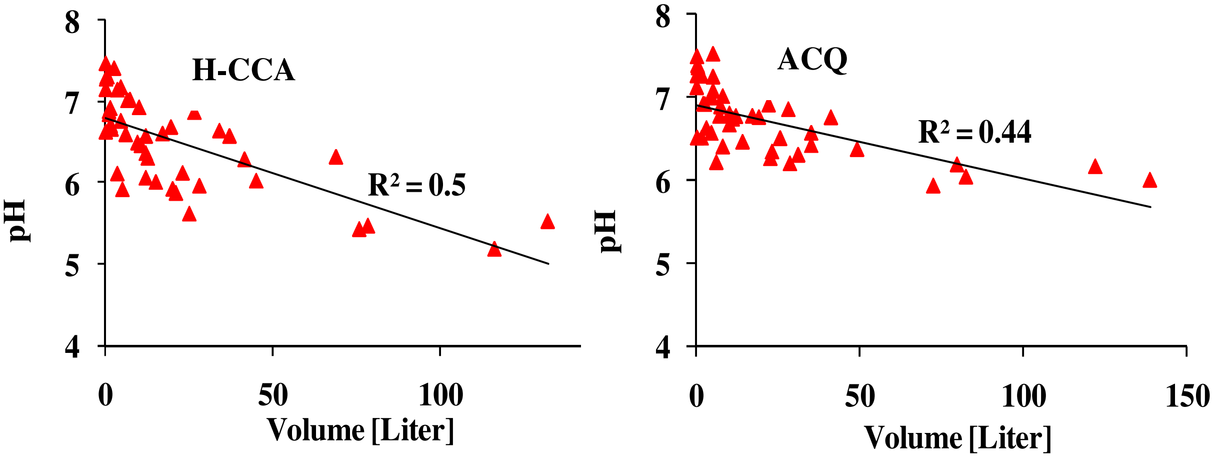


Figure A.2 pH versus water volume for H-CCA and ACQ treated wood samples.

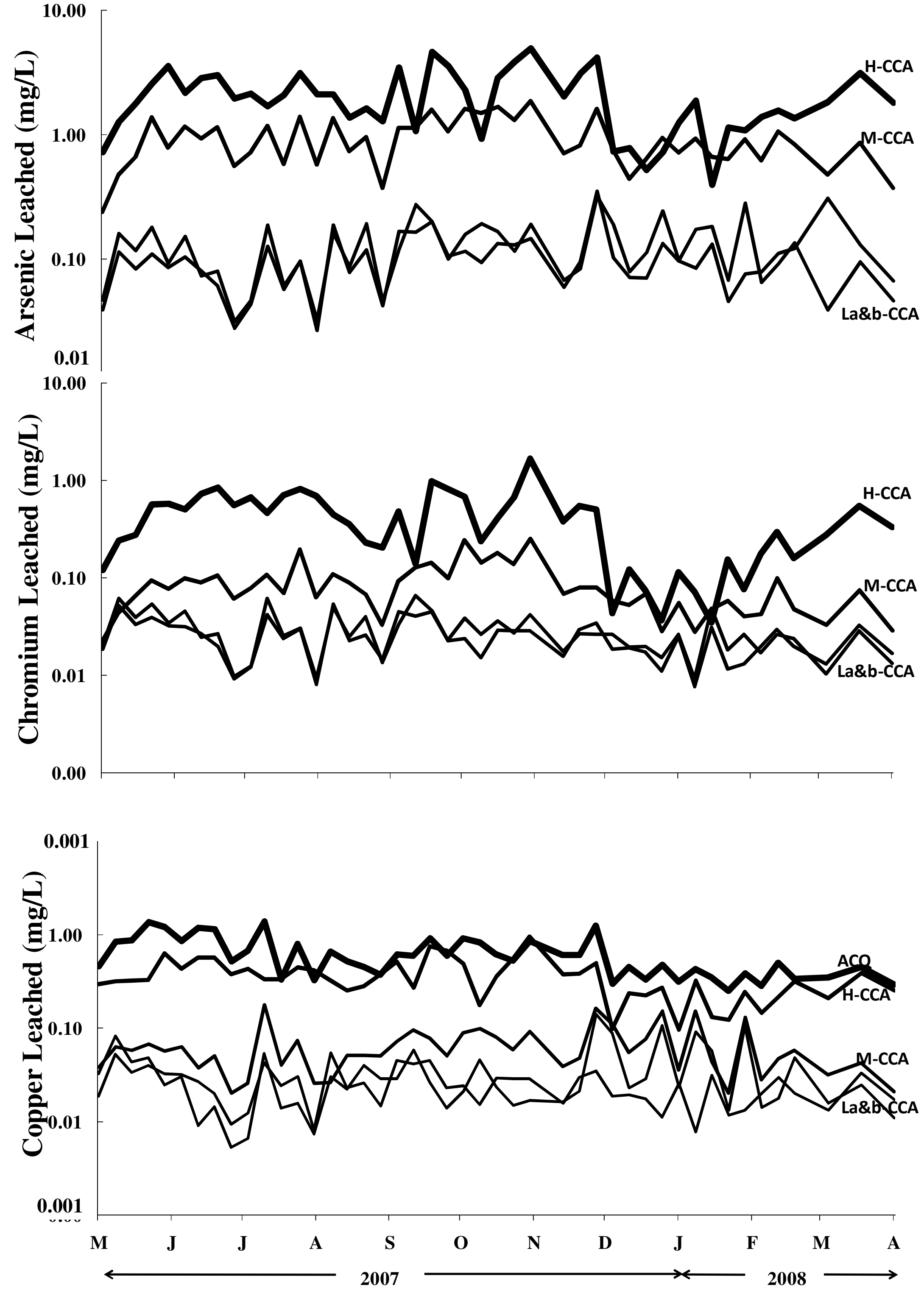


Figure A.3 Concentrations of As, Cr and Cu leached over time.

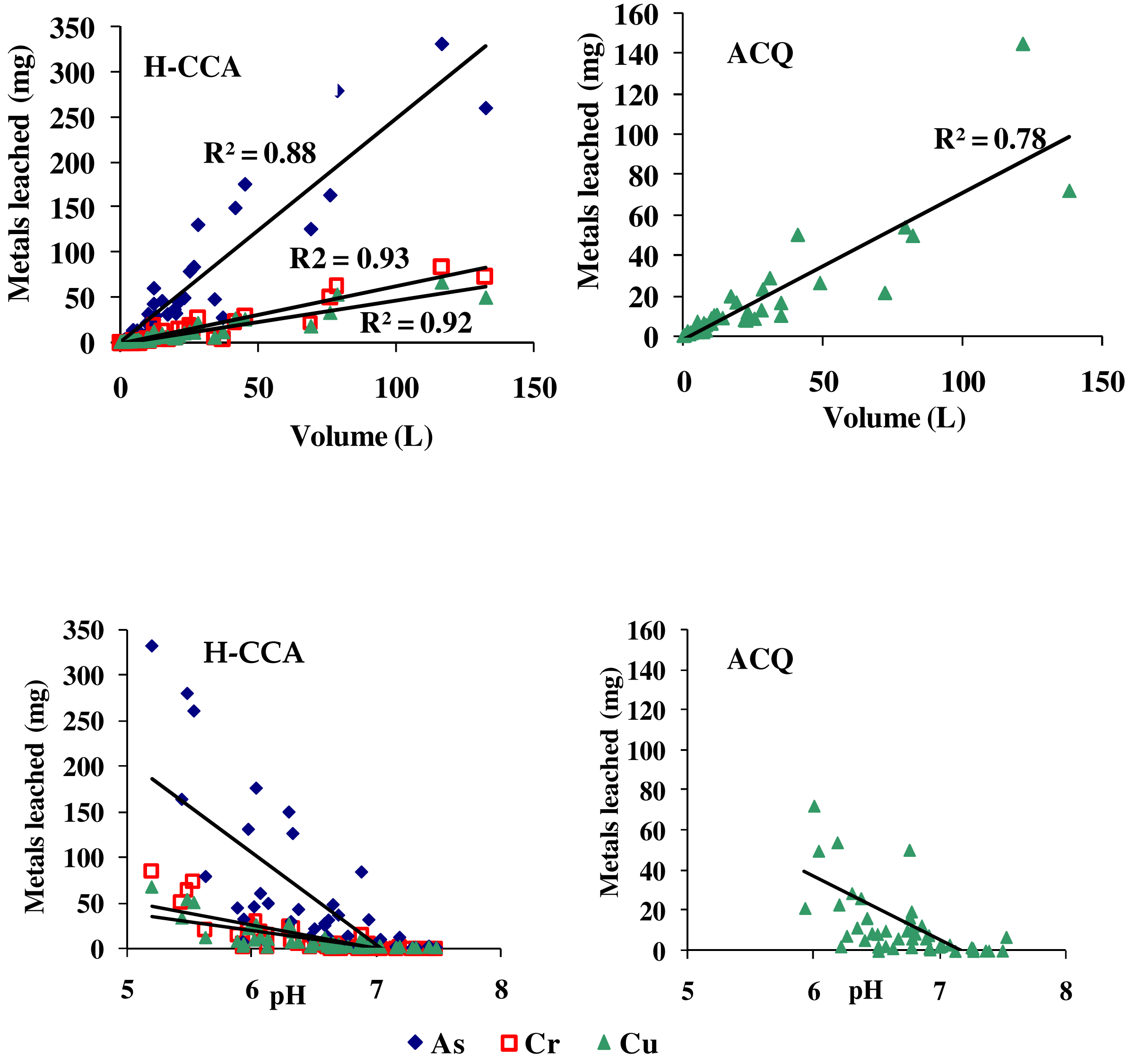


Figure A.4 Leached masses of metals relative to the collected leachate volume and its pH for H-CCA and ACQ.

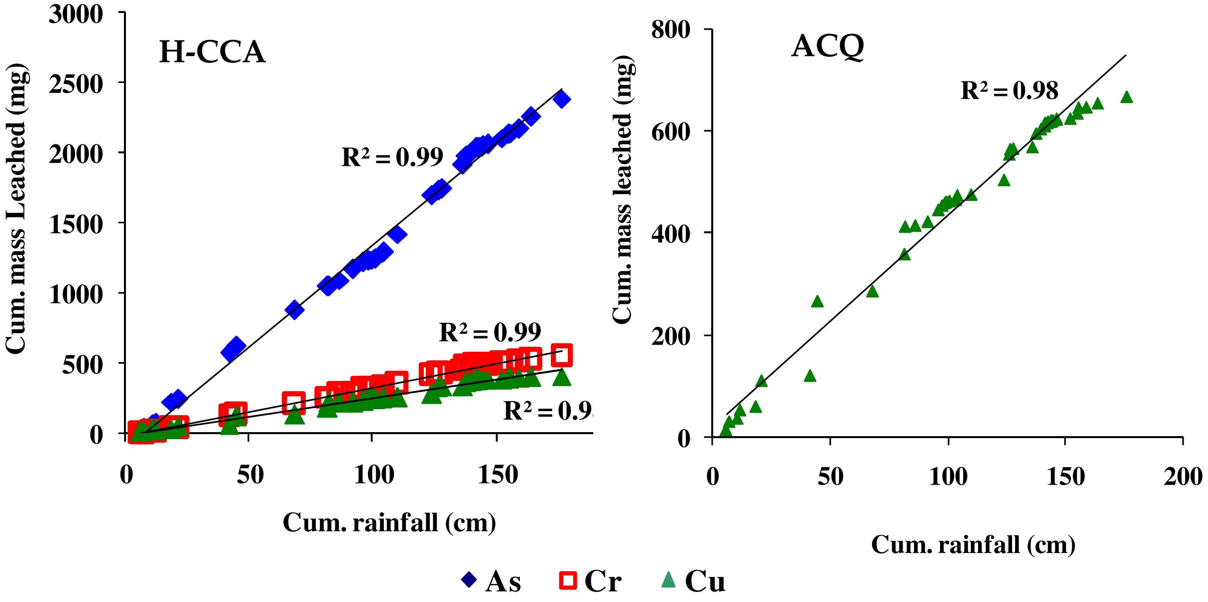


Figure A.5 Cumulative mass of metals leached versus cumulative rainfall for H-CCA and ACQ treated wood samples.

APPENDIX B: Supplementary figures for chapter 2

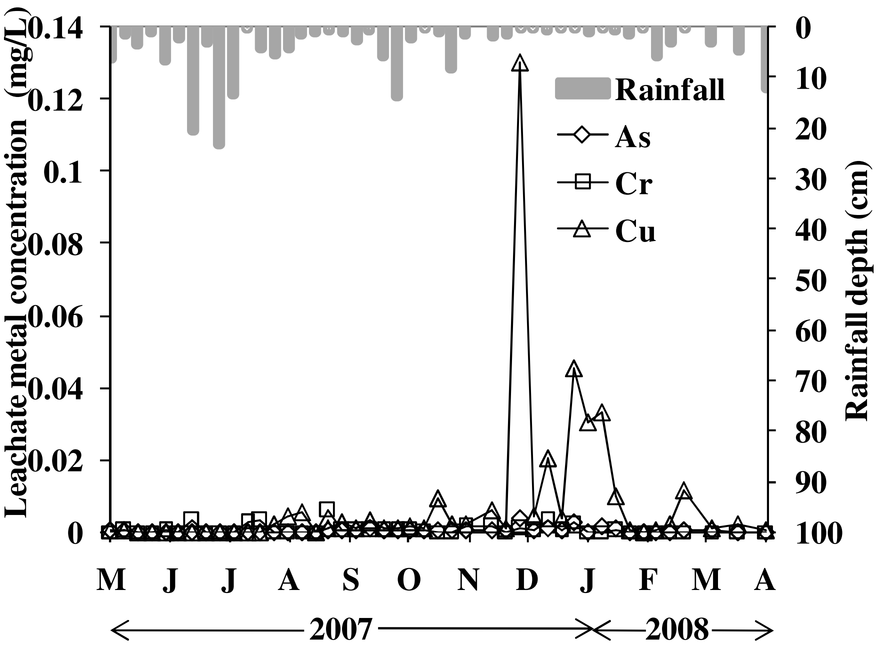


Figure B.1 Time series plots of rainfall and metals' concentrations in rainfall

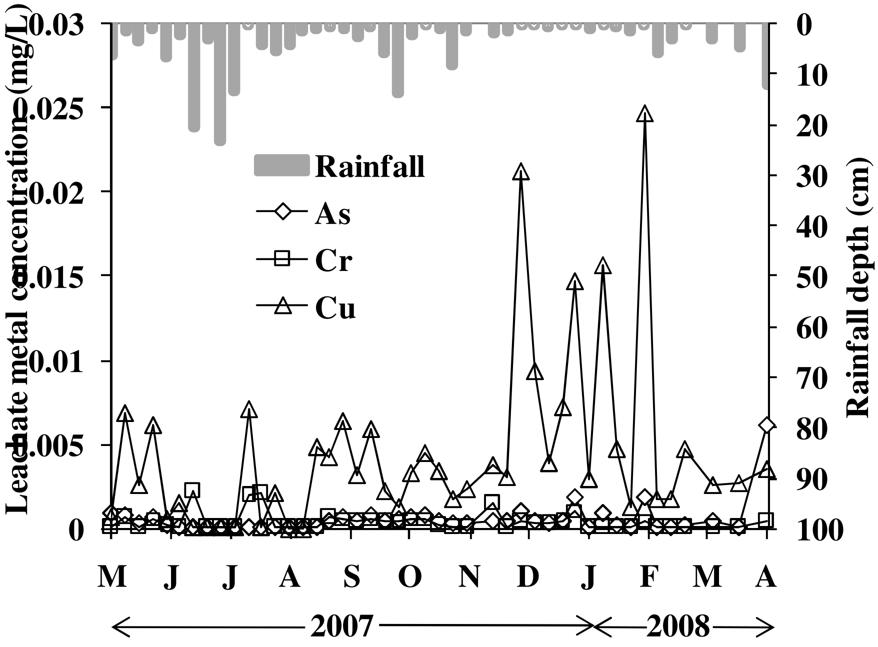


Figure B.2 Time series plots of rainfall and metals' concentrations in leachates for the untreated wood sample.

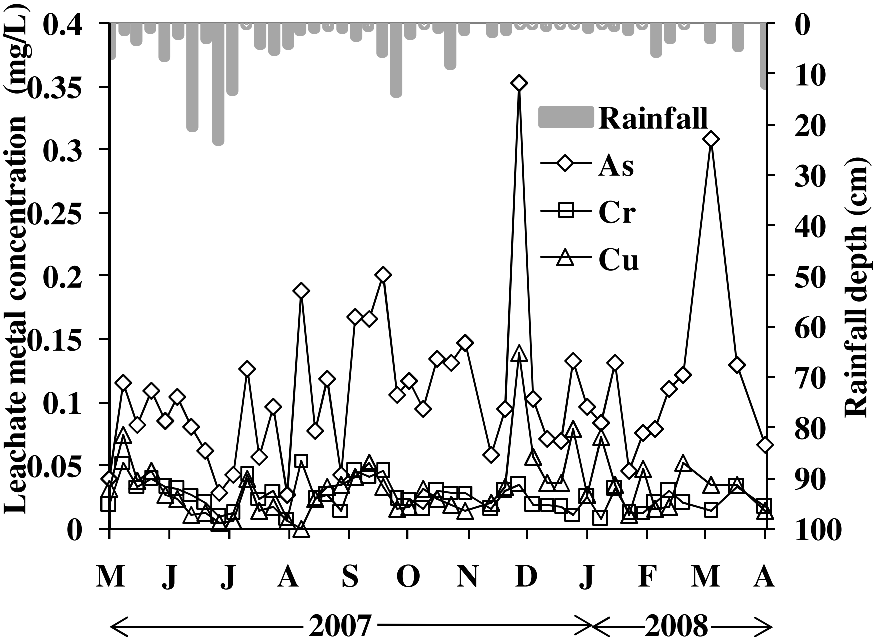


Figure B.3 Time series plots of rainfall and metals' concentrations in leachates for La-CCA treated wood sample.

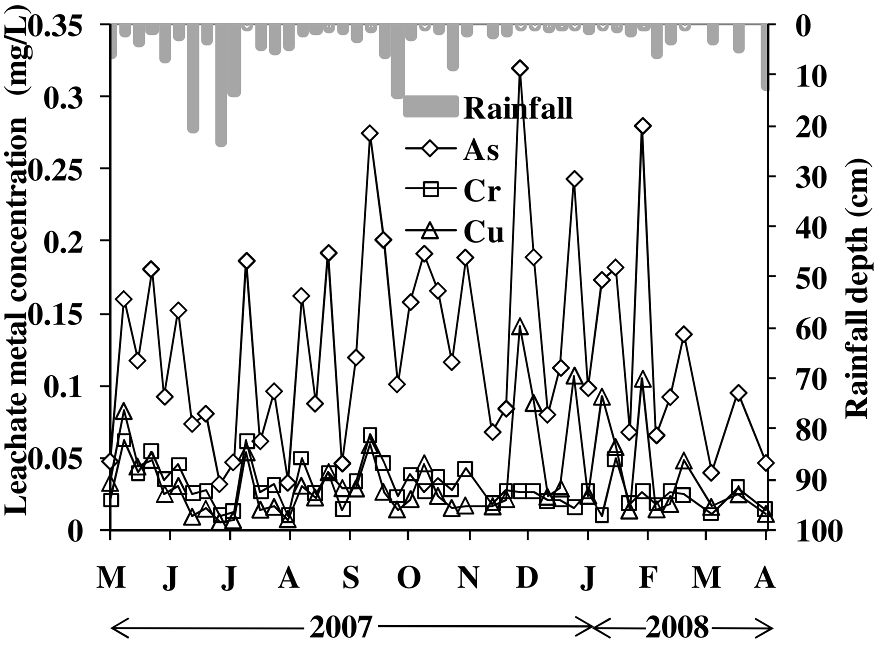


Figure B.4 Time series plots of rainfall and metals' concentrations in leachates for Lb-CCA treated wood sample.

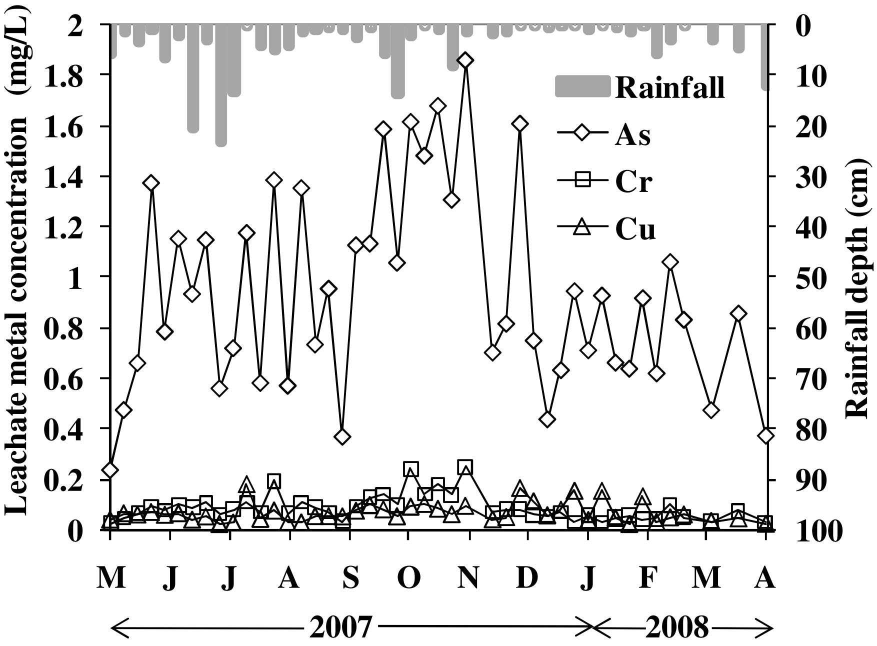


Figure B.5 Time series plots of rainfall and metals' concentrations in leachates for M-CCA treated wood sample.

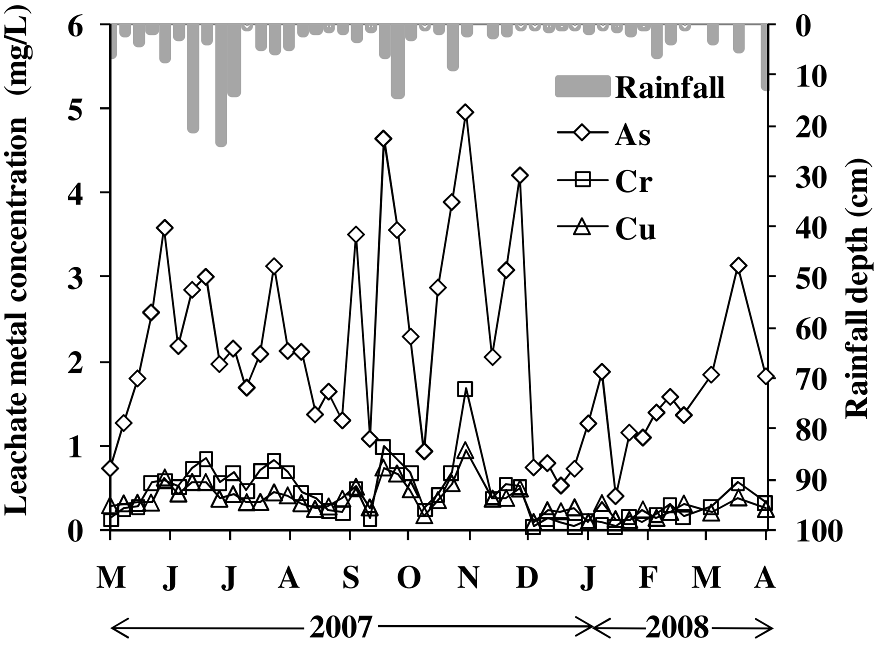


Figure B.6 Time series plots of rainfall and metals' concentrations in leachates for H-CCA treated wood sample.

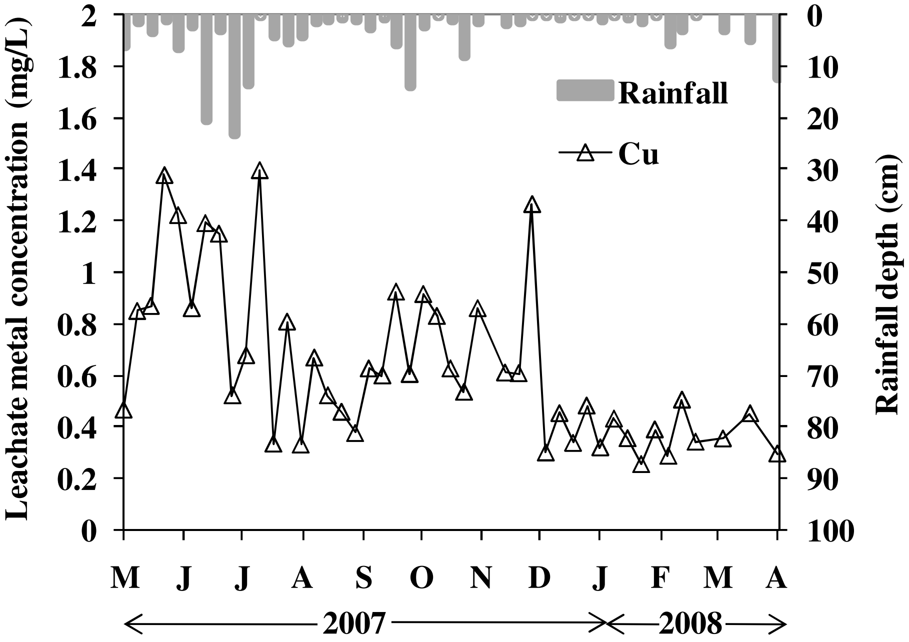


Figure B.7 Time series plots of rainfall and metals' concentrations in leachates for ACQ treated wood sample.

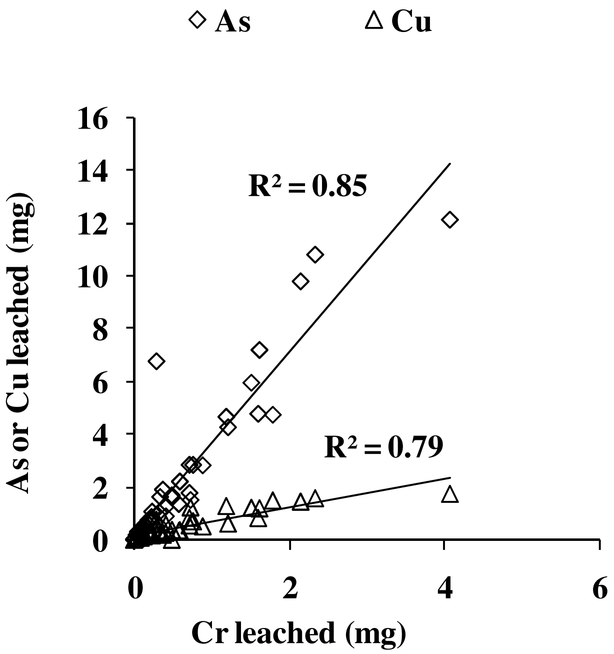


Figure B.8 Mass Leached of As and Cu relative to the mass leached of Cr for La-CCA.

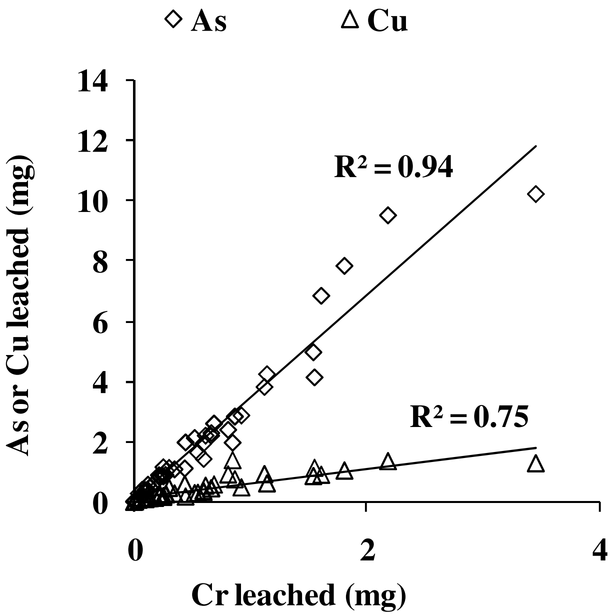


Figure B.9 Mass Leached of As and Cu relative to the mass leached of Cr for Lb-CCA.

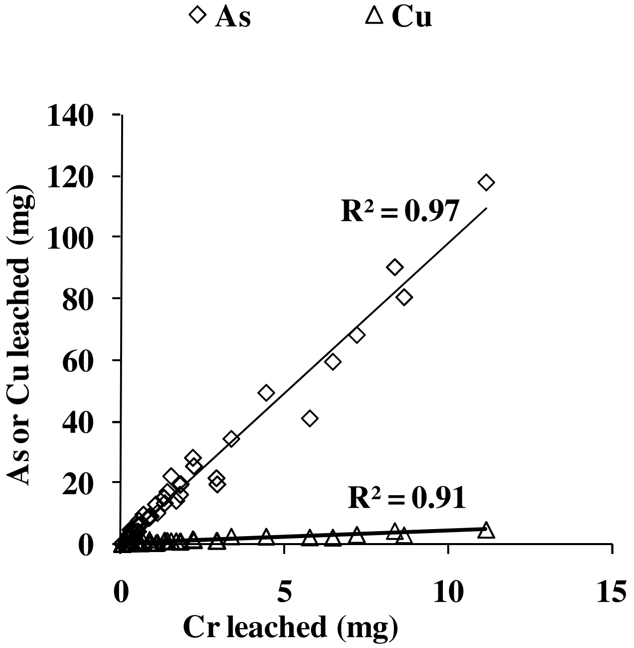


Figure B.10 Mass Leached of As and Cu relative to the mass leached of Cr for M-CCA.

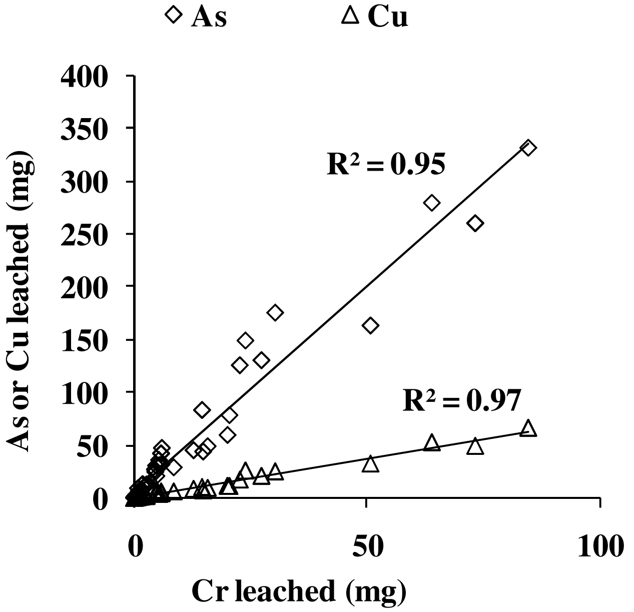
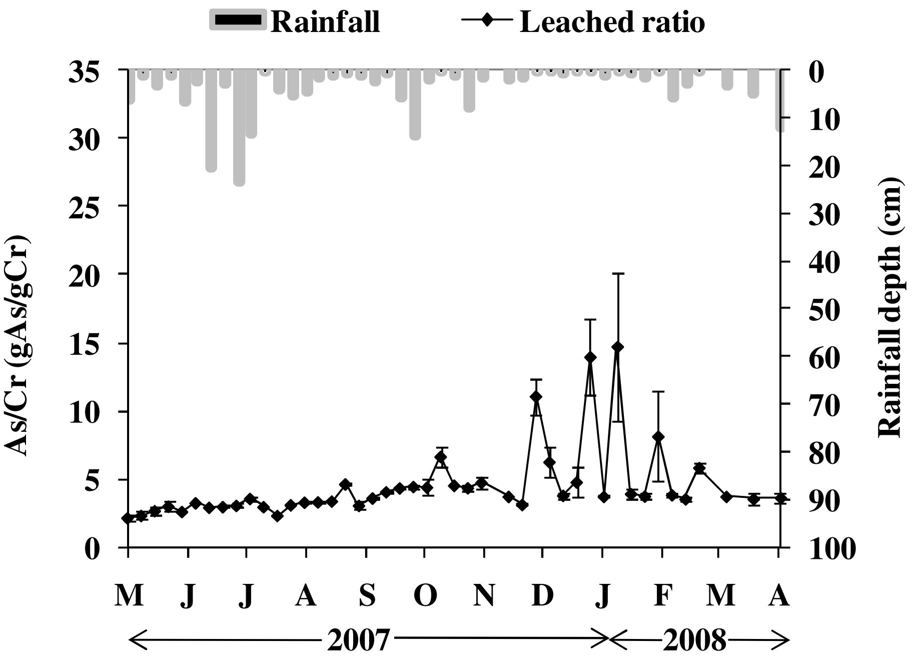


Figure B.11 Mass Leached of As and Cu relative to the mass leached of Cr for H-CCA.



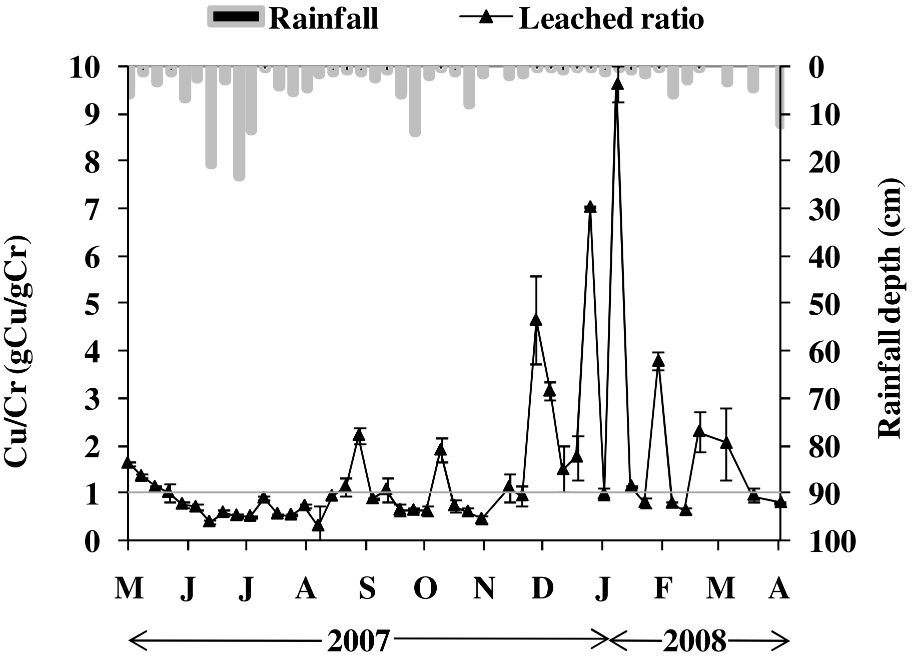
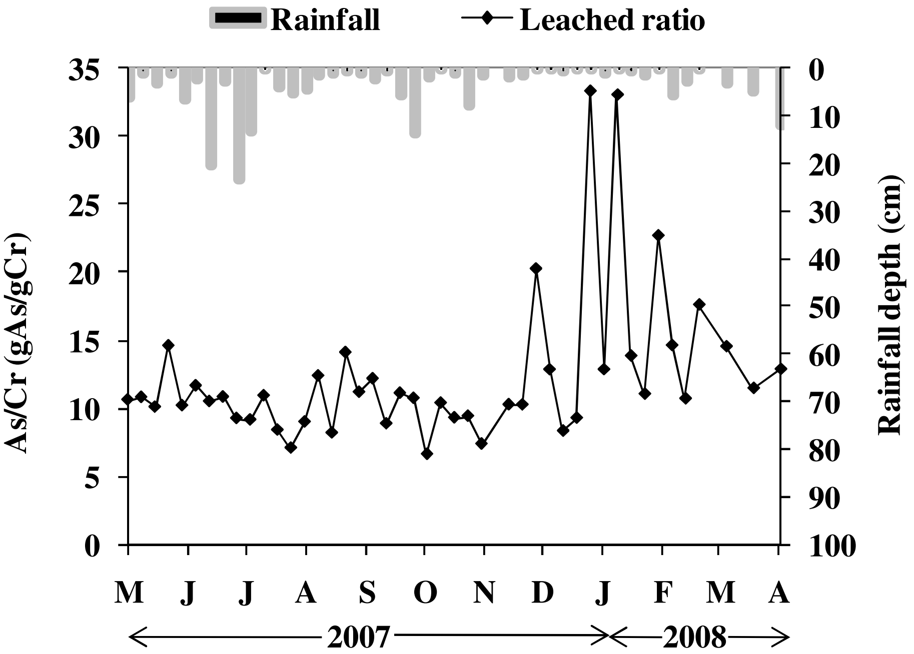


Figure B.12 Time series plots of ratios of metals' masses in leachates for H-CCA treated wood sample.



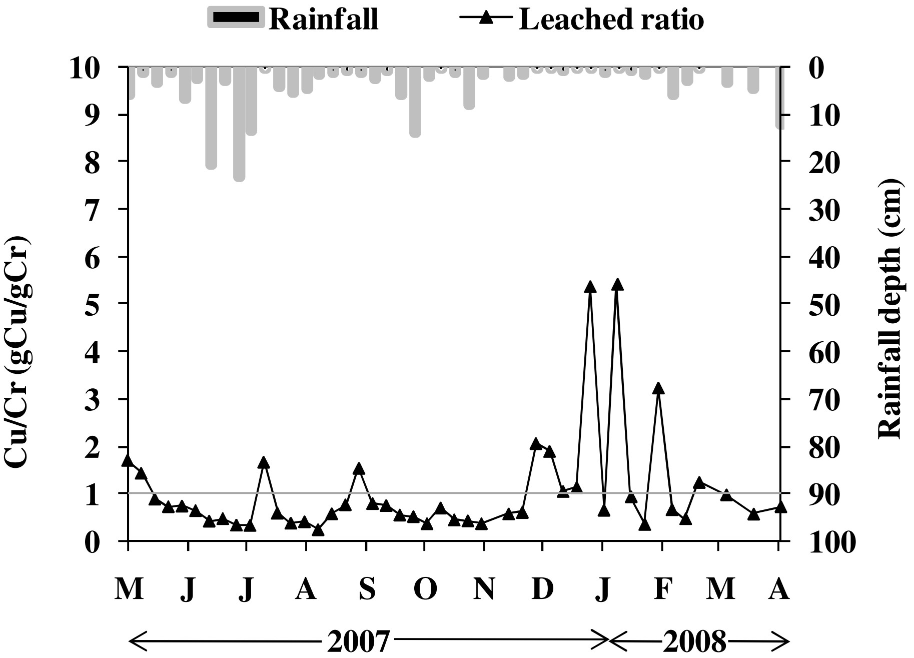
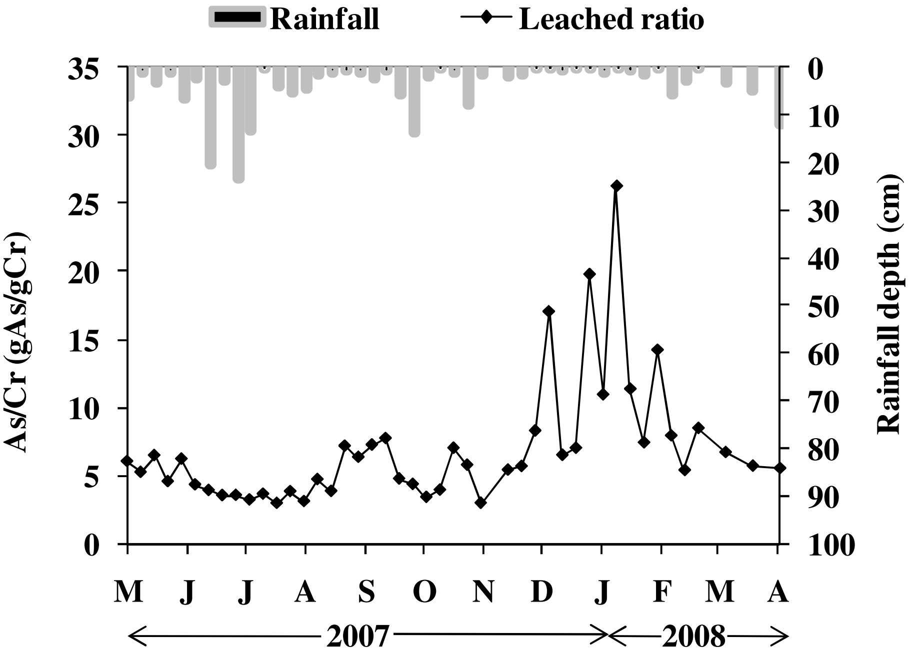


Figure B.13 Time series plots of ratios of metals' masses in leachates for M-CCA treated wood sample.



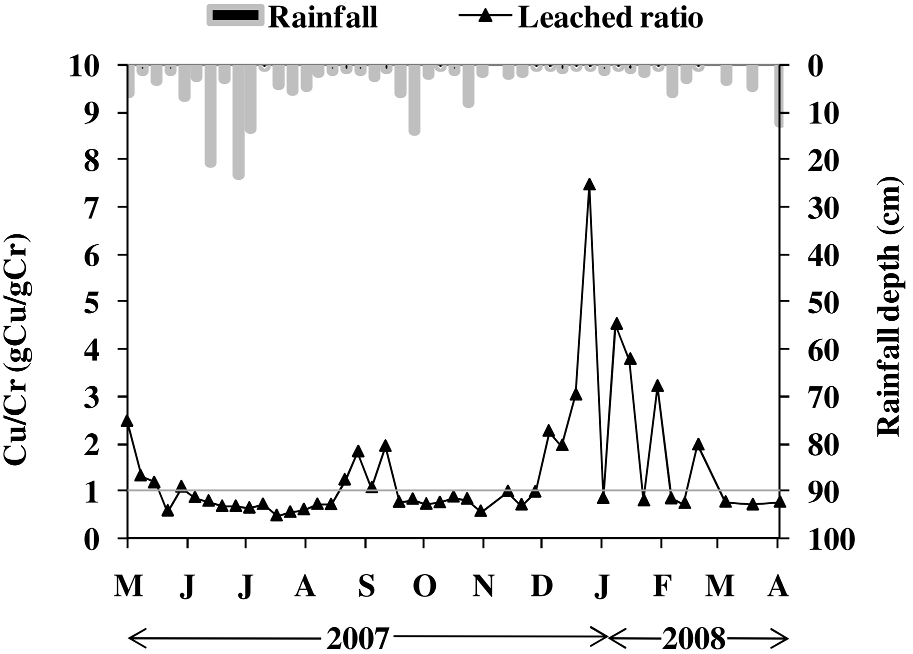


Figure B.14 Time series plots of ratios of metals' masses in leachates for H-CCA treated wood sample.

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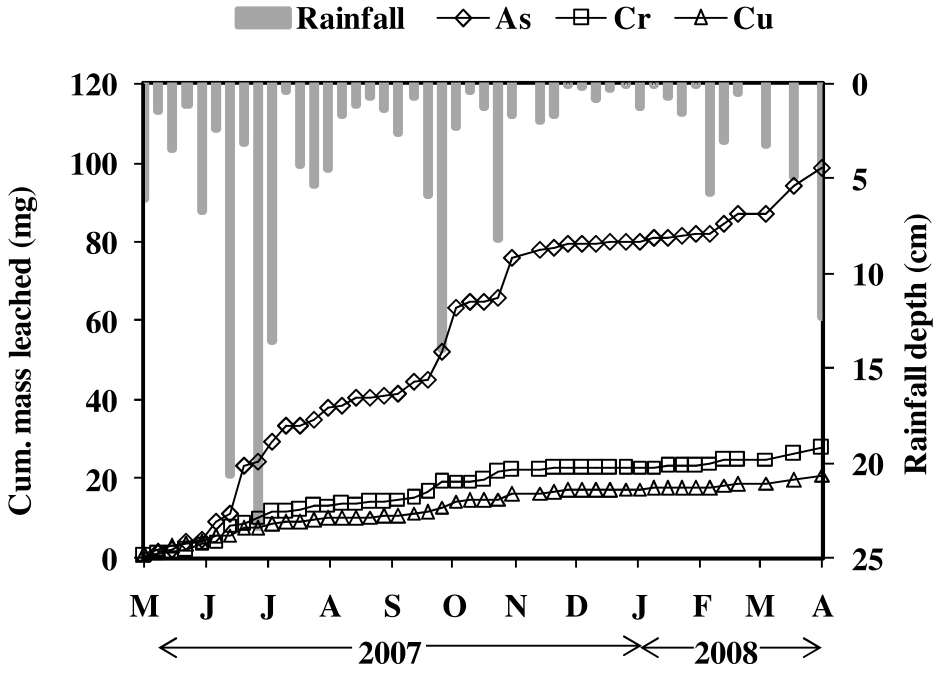

Figure B.15 Cumulative leaching of metals from wood over the experimental period for La-CCA.

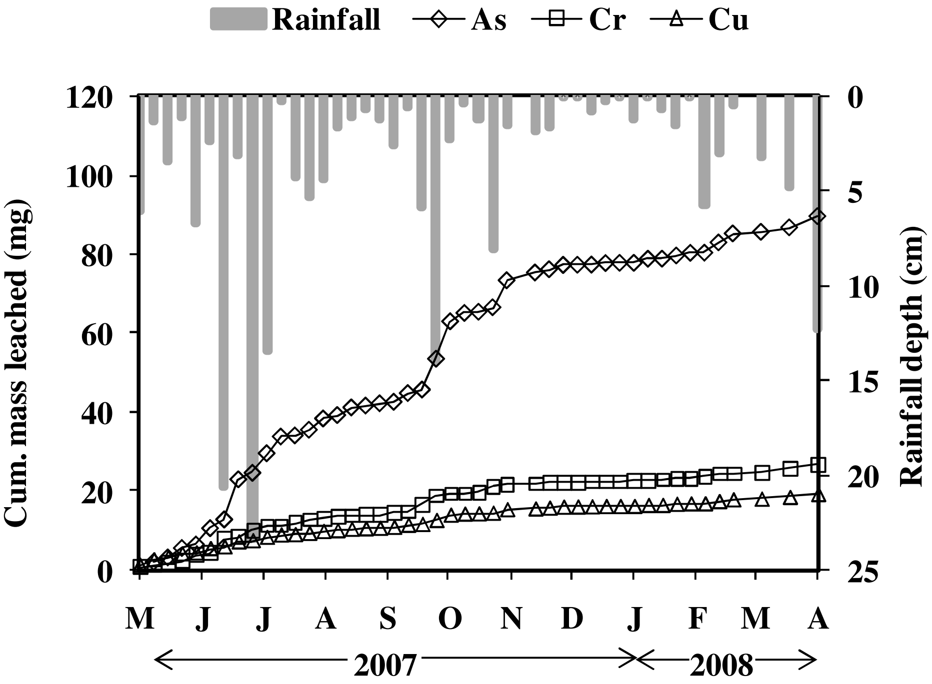

Figure B.16 Cumulative leaching of metals from wood over the experimental period for Lb-CCA.

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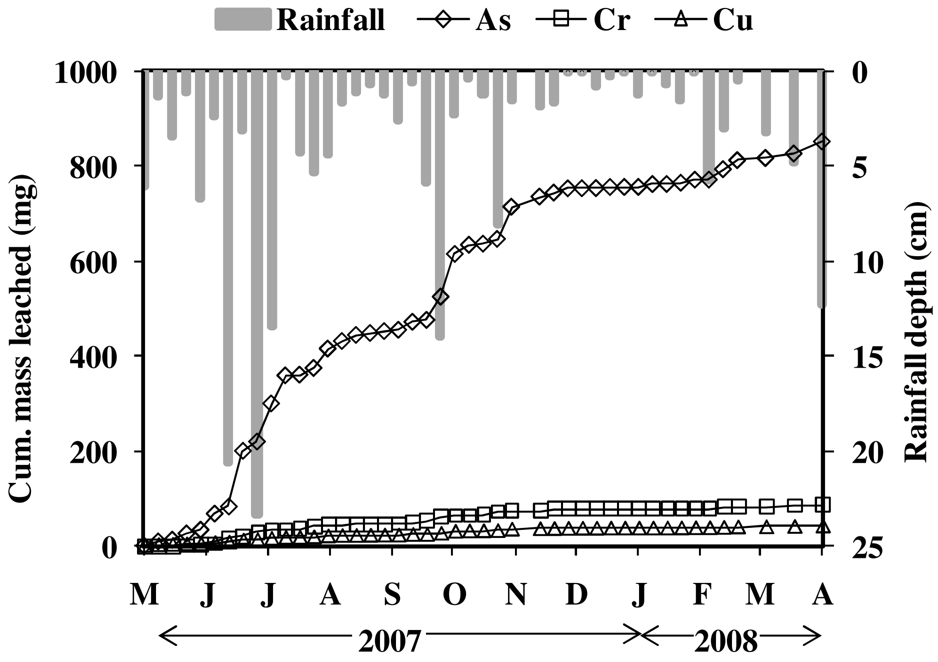

Figure B.17 Cumulative leaching of metals from wood over the experimental period for M-CCA.

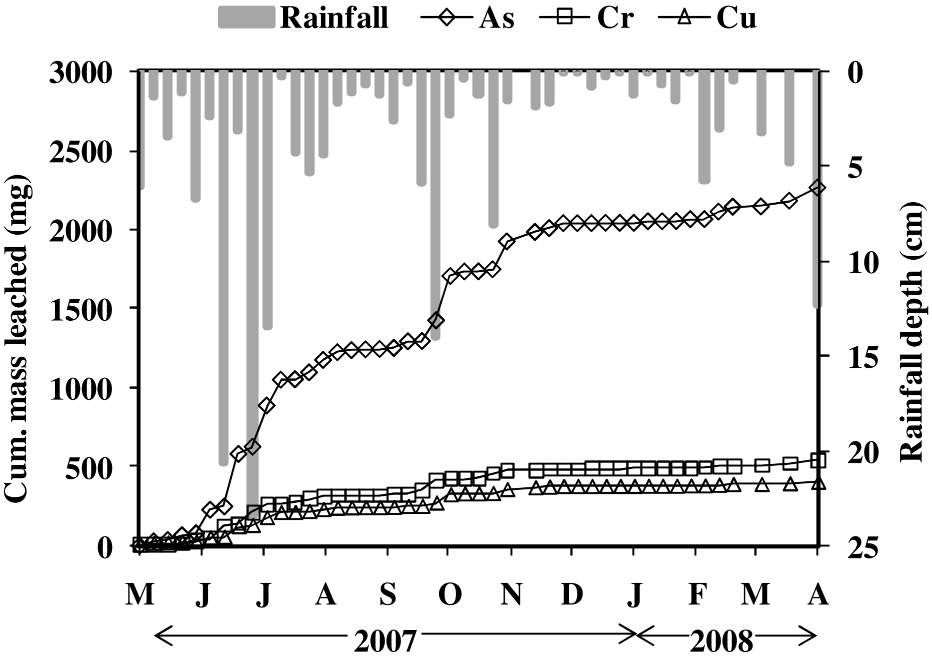

Figure B.18 Cumulative leaching of metals from wood over the experimental period for H-CCA.

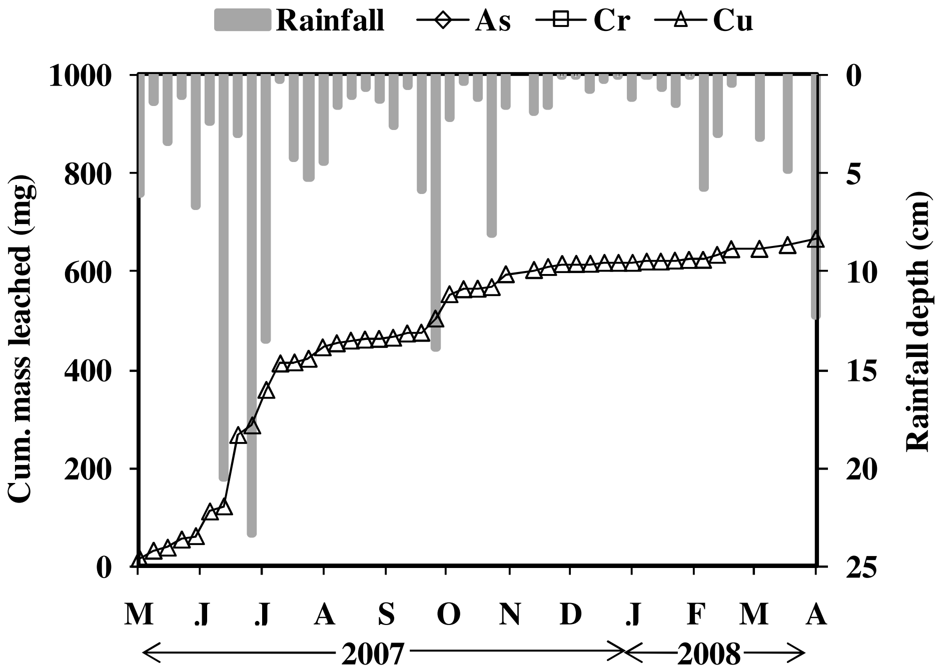

Figure B.19 Cumulative leaching of metals from wood over the experimental period for H-CCA.

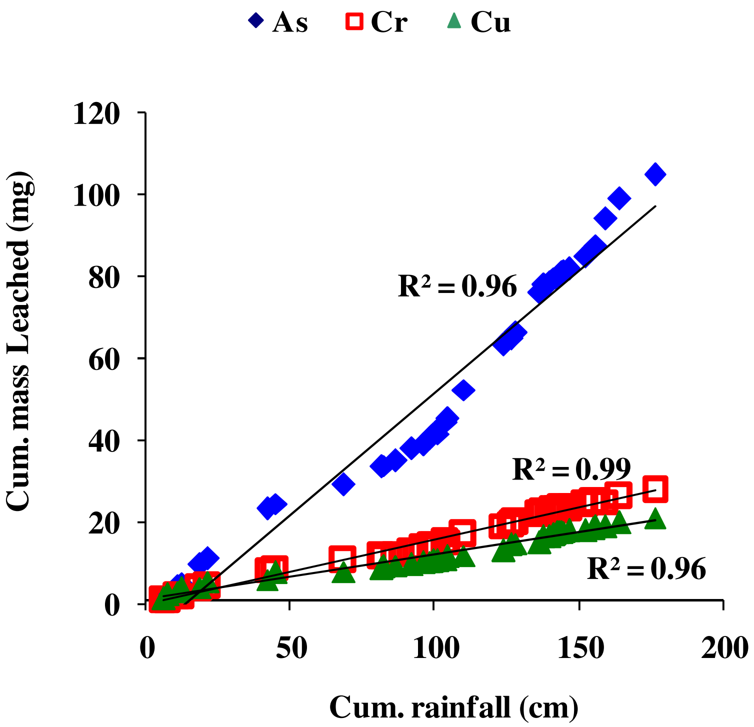

Figure B.20 Cumulative mass of metals leached versus cumulative rainfall for La-CCA.

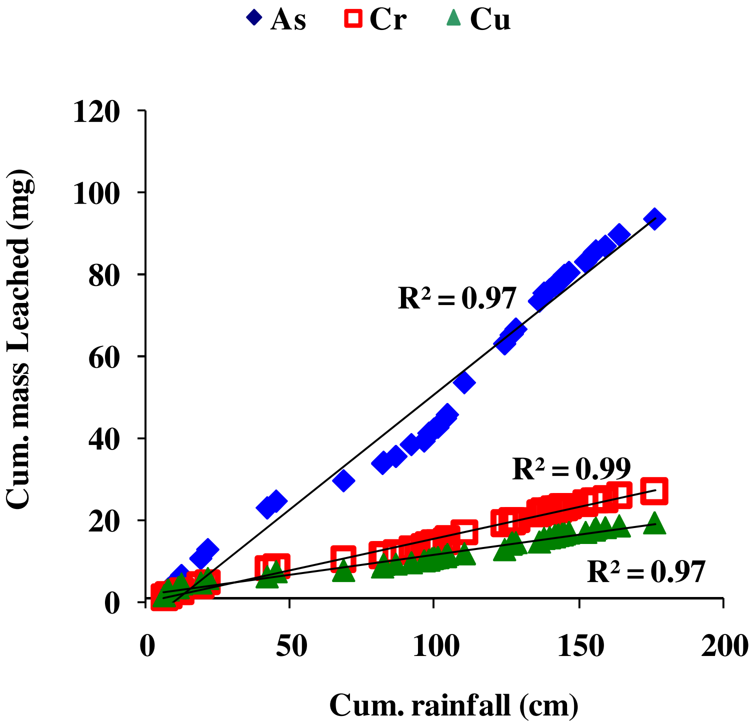

Figure B.21 Cumulative mass of metals leached versus cumulative rainfall for Lb-CCA.

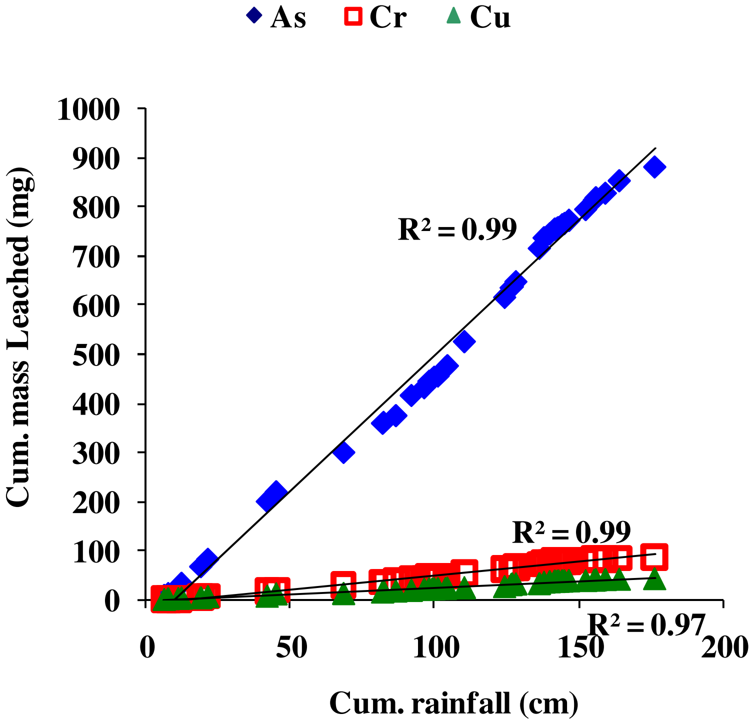

Figure B.22 Cumulative mass of metals leached versus cumulative rainfall for M-CCA.

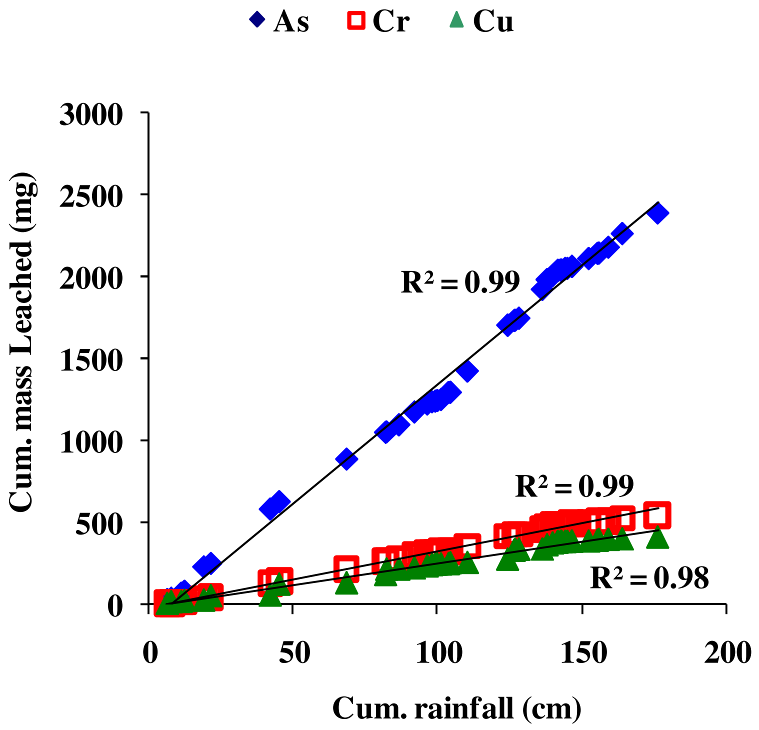

Figure B.23 Cumulative mass of metals leached versus cumulative rainfall for H-CCA.

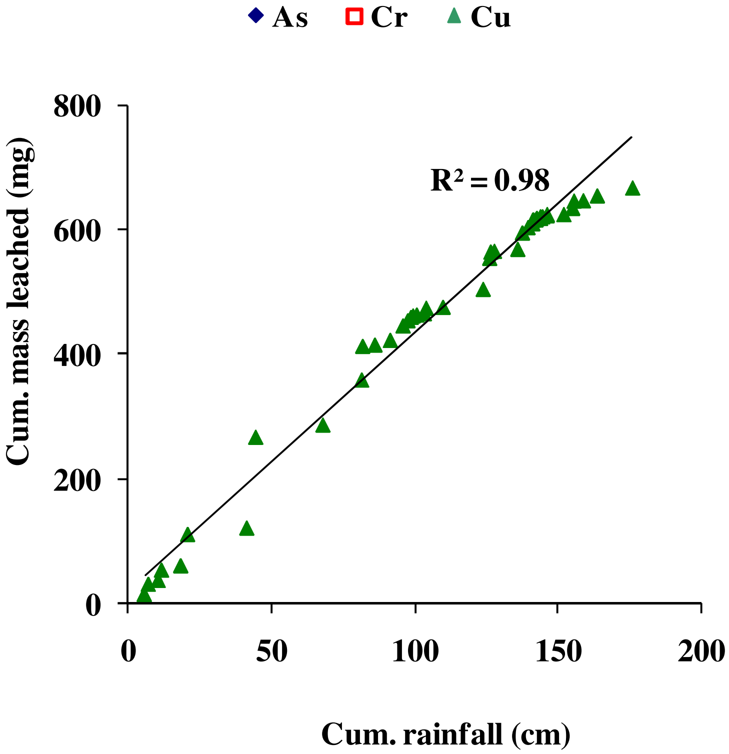

Figure B.24 Cumulative mass of metals leached versus cumulative rainfall for ACQ.

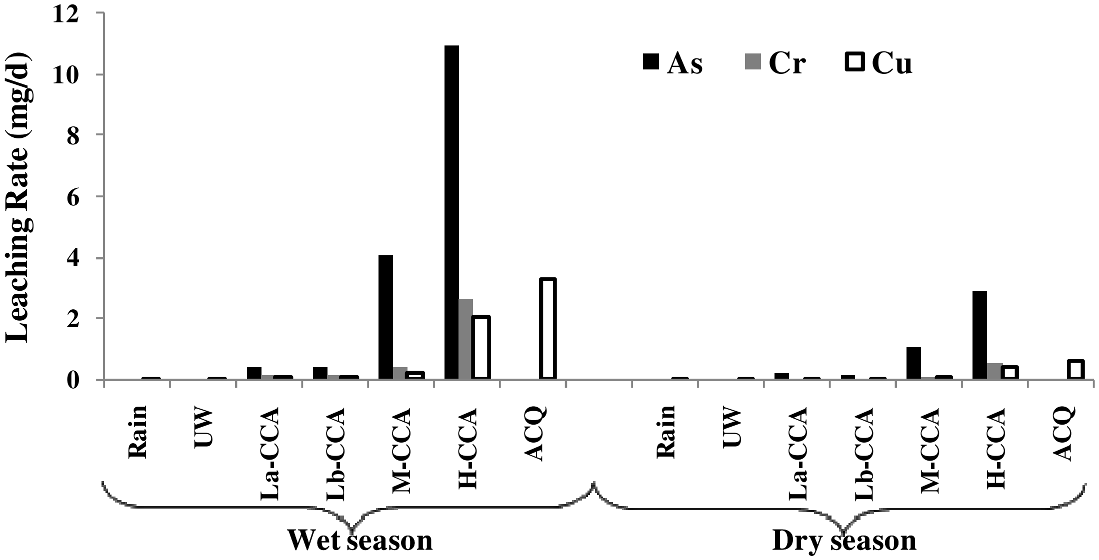

Figure B.25 Leaching rates of As, Cr and Cu leached during the wet and dry seasons.

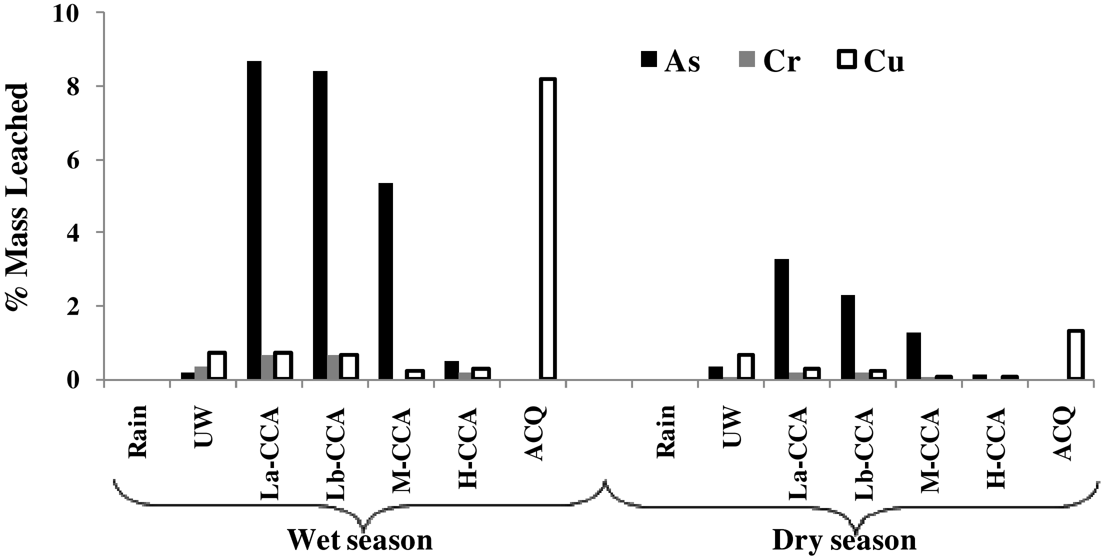

Figure B.26 Percentage leaching of As, Cr and Cu leached during the wet and dry seasons.

APPENDIX C: Justification for Equations 3.2 and 3.3

These equations relate the Cr and Cu concentrations in the wood as measured via XRF to those measured by graphite furnace atomic absorption spectrometry (GFAAS), a more traditional laboratory-based method. In chapter 2; six different types of Southern Yellow Pine wood samples were used to establish these relationships (Table C.1).

Concentrations of Cu and Cr in wood were determined by two methods, handheld-XRF and lab-analysis. The concentration measurement by handheld XRF (Innovx, α-2000S) was taken over several spots on the surface of wood pieces and avoiding knots, followed by averaging all measurements. Lab-analysis was done by analyzing the sawdust produced during cutting wood pieces to the specified dimensions, except for H-CCA, where sawdust was collected from 40 holes drilled to 1.5 cm distributed equally on its surface. Sawdust samples were digested according to the U.S. EPA method 3050B (U.S. EPA, 1996), and the concentration of Cr and Cu were measured by GFAAS (Model AAnalyst-600, Perkin Elmir, Shelton, CT, USA). Correlation between the two methods is shown in figures S1 (for Cu) and S2 (for Cr).

Table C.1 Characteristics of wood samples including number of pieces, dimensions, surface area, and wood volume.

Label[a]	No. of Pieces/shape	Dimension of each piece (cm)	XRF measurement (ppm)		GFAAS measurement (ppm)	
			Cr	Cu	Cr	Cu
UW	2, rectangular	57 x 17.8 x 3.8	74.22	0.04	14.4	0.03
ACQ	3, rectangular	49.5 x 13.8 x 3.8	275	0	5009	1780
L-CCA	3, rectangular	49.5 x 14.1 x 1.8	5655	1645	3695	1095
M-CCA	4, rectangular	8.8 x 58.5 x 8.8	7694	2680	3338	1570
H-CCA	1, cylindrical	L = 74, D = 28.5	58762	14500	10097	7500

[a] UW: untreated wood, ACQ: ACQ treated wood, L-CCA, M-CCA, and H-CCA: CCA-treated wood at low, medium, and high retention levels.

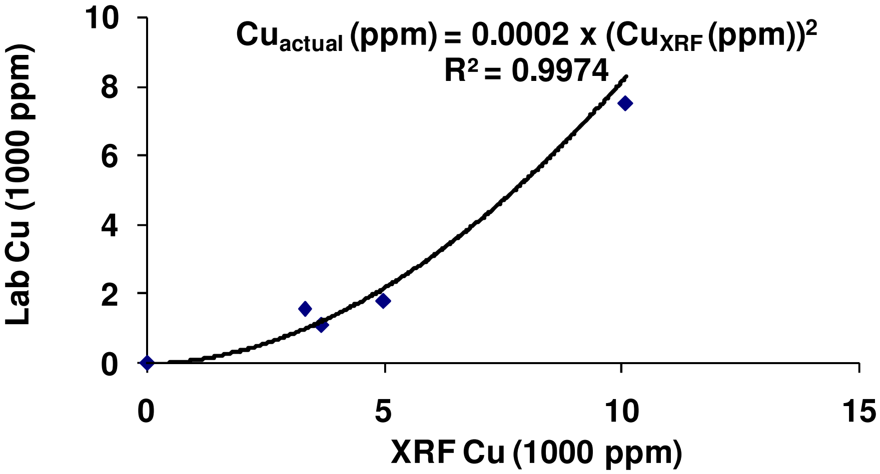

Figure C.1 Correlation between Cu concentrations in preserved wood pieces measured on the surface of wood by handheld XRF and by GFAAS.

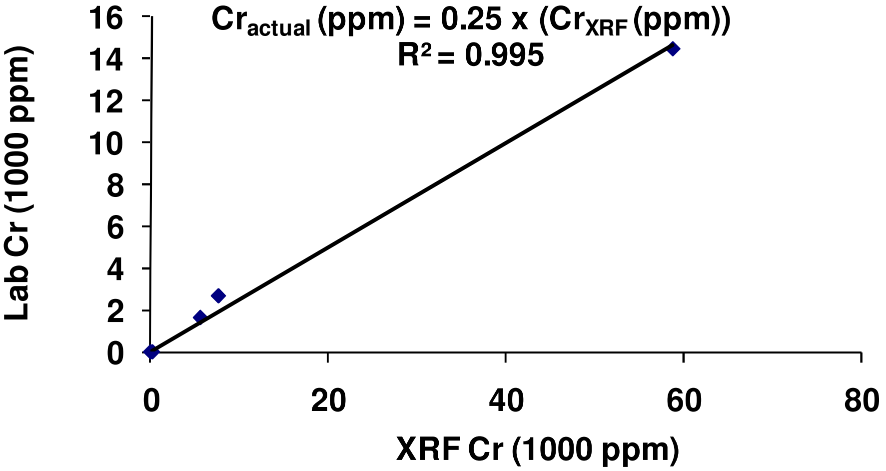

Figure C.2 Correlation between Cr concentrations in preserved wood pieces measured on the surface of wood by handheld XRF and by GFAAS.

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