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An Experimental Study of the Environmental Impacts of CCA-Treated Wood Waste Land Application

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Abstract

Chromated copper arsenate (CCA) has been the most commonly used wood preservative in the UK; up until its partial ban in 2004. The preservative prolongs the service life of wood by 20-50 years by making it resistant to biological attack. As such, in-service CCA treated wood is expected to be a major component of the UK wood waste stream in the future. Concerns over the impact of the chemical constituents of this treatment on both the environment and human health have prompted the introduction of legislation to ensure that such waste is disposed of safely in Hazardous Waste Landfills. Despite this, studies have shown that this waste can still enter into the landscape mulch market due to inadequate detection methods and increasing societal pressures to recycle.

A series of laboratory and field-based simulations were used to quantify leaching of copper, chromium and arsenic from CCA-treated wood waste mulch and evaluate the factors involved in promoting leaching. The distribution and behaviour of the metals in the soil column and leachate were also assessed. The samples generated in the study were analysed for a range of physico-chemical measurements, elemental and speciation concentrations.

Results show that arsenic, chromium and copper leaches from CCA waste wood; at times to levels exceeding regulatory thresholds by two to three orders of magnitude. Furthermore, the more toxic and mobile species of arsenic (As III) and chromium (Cr VI) were detected in both soil and leachate samples. A mass balance was produced which demonstrated that CCA wood tends to leach on initial exposure to a leachant and also during weathering of the wood. When in contact with soil, metal(loid) transport is reduced due to complexation reactions. With higher water application or where the adsorption capacity of the soil is exceeded, the metal(loid)s are transported through the soil column as leachate. Overall, there was a loss of metal(loid)s from the system that could be due to loss of water, volatilisation of arsenic and plant uptake. Due to the toxicity and concentration levels of the leached elements identified in the current study, it is apparent that adverse environmental and human health impacts may result from direct and indirect exposure to the environmental media.

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Dedications

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Go Team Shpookey, Aku suka couou ☺.

List of abbreviations and acronyms

ANOVA	Analysis of Variance
BSI	British Standard Institute
CCA	Chromated Copper Arsenate
CCATWW	Chromated Copper Arsenate Treated Wood Waste
CEC	Cation Exchange Capacity
CRM	Certified Reference Material
CS	Chrome Azurol S
DEFRA	Department for Environment, Food and Rural Affairs
DGT	Diffusive Gradient Thin Film
DI	Deionised water
DOT	Disodium Octaborate Tetrahydrate
EA	Environment Agency
EC	Electrical Conductivity
EPA	Environmental Protection Agency
EQS	Environmental Quality Standards
EU	European Union
FAAS	Flame and Furnace Atomic Absorption Spectrometries
FDA	Fluorescein Diacetate
GC-MS	Gas Chromatography Mass Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry (GFAAS)
HG-AAS	Hydride Generation – Atomic Absorption Spectrometry
HPLC-MS	High Performance Liquid Chromatography Mass Spectrometry
ICP-AES	Inductively Coupled Plasma – Atomic Emission Spectrometry
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
IRGWP	International Research Group on Wood Protection
Laser AES	Laser plasma Atom Emission Spectroscopy
LIBS	Laser-Induced Breakdown Spectroscopy
LOD	Limit of Detection
LOI	Loss on Ignition
LOM	Limit of Measurability
MARS	Microwave Accelerated Reaction System
MC	Moisture Content

OM	Organic Matter
OPSI	Office of Public Sector Information
ORP	Oxidation Reduction Potential
PAN	1-(2-pyridylazo)-2-naphthol (a colour indicator for copper)
PCA	Principal Component Analysis
PS	Particle Size
RF	Radio Frequency
RHS	Royal Horticultural Society
RSD	Relative Standard Deviation
SD	Standard Deviation
SEM	Scanning Electron Microscope
SGV	Soil Guideline Values
SHE	Standard Hydrogen Electrode
SPLP	Synthetic Precipitation Leaching Procedure
TCLP	Toxicity Characteristic Leaching Procedure
TRADA	Timber Research and Development Association
UK	United Kingdom
USEPA	United States Environmental Protection Agency
UV	Ultraviolet radiation
WHC	Water Holding Capacity
WHO	World Health Organisation
WRAP	Waste Resources Action Programme
XANES	X-ray Absorption Near Edge Structure
XRF	X-Ray Fluorescence Spectroscopy

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1 Introduction

1.1 The Use of Wood Preservatives to Prevent Deterioration

Wood is a widely used construction material and remains a significant element in modern day infrastructure (Morrell, 2006). It has many benefits as it is a renewable resource, is a strong building material (depending on the species) and is easy to produce (Hingston *et al.*, 2001). However, wood species that are not naturally durable are highly susceptible to deterioration from a range of abiotic and biotic factors (Table 1-1).

Table 1-1: Agents of Wood Deterioration (adapted from Morrell, 2006)

Abiotic	**Biotic**
Chemicals	Bacteria
Physical wear	Fungi
Fire	Insects
Sunlight	Marine borers
Hydrolysis of Cellulose	Vertebrates

One approach to protecting wood from degradation is by treating it with certain chemicals that are toxic to biotic agents and can withstand abiotic factors. These chemicals come in a variety of formulations although the majority are water-based and contain heavy metals. Preservative treatment of wood has many benefits. Firstly, the service life of the wood is prolonged, particularly for wood exposed to extreme conditions. Secondly, the need to harvest forests for wood is reduced due to the extended service life. Finally, the strength and safety of structures is improved due to increasing resistance to deterioration (Morrell, 2006).

In the UK, chromated copper arsenate (CCA) has been the most extensively used preservative over the last 50 years due to its efficiency as a preservative, leach resistance compared to other preservatives and relatively low production costs (Murphy *et al.*, 2004). The preservative is inorganic with the typical components of arsenic (As_2O_5 arsenic pentoxide), chromium (CrO_3 chromic acid) and copper (CuO copper oxide) in varying proportions. Copper acts as a fungicide and molluscicide, arsenic is an insecticide and chromium is the fixing agent that reacts with both the wood and the other two metal(loid)s (Chirenje *et al.*, 2003; Townsend *et al.*, 2004).

1.2 CCA Pressure Treatment

During CCA treatment, wood is impregnated using high pressures. This involves inserting the wood into a cylinder (Figure 1-1) and immersing the wood in the preservative solution. A series of vacuum and pressure treatment cycles are then applied. Firstly, air is evacuated and then pressure raised, forcing the solution into the wood. Once the pressure is released, a series of vacuums are applied to ensure that excess solution is recovered (Morrell, 2006). Post-treatment, the wood is left for a 32 day fixation period (BSI 4072, 1999). During this time reactions take place between the chemicals and the wood, binding the elements to the wood (Brown *et al.*, 2003). Some of the copper binds directly to the wood as CuO, whilst the hexavalent chromium is reduced to trivalent chromium in the form CrO_3. The arsenic (As_2O_5) and the remaining copper react with the chromium to produce metal complexes that are resistant to leaching. During the treatment process, fixation is never 100% complete and some unfixed preservative remains on the wood (Morrell, 2006).

Figure 1-1: Wood Being Removed From a Pressure-treatment Cylinder (courtesy of WJ Components, Hull)

1.3 In-Service Release

The most significant leaching risks associated with CCA occur during the application of the preservatives and whilst the wood is in service (WRAP, 2004). In-service treated wood can degrade over time due to biological, mechanical and chemical degradation (Enviros Consulting & The Biocomposites Centre, 2004). CCA-treated wood is almost always in contact with soil, e.g. in applications such as decking, fencing, utility poles and walkways. Various studies have shown that release of the elements from CCA-treated wood can occur whilst in-service, causing significantly elevated levels of As, Cr and Cu in the surrounding soil (Stilwell & Gorny, 1997) and impact on soil quality (Solo-Gabriele *et al.,* 2003). Levels are usually highest at ground level and immediately adjacent to the structures, decreasing with depth and distance from the structures (Zagury *et al.,* 2003).

CCA-treated wood is also commonly used for structures that are exposed to water (for example jetties and wetland walkways), in both marine and freshwater environments. The wood used in these environments tends to have higher levels of the preservative due to the severity of the exposure conditions. Higher leaching risks are associated with exposure to seawater and static systems (Lebow *et al.,* 1999; Brown & Eaton, 2000) due to a higher ionic status and accumulation of the leached preservative. Furthermore, exposure to water has been shown to increase the mobility of the elements in the environment once leached under certain conditions (e.g. high pH, low Eh).

1.4 Environmental Risks Associated with Leaching of CCA-Treated Wood

The release of the elements from CCA-treated wood can potentially contaminate soil and water resulting in toxic effects to animals, plants and/or whole ecosystems. The chemical constituents are not readily biodegradable and can accumulate in flora and fauna (WRAP, 2004). This is particularly worrying considering the reports of the leaching of the CCA chemicals into soil.

Weis and Weis (2004) studied leaching in a marine setting. They found that the metal(loid)s accumulated in the sediments and are ingested and accumulated in organisms that live directly on the wood and sediment and those that consume contaminated prey. Toxic effects on organisms are wide-ranging and include DNA damage at the cellular level, reduced growth, altered behaviour and mortality of individuals and diminished species richness/diversity at the community level. Kennedy (2004) looked at effects on soil-dwelling invertebrates and found that there was degradation in global density and also community structure. Comfort (1993) discussed a case study from Tasmania where livestock exhibited chronic copper poisoning in a pasture where CCA timber had been stored. Another case involved poultry where CCA wood was used as sawdust and shavings for litter. The birds ingested and absorbed the elements from the wood which accumulated in their bodies (Comfort, 1993).

Plants can also be adversely affected by CCA contamination in soils. Grant and Dobbs (1977) found that very high levels of CCA completely stopped the growth of all plants tested (beans, carrots and tomatoes), whilst at lower concentrations, growth was inhibited. Furthermore, the plants all had arsenic levels higher than guidelines for human health. Cao & Ma (2004) and Rahman *et al.* (2004) also looked at growth of crops in contaminated soils, in their research the soils were adjacent to CCA-treated utility poles and in raised garden beds where CCA lumber was used. They found that arsenic levels in crops were significantly higher in contaminated soils than in controls.

1.5 Human Health Risks Associated with Leaching of CCA-Treated Wood

1.5.1 Potential Contaminant-Receptor Pathways

There are many potential human health risks associated with leaching from CCA-treated wood. However, these are only present if there are contact pathways between the contaminant and receptor (Environment Agency, 2009). One contact route is through ingestion. This may be through accidental ingestion of environmental media (contaminated soil/water) or from CCA structures (i.e. hand to mouth contact in children) (Hemond & Solo-Gabriele, 2004; Shalat *et al.*, 2006). It has been established that crops can take up arsenic in contaminated soils (Grant & Dobbs, 1977; Cao & Ma, 2004; Rahman *et al.*, 2004) and livestock may also accumulate heavy metals resulting from CCA contamination. There is therefore a risk of arsenic, chromium and copper exposure to humans who eat the contaminated crops, livestock and livestock products.

Dermal absorption via cuts and lesions is another potential pathway for the uptake of arsenic. Hemond & Solo-Gabriele (2004) looked at childrens exposure to arsenic from CCA-treated wooden decks and playground structures. Uptake can be through contact with various parts of the body such as hands, lower legs and forearms. Dermal absorption has also been shown to occur in occupational settings. Comfort (1993) interviewed workers in the Tasmanian Park and Wildlife Service who frequently dealt with CCA wood. It was found that a quarter of the respondents suffered from skin rashes, infections from cuts, splinters and dust, sore throats and dizziness after handling treated timber, often without protection.

Inhalation of CCA components is a final contact route. This is especially problematic during size reduction of CCA-treated wood (such as sawing, chipping) where inhalation of small wood particles may occur. Although not directly linked with leaching, burning of CCA wood produces emissions of the toxic trivalent arsenic that can be readily inhaled (Wasson *et al.,* 2005). The resultant ash has high levels of metals from the burning process, as high as 36% of the ash by weight (Solo-Gabriele *et al.,* 2002) and is classed as a hazardous waste (Solo-Gabriele *et al.,* 2002).

1.5.2 Toxicity of Arsenic, Chromium and Copper

The health impacts associated with arsenic are generally more severe than for chromium or copper (Fleming & Trevors, 1989; Patch & Maas, 2006) as it plays no beneficial role in the body and is not safe at any levels of dosage (Plant *et al.,* 2004). Exposure is usually associated with the wood after treatment and tends to be at chronic low-level doses (Patch & Maas, 2006). The species of the metal(loid)s involved, influences its toxicity (Plant *et al.,* 2001) with inorganic species as found in CCA wood tending to be more toxic than organic species. Furthermore, there are differences in the inorganic species with Cr (VI) being 100-1000 times more toxic than Cr (III). As (III) is also more mobile and five times more toxic than As (V) (Rahman & Naidu, 2009).

Exposure to arsenic can result in a wide range of health issues. Arsenic is a known carcinogen (Plant *et al.,* 2004) and chronic exposure can cause cancers of the skin, lung, liver and bladder (Morton & Dunnette, 1994; Chen & Lin, 1994; Zakharova *et al.,* 2002; Plant *et al.,* 2005; Rahman *et al.,* 2009). The contribution of arsenic to cancer is due to the inhibition of DNA repair, resulting in mutagenic effects (Patch & Maas, 2006). Furthermore, arsenic may play a role in causing cancers and tumours to behave more aggressively (Patch & Maas, 2006). Teratogenic effects include complications and mortality at various stages of foetal development (Yip & Dart, 2001).

Chronic exposure of arsenic also manifests in a variety of health problems around the body including the respiratory, pulmonary, cardiovascular, gastrointestinal, haematological, hepatic, renal, neurological and immunological systems (Rahman *et al.,* 2009). Dermal effects are a common result of chronic exposure and include pigmentation, hyperkeratosis and ulceration/skin lesions. Cardiovascular effects associated with the thickening of the inner layer of the wall of blood vessels leads to vascular disease (DEFRA, 2002b). Respiratory effects include laryingitis, tracheae bronchitis, shortness of breath, nasal congestion and perforation of the nasal septum (Mandal & Suzuki, 2002). Gastrointestinal effects tend to be mild and include irritation and discomfort (Mandal & Suzuki, 2002). Hematological effects vary from anaemia and leucopoenia (Mandal & Suzuki, 2002). Hepatic and renal injury results from accumulation of arsenic in the liver and kidney (Burns, 1998; Mandal & Suzuki, 2002). Arsenic causes immunotoxic effects including immunosupression and lymphopenia (Burns, 1998). Significant effects to the nervous system such as neuritis, pins and needles and weakness are usually manifested over a few weeks to months (Burns, 1998). Exposure may also cause diabetes mellitus (Plant *et al.,* 2004; Rahman *et al.,* 2009).

Copper is generally non-toxic in chronic exposures to mammals and is essential for human metabolism (Flemming & Trevors, 1989; Plant *et al.,* 2001; Katz & Salem, 2005). Trivalent chromium is an essential element that is closely associated with insulin and therefore sugar metabolism. It also functions in carbohydrate and lipid metabolism for the utilisation of amino acids (Steinnes, 2009). On the other hand, hexavalent chromium can cause irritation and sensitization of the skin as well as corrosion of mucous membranes of the respiratory system and cancer of the lungs (Katz & Salem, 2005).

The health effects associated with arsenic, chromium and copper illustrate the importance of studying the impacts of CCA-treated wood. Due to the varying toxicities of the metal(loid)s, emphasis will be placed on the study of arsenic and chromium as well as the inorganic species as these present the highest risks.

1.6 Legislation Governing CCA Wood Waste

The risks of leaching from CCA wood and impacts on the environment and human health prompted the introduction of legislation worldwide. The chemical components used in CCA treatment, the treatment process and end-uses are highly regulated in the UK. The Marketing and Use of Arsenic Directive 2003/2/EC that was transposed into UK regulations (The Environmental Protection – Controls on Dangerous Substances Regulations, 2003) introduced a partial ban on the use of CCA as a preservative in the UK from the 30th of June 2004 (HSE, 2009). The ban also extended to the use of CCA-treated timber. Treated timber can only be placed on the market or reused if it is used for ‘professional and industrial use where the structural integrity of the wood is required for human or livestock safety and skin contact by the general public is unlikely’ (OPSI, 2005) (see Table 1-2). However, the restrictions do not apply to existing wood that is in service.

Table 1-2: Permitted and Prohibited Uses of CCA Wood according to the EU Marketing and Use Directive (2003/2/EC)

Permitted Uses	Prohibited Uses
Structural timber in public and industrial buildings (no human contact)	In residential areas
In bridges and bridgework	In any application where there is a risk of repeated skin contact
As constructional timber in inland freshwater areas and brackish waters, e.g. jetties	In marine waters
As noise barriers	For agricultural purposes
In avalanche control	In any application where the treated wood may come into contact with intermediate or finished products intended for human and/or animal consumption
In roadside safety fencing and barriers	
In earth retaining structures	
As electric power transmission and telecommunication poles	
As underground railway sleepers	
As debarked round conifer livestock fenceposts	

An amendment to the Directive 2006/139/EC implemented in the UK under the Controls on dangerous Substances and Preparations (Amendment) Regulations 2007 added definitions for the use, reuse and second hand market within the EU.

It has been established that CCA-treated wood leaches chemicals whilst in-service, particularly from the surface of the wood. However, limited leaching results in levels of CCA can still be high in the wood when taken out of service, particularly in the unexposed portions of the wood (Christensen *et al.*, 2006). CCA wood waste is identified as hazardous under the Hazardous Waste England and Wales Regulations 2005 and the List of Waste Regulations (WRAP, 2004; Environment Agency, 2005; OPSI 2005; DEFRA, 2006). At the end of its service life, CCA-treated wood waste must be disposed of in hazardous waste landfills unless the risk of the chemical components can be reduced (DEFRA, 2000). In response to the legislation, measures have been put in place to reduce the use of CCA by employing more environmentally friendly alternatives, pre-treatment to remove the harmful components, reusing CCA-treated wood waste for industrial application and to some degree recycling it.

1.7 CCA-Treated Wood Waste Trends in the UK

Although the use of CCA as a wood preservative is decreasing, it will still be a major component of the wood waste stream due to its long service life of 20-50 years

(Christensen *et al.,* 2006) and extensive use to date (WRAP, 2005). A study conducted by Murphy *et al.* (2004) on future projections of the CCA wood waste stream for the UK found that the amount of CCA-treated wood requiring disposal in 2004 was 62,000m^3. This figure is projected to increase to 870,000m^3 by 2061. Furthermore, the proportion of CCA-treated timber within the post-consumer wood stream is predicted to increase from 0.9% in 2001 to 12.3% in 2061 (Murphy *et al.,* 2004). Therefore, managing this waste and ensuring safe disposal will still be a major issue well into the future.

1.8 Leaching Studies Involving CCA-treated Wood Waste

Due to the risks from this material and future projections showing increases in disposal of CCA wood, several recent scientific studies have looked at the leaching properties of this waste and potential environmental and human health impacts (Cooper *et al.,* 2000; Townsend *et al.,* 2003a; Jambeck, 2004; Khan *et al.,* 2004; Shibata *et al.,* 2005; Solo-Gabriele *et al.,* 2005; Townsend *et al.,* 2005; High, 2006; Jambeck *et al.,* 2006; Khan *et al.,* 2006b; Shibata *et al.,* 2006; Hasan *et al.*, 2008). These have found that CCA-treated wood waste can leach significant amounts of arsenic, chromium and copper into the environment whilst in-service and during disposal. Townsend *et al.* (2003a) and Shibata *et al.* (2005) reported that this waste can inadvertently find its way onto the landscape mulch market due to a combination of the requirement to recycle wood waste and problems with detection of CCA components in wood. This wood usually arises from construction and demolition processes (Townsend *et al.,* 2003a; Shibata *et al.,* 2005). The authors found that leachable arsenic in commercial wood mulch was attributed to the presence of CCA-treated wood. The potential for environmental contamination lies with the larger surface area of the chipped wood particles used in this product, rendering the harmful chemicals more easily leached (Townsend *et al.*, 2003a; Yoon *et al.,* 2005). This could be a major problem in the UK particularly due to the legislation governing this waste and its classification as hazardous requiring mandatory disposal in specially designated landfill sites.

1.9 Project Motivations

The motivations for the current project arose from the potential environmental and human health impacts resulting from leaching of CCA-treated wood waste. This is compounded by future waste management challenges for this waste stream and evidence that it can inadvertently enter the landscape mulch market despite strict regulatory controls. This research aims to expand on previous leaching studies to determine the environmental effects associated with leaching of CCA-treated wood waste following application as soil mulch.

Research into this area of waste disposal was discussed at a conference for the IRGWP entitled ‘Future Directions Regarding Research on the Environmental Impacts of Preservative-Treated Wood’ (Solo-Gabriele, *et al.,* 2004c) where currently under-researched areas were considered. They identified research gaps in the field concerning the fate/attenuation of leached preservative components in soil, transformations of CCA elements, movement through soil and contamination of mulch with CCA.

This study will be placed in a UK context with regards to the natural conditions that the experiment is exposed to. To date there have been no studies that have looked at leaching characteristics of CCA-treated wood waste, let alone mulch exposed to the English climate. Therefore, this study is necessary to evaluate the potential for leaching so that comparisons can be drawn with English regulatory thresholds for arsenic, chromium and copper. The Soil Action Plan for England (DEFRA, 2004) addresses the need to minimise contamination of soils (from metal(loid)s, hydrocarbons, pathogens, organic pollutants and/or substances that enrich soils with nutrients). It also stipulates the need to protect soil functions, the environment and human health. This theme resounds in legislation covering soil and water such as Soil Guideline Values (SGV) and water Environmental Quality Standards (EQS) which provide intervention values for harmful substances, which if exceeded, can pose a threat to the environment or human health (Jeffries, 2005).

Many of the environmental impact studies of CCA-treated wood to date have focused on laboratory experiments (Yamamoto *et al.,* 1999; Lebow *et al.,* 2004; Yoon *et al.,* 2005). Although useful data have been gained from these experiments they cannot replicate natural conditions. Laboratory studies usually involve using accelerated laboratory techniques with artificial rainfall. Field studies on the other hand generate useful data particularly on in-service structures that can’t be moved. However in this setting there is very little control of the factors studied. A controlled lysimeter study allows exposure to natural conditions with some degree of control over the environmental variables.

Lysimeters are containers filled with soil of a given volume and depth with leachate collection systems at the base (Lanthaler, 2004). Field lysimeters have been employed to look at the effects of burial of CCA-treated wood waste although no studies have been found that look specifically at effects of applying CCA-treated wood waste as a soil mulch and studying its effects on the topsoil, the horizon where most of the heavy elements accumulate (Bergman, 1983; Bergholm 1989; Dagan, *et al.*, 2006). To gain a more holistic view of the leaching process, a mix of field studies and laboratory experiments were used in this work.

1.10 Aims and Objectives

The aims and objectives of this thesis are based on the issues outlined in this chapter. They are as follows:

1. To quantify the leaching of arsenic, chromium and copper from CCA-treated wood waste mulch using a combination of field and laboratory based experiments.
2. To evaluate the distribution and movement of the elements between the wood mulch, soil and leachate.
3. To determine the inorganic arsenic and chromium species present in soil and leachate.
4. To determine the factors responsible for leaching from CCA-treated wood waste mulch.
5. To compare the levels of arsenic and chromium in the soil and leachate with UK regulatory thresholds.
6. To evaluate the potential implications of the results for environmental and human health.

1.11 Thesis Structure

This thesis contains eight chapters with this overview chapter forming the first. The second chapter outlines the methodologies used in the fieldwork including experimental set-up and sampling regimes. Chapter 3 outlines the laboratory methods employed to assess leaching from CCA wood using a synthetic leaching procedure and to analyse the samples collected in the field studies. Chapters 4, 5 and 6 will present the results of the study. Chapter 4 outlines the background conditions of the field studies and physico-chemical results. Chapter 5 presents the elemental concentration results for the wood and soil samples obtained during the lysimeter studies. Chapter 6 contains the results of the elemental concentrations in the leachate. Chapter 7 discusses all of the results and contains a mass balance over time to allow evaluation of the main mechanisms of leaching and partitioning of the elements in the wood soil and leachate. The conclusions from the studies are presented in Chapter 8.

1.12 Summary

This chapter has outlined the issues behind the extensive use of CCA wood preservative in the UK and potential environment and human health effects for in-service structures and waste wood. In this study a mixture of field lysimeter studies and laboratory experiments will be used to provide a holistic account of the mechanisms taking place following addition of CCA-treated wood waste as soil mulch.

2 Methods I

2.1 Introduction

This chapter outlines the field experiments and techniques used during this research. Five separate experiments were set-up to quantify the chemical and physical processes taking place in the soil following incorporation of CCA-treated wood waste as surface mulch. The study design and methodologies follow recommendations of Lebow *et al.* (2006).

A pilot study was used to optimise the experimental design and analytical techniques for a long-term study. This is presented in section 2.2. The planning, development and monitoring of a long-term leaching experiment under natural conditions using lysimeters is covered in section 2.3. Section 2.4 outlines a short-term lysimeter leaching experiment with a controlled watering regime. The final section, 2.5, describes a series of diffusive gradient thin film (DGT) studies designed to measure *in-situ* metals. Each of the field experiments is critically assessed to justify the approaches taken and suggest areas for improvement.

2.2 Pilot Study Experimental Design and Set-Up

Pilot studies are useful as they enable trialling of procedures, measuring instruments and methods of analysis. They also check the feasibility of a study (Leedy & Ormrod, 2005). The pilot studies consisted of three soil and woodchip treatments housed in lysimeters with differing sizes, shapes and set-ups. The combinations were selected to facilitate the evaluation of short-term effects on soil physical, chemical and microbiological properties resulting from varying drainage regimes, lysimeter properties and wood chip types.

2.2.1 Soil

The combination of shallow lysimeters and top soil allows the study of leachate transport in the uppermost soil layers where previous research suggest elemental accumulation occurs (Bergman, 1983; Bergholm, 1989; Cooper *et al.*, 2005; Dagan *et al.*, 2006). The soil used in all treatments was sieved and sterilised top soil (B&Q, 10x20L bags). Commercial topsoil was selected due to the minimal effort required to standardise the soil as it was homogenised prior to purchase. The disadvantage of this is that the origin and composition of the soil are unknown and it had to be analysed beforehand to ascertain its properties. The soil was well mixed and sealed during storage to prevent drying out.

2.2.2 Woodchips

Three types of wood chip were selected for the study and passed through a commercial chipper; deciduous, coniferous and varnished furniture wood. Deciduous wood is recommended by the Royal Horticultural Society for direct mulch application whereas coniferous wood requires composting beforehand (Maya, 2008). Freshly chipped samples were collected on the 15th December 2005 from woodland behind Thwaite Hall, Cottingham. Coniferous wood chips were collected on the 13th February 2006. Coniferous wood was included in the experiment due to its availability as a waste following the Christmas holidays and also as a ‘blank’ reference point for the CCA-treated wood waste. Softwood coniferous tree species are usually favoured for treatment with CCA (Plackett, 1984; Suzuki & Sonobe, 1993; Crawford *et al.,* 2002; Khan *et al.,* 2004) and were utilised as a control in a similar study by Townsend *et al.* (2003a). The varnished furniture wood chips were taken from the legs of a discarded wooden desk. Although not treated with CCA, this particular wood waste was selected to try out analytical techniques prior to using the more hazardous CCA-treated wood waste. Chipping took place on the 13th February 2006. All the chippings were stored separately in a cool dark room prior to experiment set-up on the 10th April 2006.

2.2.3 Lysimeter Prototypes

Lysimeters are conventionally used for water-balance and waste studies although they can be used to evaluate the behaviour of trace elements, heavy metals and microorganisms (Takamatsu *et al.,* 2007). Smith (2005) discusses the main parameters that need to be addressed when designing lysimeters. These include size and shape, length of time required for experiment, type and frequency of monitoring, environment and the number of replicates. Melcher & Peek (1996) studied the migration behaviour of a chromium-fluorine-boron preservative using different types of lysimeters to determine the influence of dimensions. They found that dimensions are of secondary importance in wood preservative leaching experiments but that there are limits such as a test period of at least 6 weeks, a lysimeter diameter of at least 5cm and the use of a transparent column. Three plastic lysimeter prototypes of varying proportions were selected to evaluate the impact of surface area, depth, drainage and inclination (Table 2-1).

Table 2-1: Lysimeter Properties

Lysimeter Number	Lysimeter Type	Lysimeter Inclination	Woodchip Type	Incorporation Depth
1	Large (A)	8 °	Deciduous	To base
2	Large (A)	10 °	Coniferous	To base
3	Large (A)	35°	Treated	To base
4	Small (B)	8 °	Control	To base
5	Small (B)	14 °	Deciduous	To base
6	Small (B)	14 °	Coniferous	To base
7	Small (B)	8 °	Treated	To base
8	Cylindrical (C)	0 °	Deciduous	Surface mulch (2cm)
9	Cylindrical (C)	0 °	Coniferous	Surface mulch (2cm)
10	Cylindrical (C)	0 °	Treated	Surface mulch (2cm)
11	Cylindrical (C)	0 °	Control	Surface mulch (2cm)
12	Cylindrical (C)	0 °	Deciduous	Surface mulch (2cm)
13	Cylindrical (C)	0 °	Coniferous	Surface mulch (2cm)
14	Cylindrical (C)	0 °	Treated	Surface mulch (2cm)

The largest prototype was 65cm x 35cm x 9.5cm deep with a surface area of 2275cm^2 (type A; Figure 2-1). The smaller prototype was 40cm x 29cm x 16cm deep with a surface area of 1160cm^2 (type B; Figure 2-2) and the final prototype was circular and 29.5cm in diameter x 23.5cm in height with a surface area of 683.49cm^2 (type C; Figure 2-3).

Figure 2-1: Largest Lysimeter Prototype (A).

Figure 2-2: Smaller Lysimeter Prototype (B).

Figure 2-3: Cylindrical Lysimeter Prototype (C).

Simple lysimeters were selected because there are less factors that need to be taken into account such as weighing mechanisms, intricate water application systems and leachate collection systems. The disadvantages include reduced replication of natural conditions.

More intricate lysimeters can be designed to collect leachate water gravimetrically at the base, simulate groundwater levels, incorporate weighing equipment and seepage water systems (Lanthaler, 2004; Takamatsu *et al.*, 2007). They can also be made out of more robust materials. However, the simple design proved adequate for the study as leachate was measured volumetrically on collection, materials were weighed out prior to experiment set-up and groundwater levels did not need to be simulated at the depth of soil studied.

Lysimeter types A and B were housed in specially designed wooden structures with 2 holes at the base for leachate collection (Figure 2-4). Different inclinations were also trialled to determine which was most effective for drainage. The cylindrical lysimeters (C) were purchased with drainage trays and pre-punched drainage holes. These were selected as they are widely used in gardening and provide an insight into leachate transport in smaller containers. They have also been used by other authors studying preservative leaching into soil (Wang *et al.,* 1998; Crawford *et al.,* 2002).

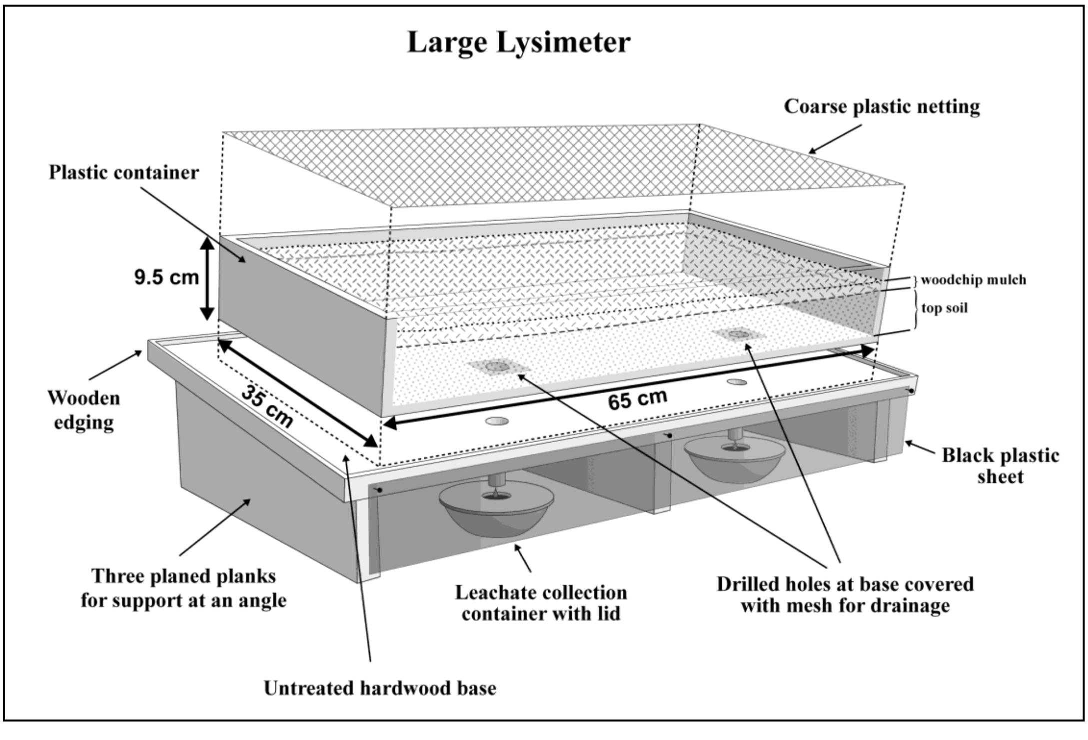

Figure 2-4 : Lysimeter Storage Frame Design

2.2.4 Treatments

The woodchips were first weighed out and the incorporation rate calculated. 20L of well-mixed soil was added to lysimeter prototypes A and B and 1kg of woodchips was added to the experimental lysimeters and mixed in thoroughly. This high incorporation rate and mixing into the soil as opposed to surface mulching, allows for maximum contact between the woodchips and soil to accelerate any potential effects in the short time-scale of the study. A control lysimeter was left untreated. The remaining soil was distributed evenly between the cylindrical lysimeters (C). A 2cm layer of woodchip was added to the surface as mulch on all but the control.

2.2.5 Experimental Conditions

The lysimeters were all placed in a secure outdoor location (University of Hull Botanic & Experimental Garden, Cottingham) and exposed to natural rainfall. Meteorological data for the experimental period was collected by the Ridings branch of the Environment Agency (EA) at their Cottingham site (Grid Reference : TA 048342), approximately 1.5km northwest of the experimental site. The lysimeters were also covered with a coarse plastic mesh to protect them from small animals.

2.2.6 Sampling Regime

Lysimeters were sampled for soil, wood and leachate over a 4-month period from 26th May 2006 following an intial 'settling period' of seven weeks. Lysimeter prototypes A and B were subsequently sampled every three weeks (16th June 2006, 7th July 2006, 28th July 2006 and 18th August 2006). Sampling of the cylindrical lysimeters was staggered due to the small surface area and material available for sampling.

On each sampling occasion the lysimeters were weeded if required. Mulching is known to suppress weeds to some extent and where this was not the case, removal was important to exclude the influence of plant uptake factors. Any leachate was collected from the base of all the lysimeters and stored in 100ml nalgene containers prewashed with ultrapure water (resistivity of 18Ωm cm^{-1}, Pearson *et al.*, 2007). The soil and woodchip mixtures were extracted from each selected lysimeter using the sampling methods outlined by Crepin & Johnson (1993). A rough core was taken using a trowel to 10cm depth and the samples transferred into plastic zip lock bags. As soon as possible after sampling, the soil and leachate samples were frozen to -20ºC and analysed within a month. Deep freezing rather than refrigeration was the preferred method of storage as this prevents microbial growth (Ahmad *et al.*, 2001).

2.3 Long-Term Leaching Study

The design of the main series of leaching studies was based on the results of the pilot study. The large lysimeter prototypes (A and B) were selected as they performed best in terms of drainage, ease of sampling and consistency of results. The prototypes were raised and plastic washers with tubing were attached to the base to facilitate leachate sampling. The collection dish was a plastic container with a drilled hole in the lid to allow the leachate to drip through from the tubing and prevent evaporation, overflow or external contamination. The lysimeters were all tilted at 3-4° and a black plastic cover was pinned to the front of the wooden framework to protect the leachate from insects and minimise evaporation (Figure 2-5).

Figure 2-5: Modifications to Lysimeter Design

2.3.1 CCA Wood Treatment

Due to the partial ban on the use of CCA preservative and manufacture of CCA wood in the UK, fresh wood was treated with CCA in the laboratories of the Forest Products Research Centre, High Wycombe. This provided a useful comparison with CCA-treated wood waste and allowed precise measurements of initial components. Scots Pine (*Pinus sylvestris* L.) wood was used as it is a common reference material and is highly permeable to wood preservative (Sawyer, *pers com.*, 2006). Sapwood blocks measuring 50mm long x 40mm wide x 10mm thick were identified with a solution of ortho-anisidine following a method developed by Stalker (1979) where sapwood is stained dull orange colour and heartwood deep pink to scarlet. The CCA solution used was Celcure 'A' formerly manufactured by Rentokil Ltd. (Table 2-2). The strength of the solution was determined with a nomograph using specific gravity taken with a hydrometer and thermometer according to BSI 4072: 2 (1987). This was found to be 0.8%. A modified version of vacuum impregnation following BS 4072 (1999) and BS

4072:2 (1987) was undertaken on a laboratory scale. The Scots Pine blocks were weighed and placed in a container inside the treatment vessel where an initial vacuum of -0.8 bar (-80kPa) was applied. The preservative was then added until the blocks were submerged and the vacuum released for thirty minutes. The blocks were left for a further two hours under 1 bar of atmospheric pressure to allow for impregnation. Uptake rate was calculated with the mean loading on the blocks of 5.86kg CCA/m^3 ± 0.04. The wood was left in sealed plastic bags for 24 hours before being brought back to the University of Hull and dried at ambient conditions (24 ± 2°C) for thirty two days in accordance with BS 4072 (1999) to allow for chemical binding of CCA components to the wood (Brown *et al.*, 2003; Lebow *et al.*, 2004).

Table 2-2: Celcure A Composition

	Celcure A (BS 4072 Type 1)
$CuSO_4.5H_2O$	32.6%
$Na_2Cr_2O_7.2H_2O$	41%
$As_2O_5.2H_2O$	26.4%
Total	100%

2.3.2 Field Based Methods for Identifying CCA-treated Wood Waste

2.3.2.1 Visual Observation

A number of methods are used to identify CCA-treated wood waste. Visual observation can be used to detect greenish tinges characteristic of wood treated with a copper compound. However, over time the wood can lose colour due to in-service leaching and therefore may be overlooked. Untreated wood waste can also be incorrectly identified as treated wood if covered with moss, green paints or stains. Blassino *et al.* (2002) conducted a study to determine the effectiveness of visually sorting CCA-containing wood waste piles and showed that it can reduce the amount of CCA-treated wood by 60-70%. However, Solo-Gabriele *et al.* (2004a) reported that visual sorting resulted in throughput of more than 9% CCA wood into an untreated pile, too high for recycling wood as mulch or wood fuel.

2.3.2.2 Chemical Stains

Chemical stains are relatively inexpensive to make and are easy to use on small quantities of wood. PAN (1-(2-pyridylazo)-2-naphthol) to identify metals in wood was originally formulated by Blassino *et al.* (2002) and is used to assist with sorting (Jacobi *et al.,* 2007). It is fast acting and reacts with metals to stain a destructive magenta colour, with untreated wood staining orange. However, this method can produce false positive results (Blassino *et al.,* 2002; Sawyer & Irle, 2005b; Jacobi *et al.,* 2007) and needs to be confirmed with more targeted stains. Rubeanic acid and Chrome azurol S (CS) are used for the detection of copper-based preservatives (Blassino *et al.,* 2002; Sawyer & Irle, 2005c). Chrome Azurol S reacts to give a strong blue colour whereas untreated wood remains yellowy orange. Rubeanic acid stains copper containing wood an olive green colour. CS is slower acting than the PAN stain but is useful to differentiate CCA-treated wood waste where results are uncertain. It is also less likely to suffer from interference reactions than rubeanic acid (Blassino *et al.,* 2002). The identification of copper compounds is an indication that the wood has been treated but does not identify the formulation used. Further identification is required to distinguish between CCA and other copper-containing preservatives. Stannous chloride is a stain that can be used to achieve this by identifying the arsenate portions that are specific to CCA-treated wood (Omae *et al.,* 2006).

2.3.2.3 Laser and X-Ray Technologies

More complex and accurate analytical methods can be used to identify CCA-treated wood in the field although these are time consuming and expensive. Laser-induced breakdown spectroscopy (LIBS) has been used in pilot studies to detect the presence of chromium, giving high sorting efficiencies of >95% (Solo-Gabriele *et al.*, 2006). This device operates on samples using a high powered laser to create a small microplasma at temperatures greater than 20,000°C. This area of the sample vaporises, emitting light from the atoms present through the process of atomic emission (Peylo & Peek, 1998). The intensity of the emission is then read on a spectrometer and correlated with the quantity of each element in the sample (Solo-Gabriele *et al.,* 2006). Despite the high sorting efficiency of this technology, the authors argue that it still requires further fine-tuning to overcome inefficiencies with readings taken from weathered, rotted and thick pieces of wood.

Solo-Gabriele *et al.* (2006) and Block *et al.* (2007) suggest the use of hand-held x-ray units (based on x-ray fluorescence spectroscopy) for identifying and quantifying CCA chemicals in wood. This works by using an excitation source (such as UV light) on the sample causing the atoms to become excited and fluoresce at specific energies for each element (Kalnicky & Singhvi, 2001). They found that they could use handheld probes to detect very low levels in around 2 seconds, however, the wood needed to be within 2cm of the detector and the labour and capital costs are high. This technique has also been used on contaminated soils, although hand held units have lower LODs and accuracies than bench top systems (Vanhoof *et al.*, 2004).

2.3.2.4 Identifying CCA-treated Wood in the Long-Term Study

A range of methods were utilised to identify CCA wood in order to overcome the shortcomings discussed above. Visual observations were reinforced with qualitative identification stains and quantitative ICP-OES analysis (a laboratory technique to determine trace elements). The above methods were trialled on freshly treated CCA wood, suspected CCA wood structures and uncontaminated wood.

Visual observations were used to detect the colour of the wood and the combination of stains recommended by Solo-Gabriele *et al.* (2006) were used. PAN (1-(2-pyridylazo)-2-naphthol) was followed up by chrome azurol to test for the presence of copper (prepared in accordance with BSI 5666 Pt 2, 1980). A further colour indicator technique (stannous chloride stain) was used to identify the arsenate (prepared in accordance with Omae *et al.*, 2006). In the presence of arsenate, the solution and wood shavings turn a deep blue within an hour.

The qualitative stains were trialled on the freshly treated CCA wood and CCA wood structures around the university. Results for the PAN and chrome azurol indicators were highly visible. There were poor results for the stannous chloride stain for arsenic (Figure 2-6). This highlights the potential problems faced when using simple qualitative stains for sorting wood waste if only one stain is used as an indicator.

Figure 2-6: Indicator Techniques for the Presence of Copper in Treated Wood. PAN stains orange and CS stains a deep blue. Results were negative for the stannous chloride test for arsenic

Samples of CCATWW were collected from a local industrial source. These were tested with the qualitative colour indicators outlined in section 2.3.2.2. The stains showed up as positive for copper and negative for arsenic (Figure 2-7). Even when the tests for arsenic were carried out on wood shavings from the planks over a 16 hour period (as recommended by Omae *et al.* 2006), there was no obvious change in colour. Further analysis using ICP-OES confirmed mean levels of arsenic, chromium and copper to be high; 5429.74 ± 1343.55ppm, 10647.95 ± 3345.23ppm and 2920.74 ± 968.19ppm respectively. Again, this highlights the shortcomings of some qualitative methods currently used to identify CCATWW and illustrates how waste can be misidentified during sorting.

Figure 2-7: Colour Indicators for CCATWW.
PAN stain for Cu is positive (orange) on the right and stannous chloride stain for As is negative on the left

2.3.3 Untreated Wood

Following confirmation of CCA preservative in the wood waste, samples were sent off to the Forest Products Research Centre, High Wycombe for identification. The wood was identified as *Picea excels* which is commonly marketed as Norway Spruce or European whitewood (Sawyer, *pers. comm.,* 2007). This identification was used to obtain similar blank wood for the study.

2.3.4 Collection and Chipping of Wood

CCA-treated wood waste that had previously been used in a cooling tower for at least 15 years (Wilson, *pers comm.,* 2008) was collected on 19th April 2007. Untreated wood (European Whitewood) was purchased from Gresham's Timber Yard, Brough on the 30th of April 2007. Both were chipped using a Jensen Industrial Chipper (Figure 2-8) with the blank wood processed first to avoid contamination. In between chipping, the machine was brushed out and cleaned with compressed air. All woodchips were stored separately in cool and dry conditions prior to use. Particle size reduction has been identified as a controlling factor on leaching of preservative, however, in a similar lysimeter study, Gifford *et al.* (1997) justify the use of chipped wood as it allows for easier packing into the lysimeter, is representative of the varying wood particle size experienced in wood waste streams and accelerates the rate of leaching.

Figure 2-8: Chipping of Blank Wood and CCATWW

2.3.5 Long-Term Study Experimental Design and Set-up

The long-term leaching study was set-up between the 7th to 9th May at the same site as the pilot study. The experimental design consisted of fourteen lysimeters with modifications (outlined in Section 2.3). Three further lysimeters (monofills) were set-up and filled with soil, untreated wood or CCA-treated wood waste. All leachate collection containers and lysimeters were acid washed with 5% nitric acid followed by a rinse with ultrapure water to remove any contamination. All equipment was also acid washed. A protective ground sheet was laid beneath the lysimeters to prevent growth of weeds and to limit pests.

The total depth of the lysimeters was 16.5cm. In order to follow the recommended mulch depth specified by the RHS (Maya, 2008), soil was added to a depth of approximately 7.5-8cm. This was repeated with three lysimeters and the average weight of the soil used per box was calculated (20kg). The same weight of soil was added to all other lysimeters. Lysimeters with the untreated wood were filled first to prevent contamination of the wood, soil and/or equipment with CCA components. The untreated wood was well mixed and added to seven lysimeters as surface mulch to an approximate depth of 7.5cm. The weight of the added woodchips averaged 4.5kg. The CCA-treated wood waste was handled in the same way as the blank wood with thorough mixing followed by the application of 4.5kg to the remaining seven lysimeters. Filter membranes (0.2µm) were attached to the base of two lysimeters, one with untreated wood and soil and one with CCA-treated wood and soil to gauge if it was an appropriate method to sterilise the leachate by retaining microbes whilst leachate percolated into the leachate containers (Servais *et al.,* 1989). This method may also prevent microbial growth which can alter the heavy metal composition in the leachate.

All 17 lysimeters were set-up as in Figure 2-9. It was decided that the Environment Agency's Cottingham data logger used in the pilot study was situated too far from the experimental site to provide useful data on the conditions and microclimate of the site. Therefore rainfall and temperature data for the experimental period were recorded onsite on an hourly basis with a Cambell Scientific™ Basic Mounted Weather Station. This data was collected on a three-weekly basis.

Figure 2-9: Long-Term Leaching Experiment Layout

2.3.6 Sampling Regime

The experimental period began on the 9th of May 2007 and ran for twenty one weeks. Leachate samples were collected after periods of rainfall with volume measured using a graduated cylinder and redox potential measured with a handheld ExStik$^{\text{TM}}$ ORP RE300. Leachate volumes were not uniform across all lysimeters due to loss of leachate from overspill caused by flooding, absorption of rainfall by the wood and/or soil and possible differences in the distribution and amount of rain reaching each lysimeter (Hasan *et al.,* 2008). On all occasions leachate from lysimeters with the untreated wood were measured first. Upon emptying, the leachate collection dishes were washed out with ultrapure water and wiped clean before replacing. Leachate samples were transferred into cleaned 100ml nalgene containers. These were immediately returned to the lab where one set was frozen for elemental speciation analysis and the other stored at 4°C for measurement of pH and elemental analysis. In all, twenty batches of leachate were measured and eighteen collected and stored. In some cases collection bottles were not available due to excessive leachate production. Furthermore, there were some inevitable losses of leachate due to broken and lost sample tubes. In addition, not all boxes had leachate present to be collected. As such a full range of samples was not available.

Soil and woodchips were sampled every three weeks to allow sufficient time for laboratory analyses to take place. Samples were taken from two CCA-treated wood and soil lysimeters, two untreated wood and soil lysimeters and all of the monofill lysimeters on each sampling date. This sampling regime ensured that each of the soil and woodchip treatment lysimeters were only disturbed twice. During sampling, the top layer of woodchips from the selected lysimeters was scraped off and placed in ziplock plastic bags. Redox potential was measured on the soil and cores were taken using a trowel.

2.3.7 Changes to Experiment

Over the course of the study, the experiment was amended slightly to make sampling easier and to improve the consistency of results. Early into the experiment, the lysimeters were raised onto bricks to allow easy access to the sample collection containers. The drainage holes had plastic tubing added for leachate to pass straight into the collection container, minimising leachate loss. On the 17th May 2007, the filters were removed as leachate was not draining effectively with resultant pooling in the lysimeter. It was decided that simply sampling after major rainfall events would ensure that the metal(loid)s present would not have time to undergo changes due to microbial transformations. Two Tiny Tag^{TM} Soil Probes (model TGP-4017) were added to two lysimeters on the 11th June 2007 to record the temperature of the soil for the rest of the experimental period. These were wrapped in plastic zip lock bags and buried in the soil at the mulch/soil interface (7.5cm) and in the soil profile (11cm).

2.4 Short-Term Greenhouse Leaching Study

A short-term leaching study was set-up to augment the results of the long-term study. Exceptional quantities of rainfall were delivered to the lysimeters in June 2007, equivalent to a 1 in 150 year flood event (Coulthard *et al.,* 2007). Many of the lysimeters became waterlogged and leachate was lost as a result (Figure 2-10). Although this type of extreme event has not been experienced in other CCA leaching studies and is therefore useful to evaluate the impact of such events, it was decided that further lysimeters should be set-up with controlled watering based on more normal rainfall conditions. This is important as most authors argue that CCA metal(loid) components leach out more readily in the early stages (Hingston *et al.,* 2001). This may also be the case with the CCA-treated wood waste mulch as the chipping process exposes surface areas, previously unavailable for leaching and a short-term study with controlled watering and more frequent sampling would allow this to be evaluated.

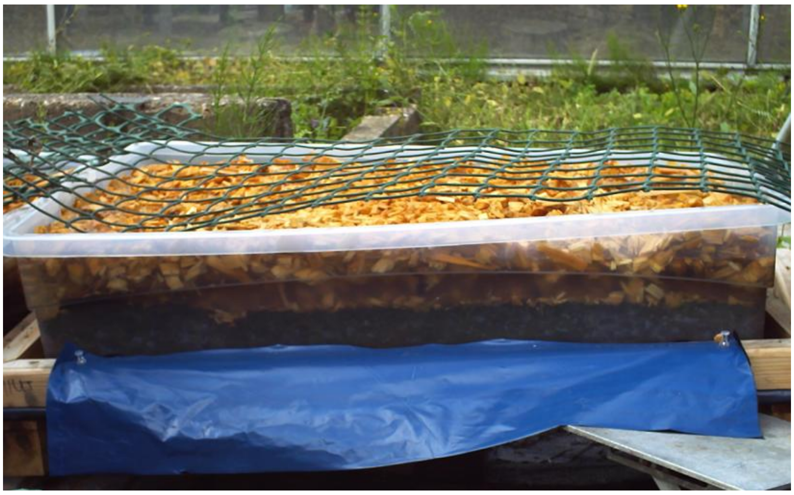

Figure 2-10: Waterlogging in a Lysimeter

Six lysimeters with untreated wood and soil and six with CCATWW and soil were set up in the same way as in the long-term study. These were installed inside the greenhouses at the University of Hull Botanic Gardens, Cottingham. The watering regime was based on winter and summer averages of the area over the last five years taken from Environment Agency records. Averages for the summer months used June, July and August data and for the winter months used data for December, January, February for the years 2002-2006 (see Table 2-3).

Table 2-3: Winter and Summer Rainfall Averages (2002-2006)

	Summer	**Winter**
Monthly	56.7mm	58.2mm
Weekly	14.2mm	14.6mm
Daily	2.03mm	2.1mm

The rainfall application was calculated as appropriate for the surface area of the lysimeters. Lysimeters were divided into six pairs (untreated and treated wood) with each pair receiving the same amount of water. Three of the pairs received the summer average rainfall with one pair receiving the monthly average in one application, another pair watered weekly and the final pair had water applied daily. The same approach applied for the lysimeters receiving winter average rainfall. Two Tiny Tag^{TM} Soil Probes (model TGP-4017) were added to two lysimeters to record the temperature of the soil. These were wrapped in plastic zip lock bags and buried in the soil.

The experiment ran for a 4-week period from the 3rd October 2007 – 31st October 2007. Ultrapure water was applied in the required amounts using a standard plastic watering can. The monthly totals were applied to the appropriate boxes at the start of the experimental period. Weekly watering took place at the start of each week (days 1, 8, 15 and 22) and sampling of leachate, soil and woodchips from all lysimeters took place at the end of each week (days 7, 14, 21 and 28). Leachate volume and redox potential of the soil and leachate were measured during sampling. Samples were collected and stored as described in section 2.3.6.

2.5 Speciation and Measurement of Mobile Elements in the Soil Profile

In order to evaluate the distribution and movement of the CCA elements along the soil profile, further experiments were set-up using deeper containers. There are a range of methods that can be used to look at distributions of elements along the soil profile. A commonly used one is to sample soil at various depths and return the samples to the laboratory for total elemental analysis following digestion (Stilwell & Gorny, 1997; Lebow & Foster, 2005; Dagan *et al.*, 2006). However, this method is destructive and species of elements present in the soil can transform following removal and exposure to oxygen (Zhang *et al.*, 1998).

Measuring individual species and forms of an element is important for understanding mobility and partitioning in the soil. The available methods for this are limited (Cai *et al.*, 2006). Arsenic speciation can be carried out in the field using x-ray absorption near edge structure (XANES) spectroscopy or x-ray fluorescence (XRF). However, Cai *et al.* (2006) argue that the methods are limited by sensitivity when used on environmental samples. Arsenic species can also be extracted from collected samples using phosphate. However conversion of species can occur due to micro-organism activity and hydroxides of iron, aluminium and manganese (Cai *et al.*, 2006). Although stabilisation of the arsenic species was achieved through complexation with sodium diethyldithiocarbamate, this extraction method is still destructive and doesn’t allow measurement *in situ*. Extractions can also be done sequentially by treating the soil with a series of reagents to partition fractions of the soil by releasing metal(loid)s from the soil matrix (Ure & Davidson, 2002). This method has been used by Balasoiu *et al.* (2001) in their study of CCA contaminated soils although problems dealing with interpretation due to ‘limited selectivity and redistribution of metal(loid)s’ were reported (Balaisou *et al.*, 2001). Measurement of the highly mobile Cr (VI) species in the soil requires an alkaline digestion procedure using 0.28M Na CO /0.5M NaOH to preserve the species before analysis (Cai *et al.,* 2006). A novel technique called Diffusive Gradient in Thin Film (DGT) can overcome the above mentioned issues and has not been utilised in CCA leaching studies to date.

2.5.1 Diffusive Gradient in Thin Film (DGT) Study

DGTs are devices that accumulate dissolved substances onto a binding gel after passing through a diffusion layer (Fitz *et al.,* 2003). The devices consist of a plastic base with a layer of resin embedded in a hydrogel overlain by a layer of diffusive hydrogel and a protective membrane filter (Zhang *et al.,* 2001). A tight plastic casing holds the device in place (Figure 2-11) and once deployed in the soil, metal(loid) ions diffuse in to accumulate in the resin layer (Zhang *et al.,* 2001).

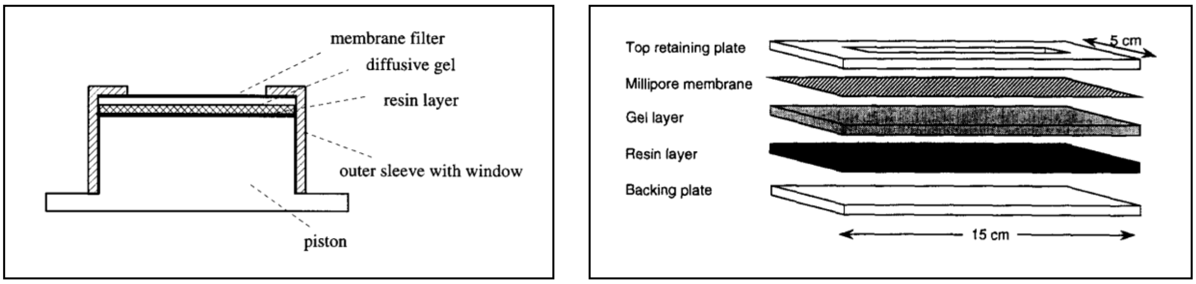

Figure 2-11: (a) Schematic Representation of a Cylindrical Soil Moulding DGT (after Zhang *et al.*, 1998) (b) Schematic Representation of a Sediment Probe Moulding DGT (after Zhang *et al.*, 1995)

They can be used to measure the mean flux of labile species from the soil and this can be interpreted as the mean concentration of metal(loid) ions in the pore-water at the surface of the device (Zhang *et al.,* 1995). Furthermore, the concentration can be related directly to the effective concentration of labile metal(loid), C_E, which represents the supply of metal(loid) from both the soil solution and the solid phase (Fitz *et al.,* 2003) through resupply mechanisms. The solutes pass through the filter and along the diffusion layer (of known thickness) where a steady-state concentration is assumed (Menzies *et al.,* 2005) to the binding gel where ion exchange processes take place (Figure 2-12). This allows metal(loid) concentrations to be measured. The technique is based on Fick’s first law of diffusion where the flux of a diffusing species is proportional to the concentration gradient and will move toward lower concentration giving time-averaged concentrations (Garmo *et al.,* 2003). For a detailed account of the theory see Zhang & Davison (1995) and Cussler (1997).

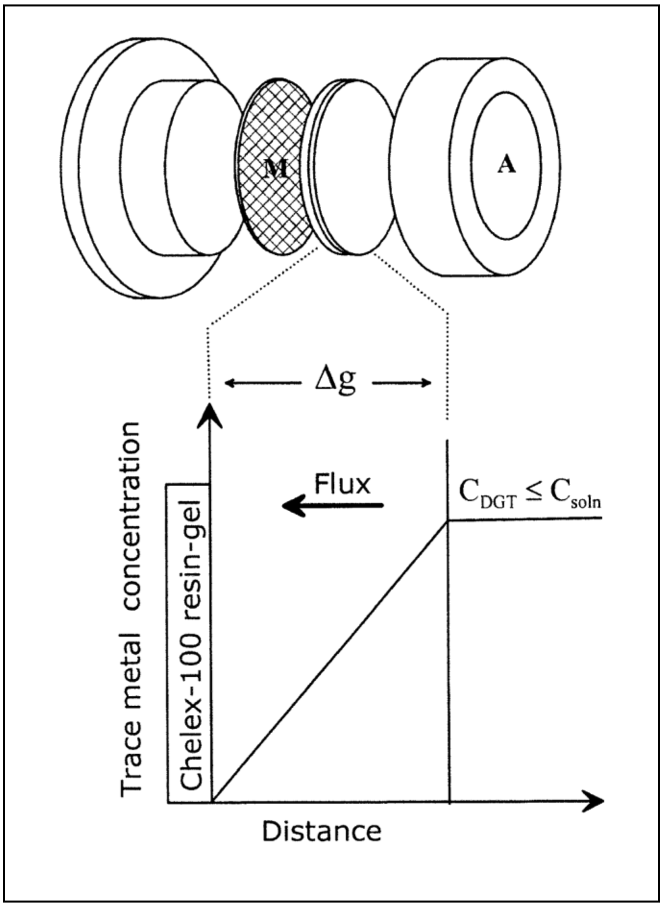

Figure 2-12: View of the DGT Device and Concentration gradient in the Diffusion Gel (After Ernstberger, *et al.*, 2002)

2.5.2 Uses of DGT

DGTs have been used to measure metal(loid) concentrations in a range of media including soil (Zhang *et al.,* 2001; Fitz *et al.,* 2003; Nowack, *et al.,* 2004; Zhang *et al.,* 2004; Hooda *et al.,* 2005; Menzies *et al.,* 2005) water (Davison & Zhang, 1994) and sediment (Zhang *et al.,* 1995). They have also been used for *in situ* measurements of speciation, bioavailability and profile studies.

In this study, the devices were used to gain an understanding of the *in situ* metal and speciation release from CCA-treated wood waste mulch in the soil, both at the mulch/soil interface and below this in the soil profile. The advantage of using DGTs over conventional sampling methods is being able to measure the distribution and behaviour of the metals *in situ,* so that the physical-chemical equilibrium of the soil is that of field conditions (Zhang *et al.,* 1998). Furthermore, alternative methods that are frequently used to measure the labile fractions (such as extraction) are destructive methods, requiring disturbance of the soil for sampling and increasing the risk of species transformation during storage.

DGTs are also capable of speciating certain metals *in situ*. For chromium this is possible due to the narrow-pore hydrogel allowing only the smaller Cr species (III) through to accumulate in the Chelex binding gel whilst the larger Cr (VI) species remains in the diffusive layer. Again, the measurement of speciation *in situ* reduces the potential to alter species post-sampling. Arsenic may also be speciated in the Fe-oxide gels, although this hasn't been confirmed in previous studies.

The results from these studies can give a greater understanding of the transformation mechanisms in the soil during the long-term leaching studies. They require the soil to be completely saturated for the devices to work, so in that respect, they are comparable to the extremely wet conditions of the long-term leaching study. However, some disadvantages of using DGTs were found during the study. DGTs can only be deployed for a short period of time and therefore separate devices need to be used in studies lasting longer than a week. Furthermore, they are very costly to purchase and with regards to this study could only provide a snapshot of the processes taking place in the soil following the application of mulch.

Fully loaded and assembled DGT devices were purchased from DGT Research Ltd. (Lancaster, UK). Cylindrical soil deployment mouldings (Zhang *et al.,* 1995) were prepared using a polyethylene base and casing with an exposure surface area of 2.54cm^2. For measurement of copper and chromium in the binding gel, Chelex gel resin was impregnated within a layer of polyacrylamide gel (0.4mm thickness). Separate DGTs were used for measurement of total arsenic using an Fe-oxide gel impregnated with ferrihydrite (Fitz *et al.,* 2003; Plant *et al.,* 2004). The diffusive gel was prepared from agarose polacrylamide gel (0.8mm thickness). The gels were overlain with a 0.45µm pore size Millipore cellulose nitrate membrane. Sediment probe mouldings were prepared in a similar manner but were encased in a rectangular moulding with an exposure surface area of 22.5cm^2. DGT devices were stored in sealed clean plastic bags containing a solution of 0.01M $NaNO_3$ at 4°C.

2.5.3 DGT Experiment Design and Set-Up

Three DGT experiments were designed. The first was a preliminary study using standard soil mouldings to look at the concentration of copper, chromium and arsenic at the mulch/soil interface over a 24 hour period. The second was a further week-long study to examine how the metal(loid)s are distributed in the soil profile and the final study was a speciation experiment.

All experiments used two untreated wood and soil containers and two CCA-treated wood and soil containers. These had to be deep enough to hold the DGT discs and probes and strong enough to withstand the pressure exerted by the saturated soil against the side walls. Four polypropylene Addis 48L bin bases were used with a depth of 52.5cm, length of 34cm and width of 30cm. They were scrubbed and rinsed out with ultrapure water prior to use.

The soil and woodchips were prepared as in section 2.2.1and 2.3.5 respectively. 20kg of soil was added to each of the four bins. The soil was then wetted over a period of four days until it had the consistency of a slurry (soil moisture content >80%) as specified by Fitz *et al.* (2003). This high water content is required to decrease tortuosity of the diffusion pathway and increase the effective area of contact (Menzies *et al.*, 2005). Two Tiny Tag^{TM} Soil Probes (model TGP-4017) were inserted to measure soil temperature.

2.5.3.1 DGT Deployment

The DGTs were placed in the containers (cylindrical DGTs were applied on the surface and soil sediment probes inserted into soil (Figure 2-13)). Following application of the DGT discs, 4.5kg of woodchip was applied on top of the soil as mulch. 500ml of water was applied to each box to keep soil moist and leach metal(loid)s from the wood.

Figure 2-13: Set-up of Soil DGT Mouldings

The preliminary study commenced on the 3rd October 2007 with a deployment time of 24 hours in line with the suggestions of Menzies *et al.* (2005). Two soil deployment mouldings were added to each lysimeter; one for chromium and copper and a second for arsenic. The soil profile study was setup on the 15th May 2008 with a deployment time of 168 hours (one week). One Chelex resin-containing device and one Fe-oxide resin-containing device were put in to the hollow created by a plastic ruler ensuring that all the gel was covered. At the end of a one week period, the DGTs were removed. The final study to investigate speciation was carried out on the 15th May 2008 with a deployment time of 50 hours as suggested by Ernstberger *et al.* (2002).

2.5.3.2 DGT Retrieval

On retrieval of the discs, the DGT units were rinsed with ultrapure water to wash off any adhering soil particles and dabbed lightly with a tissue. For all cylindrical devices, the cap was broken off and the filter peeled off. The resin and diffusive gel components were removed and added to 2ml of 1M HNO_3 in 10ml plastic sample containers. For the speciation study, the gels were left for two hours to allow the Cr (III) to fully migrate to the binding gel before adding to the acid (Ernstberger *et al.,* 2002). For the sediment probes, the gel and filters were cut out of the exposure window using a glass cover slip and cut into 2.5cm sections before adding to the acid. All the gels were left for approximately two weeks to allow elution to take place and for easier handling when pipetting (Zhang *pers comm.,* 2007).

2.6 Summary

This chapter has covered the four types of fieldwork experiments conducted during the project. Justifications for each of the field studies were placed in the context of previous work performed by others in the discipline. The advantages and disadvantages of the methods selected were discussed as well as potential alternatives. The next chapter will focus on the laboratory methods used on the leachate, soil and woodchip samples collected during the field studies.

3 Methods II

3.1 Introduction

The aim of this chapter is to present and assess the laboratory methods and techniques used on the samples collected during fieldwork (Chapter 2). Section 3.2 will cover the main techniques used in this study to analyse soil, woodchip and leachate physico-chemical properties. Section 3.3 presents the statistical analyses methods used on the data and the final section, 3.4 summarises the chapter.

3.2 Physico-Chemical Measurements

Physical and chemical measurements of the soil, woodchip and leachate can provide an indication of how the CCA elements might behave once leached out of the mulch. Measurements used in this study included pH, organic matter, particle size analysis, electrical conductivity, redox potential, total elemental concentrations and inorganic element species.

3.2.1 Soil Moisture Content

Measurements of soil moisture content (MC) were carried out on soils collected from the pilot study, long-term leaching study and greenhouse leaching study. MC is one of the most commonly used analyses for soil studies as it affects much of the behaviour and condition of the soil (Topp, 1993). It is also a requirement for calculations of other physico-chemical parameters (Hesse, 1971), in this case loss on ignition (LOI), particle size (PS) and total elemental concentrations in soil. A number of techniques to measure soil MC, both directly and indirectly are reported in the literature (Gardner, 1965; Bascomb, 1974; Baize, 1993; Topp, 1993). They all involve separating the water fraction from the soil and inferring or measuring the amount of water that is removed (Gardner, 1965).

The most frequently used technique is gravimetric with oven drying (Gardner, 1965). It is a simple method that involves weighing approximately 10g of field moist soil into a porcelain crucible and oven-drying at 105°C overnight. After cooling, the crucible and sample are re-weighed and the % moisture content is calculated as the mass of water lost as a percentage of the mass of oven-dried soil.

Despite the simplicity of the method compared to other MC techniques, there is a significant disadvantage described by Topp (1993). Soil samples analysed using this technique may not be dried to a constant weight. There are three possible reasons for this. Firstly, water is bound to a variety of components in the soil that require different heat levels to remove the water. As a result, the mass of the soil samples can continue to decrease over a number of days if left in the oven (Gardner, 1965). Secondly, a portion of the organic matter (OM) in the soil may be oxidised or volatilised at 105°C so some of the decrease in mass can be attributed to a loss in organic matter. Thirdly, temperature control can be a problem in laboratory ovens where the actual temperatures of the soil sample are not measured, only the air temperature in a specific section of the oven. The problem of reaching a constant weight was overcome by drying replicate samples and checking the weights until they were constant. Samples were cooled in the open and may have absorbed moisture, thus affecting results. In future studies it would be more appropriate to dry samples in a dessicator.

3.2.2 Soil Organic Content

Soil organic matter (OM) content analyses were carried out on soils from the pilot study, long-term leaching study and greenhouse leaching study. Earlier CCA-treated wood studies have reported that soils with high OM (and therefore high levels of fulvic and humic acid) have a greater tendency to leach out the components of CCA-treated wood waste (Bergman, 1983; Bergholm 1989; Cooper *et al.*, 2001; Kartal *et al.,* 2005, Dobran & Zagury, 2006). Therefore it is necessary to measure the OM content of the soil mixtures used in the study.

Soil organic content can be calculated gravimetrically. There are three methods for determining soil organic matter content; the first is ignition of the soil at low temperatures (350-400°C), the second is ignition at high temperatures (800-900ºC) and finally there is treatment with hydrogen peroxide (Hesse, 1971). Loss on ignition (LOI) at a low temperature can be problematic as it may not differentiate between losses from organic matter and mineral matter (Hesse, 1971). The LOI method at high temperatures is also considered a very approximate method as loss in weight can result from clay mineral and structural water. However, this method was selected as it is simple and widely used. It involved weighing out oven dried soil in replicate and placing in a furnace for 30 minutes at 850ºC as outlined by Bascomb (1974). The combustible organic matter is burned off in the process leaving only the mineral soil fraction (see

Figure 3-1). The organic matter % is calculated as the mass of the oven-dried soil lost as a percentage of the mass of ignited soil.

Figure 3-1: Samples Following Loss on Ignition

3.2.3 Soil Particle Size Analysis

Soil particle size (PS) analysis was selected to gauge the physical properties of the soil used in the study. It is used for determining the distribution of mineral particles (sand, silt and clay) in size classes to ascertain the textural character of the soil (Baize, 1993). Sand particles are defined as those that fall into the range of 0.06 – 2.0mm. Silt particles range from 0.006 – 0.02mm and finer material is classed as clay. Although the topsoil used in all studies was pre-purchased, there was no evidence of a classification scheme and as such, this measurement was required to understand the soil medium used. In leaching experiments, soil particle size is likely to contribute significantly to permeability and therefore leaching potential of CCA components.

The technique used was based on Bascomb (1974) and Sheldrick & Wang (1993). It differentiates size classes using sieves and a settling procedure. There are a number of pre-treatments that can be used to remove carbonates, OM and/or soluble salts (Sheldrick & Wang, 1993). In this study OM was removed from the soil samples using heated hydrogen peroxide and the sample was then left to dry overnight. The dried soil was agitated with sodium hexametaphosphate and water in an ultrasonic bath to disaggregate all the particles. The gravel fraction was removed by wet sieving. After drying, the rest of the material was passed through a series of sieves of different sizes (equating to different sized sand fractions) (Table 3-1). The remaining silt and clay in the base pan was transferred to a sedimentation tube where it was thoroughly suspended. According to Stoke’s Law, the final fractions will settle out to a certain depth after a certain time depending on the particle size (Table 3-2). Therefore, pipetting from these depths at set times (followed by drying and weighing of samples) will allow the calculation of the quantity of material within specific size limits.

Table 3-1: Sieved Sand Fractions

Sieve Size	Texture
2.00mm	Gravel
0.6mm	Coarse Sand
0.2mm	Medium Sand
0.06mm	Fine Sand

Table 3-2: Silt and Clay Fractions

Settling Time	Equivalent Diameter
4 minutes, 48 seconds	0.02mm
1 hour	0.006mm
8 hours	0.002mm

It should be noted that this method of determining particle size has inherent limitations. The final calculation involves estimating the material within the range 0.06-0.02mm by subtracting the total of all the other size range percentages from 100%. This can be an inaccurate representation of the size class. Furthermore, it is a lengthy process where many small errors can occur (such as disturbing the sedimentation process when pipetting), resulting in a larger source of error in the final result. Despite the fundamental shortcomings of the method, Wang *et al.,* (1998) maintain that measurement of soil texture is the most significant measurement for soil physical property. In this study it also proved a useful measurement.

3.2.4 Soil and Leachate pH

pH is defined as 'the negative logarithm of hydrogen activity' (Foth, 1990). pH readings were carried out in the laboratory on all collected leachate and soil samples. pH measurements are widely used in soil and water studies as it is a cheap and easy method, with informative results. In terms of this study, pH will greatly influence many soil functions and processes including microbial activity, nutrient levels and soil leaching properties. Previous CCA-treated wood leaching studies found pH to be the most influential factor on both leaching and elemental species (Bergman, 1983; Bergholm 1989; Kim & Kim, 1993; Aceto & Fedele, 1994; Van Eetvelde *et al.,* 1995a,b; Wang *et al.,* 1998; Balasoiu *et al.,* 2001; Hingston *et al.,* 2001; Cooper *et al.,* 2001; Crawford *et al.,* 2002; Schultz *et al.,* 2002; Townsend *et al.,* 2003a; Khan, 2004; Lebow *et al.,* 2004; Townsend *et al.,* 2004; WRAP, 2004; Solo-Gabriele *et al*., 2005; Moghaddam & Mulligan, 2008).

There is conflicting evidence however as to what pH conditions promote or hinder leaching. The study by Townsend *et al. (*2004) found that extremes of pH produce maximum rates of leaching in both freshly treated and weathered CCA-treated wood. At low pH levels, increased hydrogen ion concentration increases the solubility of the CCA chemicals through acid-ion-exchange reactions (Aceto & Fedele, 1994). These reactions form water-soluble chelates with copper and chromium (Kim & Kim, 1993; Cooper, 1994; Wang *et al.,* 2001). At this extreme, it is the copper that leaches the most readily of the three elements considered (Aceto & Fedele, 1994). Warner & Solomon (1990) studied the response of metal(loid) leaching at low pHs and found that copper leached out in large amounts before plateauing, chromium leached out exponentially and arsenic was released linearly.

At high pH levels, increased leaching of arsenic, copper and chromium also occurs due to the dissolution and mobilisation of the organic matter to which the compounds are chelated or complexed (Chirenje & Ma, 2006). Copper leaches out most readily followed by arsenic and chromium (Moghaddam & Mulligan, 2008). Townsend *et al.*, (2004) reported that within the near-neutral pH range as observed in both the long and short-term leaching experiments, pH has little effect on leaching.

Findings from other CCA leaching studies disagree with leaching at pH extremes. Wang *et al.* (1998) found no correlation between soil pH and leachability of CCA, whilst Warner & Solomon (1990) found leaching of arsenic, chromium and copper in leachate at all the pH levels studied (3.5 - 8.5). Furthermore, Van Eetvelde *et al.* (1995a, 1995b) and Taylor & Cooper (2005) reported that chromium and arsenic have maximum leaching levels at neutral pHs. This may be due to the presence of organic acids in the soil which have been shown to influence leaching in near-neutral pH ranges (Lebow *et al.*, 2004). Therefore, it is possible that the near-neutral pH levels observed in the long and short-term leaching studies may cause increased leaching of arsenic and chromium.

In the current study all samples were measured with a Fisherbrand Hydrus 300 pH probe in accordance with the manufacturers' instructions. The pH of the soil was measured using a soil-deionised water suspension as described by Rowell (1994). Although pH measurements can also be carried out using $CaCl_2$ or KCl mixtures, mixing with water yields pH results closest to the pH of soil solution in the field (Hendershot *et al.*, 1993). Soil samples were mixed with deionised water (ultrapure water with a resistivity of 18Ωm cm^{-1}, Pearson *et al.*, 2007) and the pH electrode placed in the solution (Figure 3-2). Readings were taken once the mixture had reached equilibrium. The major concern with adding water to the soil is that it could potentially increase the pH values (Hendershot *et al.*, 1993). This was minimised in the measurements by keeping the ratio of soil:water constant and as low as possible. A further problem as highlighted by Elberling & Matthieson (2007), is the degassing process and biased pH values when measuring soil pH in the laboratory as opposed to *in situ*. They found that pH measured in the laboratory was consistently more alkaline. In this study the effect was minimised by storing soil samples in air-tight plastic bags and analysing within 24 hours of sampling.

Figure 3-2: Measurement of pH on Leachate Samples

Leachate samples were measured directly without dilution once they had been removed from refrigeration and left to adjust to room temperature (21°C). This served to stabilise the readings. For measurements of both soil and leachate samples, regular calibration of the instrument was carried out with two pH buffer solutions at pH 4.0 and 7.0. All untreated samples were tested first to prevent cross-contamination and the electrode was rinsed with deionised (DI) water between samples. Replicates of selected samples were tested for quality control. This involved picking samples from each treatment.

3.2.5 Soil Electrical Conductivity

Electrical conductivity (EC) in soil solutions is an indirect indication of the concentration of ions present (salinity) and their electrical charge (Rowell, 1994). The salinity of the environment that the CCA-treated wood is exposed to can greatly influence the leaching properties of the components. Studies have illustrated that soil and leachant electrical conductivity (salinity) can have an effect on leaching (Lebow *et al.*, 1999; Kartal *et al.*, 2005). Salinity is a measure of all dissolved solids such as sodium, chloride, sulphate, magnesium, calcium, potassium bicarbonate, boron and strontium (Lebow *et al.*, 1999). Kartal *et al.* (2005) found that with exposure to saline conditions such as in marine environments, arsenic leached out in greater amounts (and copper and chromium in lesser amounts) than with exposure to distilled water. Lebow *et al.* (1999) found that in sea water, copper and arsenic were released in greater amounts and chromium remained fixed when compared with deionised water. Plackett (1984) also studied the effect of inorganic salt solutions on the leachability of CCA. Copper was found to leach more readily with increased salt solution concentration. He concluded that horticultural soils with a high concentration of salts including calcium, magnesium, potassium and phosphorus would have a higher potential to leach CCA components than soils with a lower concentration.

In this study, EC was measured using a Hanna DiST®5 Waterproof EC/TDS/°C/°F handheld meter (Hanna Instruments). The samples were treated according to the manufacturer’s instructions and the method of Janzen (1993). Janzen (1993) outlines a number of techniques to measure soil salinity including *in situ* measurements such as electromagnetic induction sensors and time-domain reflectometry as well as extraction methods such as direct extraction and fixed-ratio extract (used in this study). The *in situ* methods are more time consuming and costly than the extraction methods. The fixed-ratio method was selected as it provides a very quick and easy estimation of the total solute concentration in the soil and can use the same samples as those used to measure soil pH. The method involves mixing soil and water to a ratio that is fixed for all samples.

3.2.6 Soil and Leachate Redox Potential

Soil and leachate reduction-oxidation (redox) potential measurements were taken in the long-term and short-term leaching studies and in the DGT experiments. Reduction reactions involve the gain of electrons/hydrogen or a loss of oxygen. Conversely, oxidation reactions involve the loss of electrons/hydrogen or gain of oxygen.

Redox potential controls the reduction or oxidation of compounds and therefore the level of reduction or oxidation in soils. Redox is a semi-quantitative measurement (Lillie & Smith, 2009) that is most commonly measured using Eh which denotes electrode potential against hydrogen electrode (Smith, 2005). The redox status of the soil can be categorised according to Patrick & Mahapatra (1968) (Table 3-3).

Table 3-3: Classification Scheme of Redox Potential (Patrick & Mahapatra, 1968)

Redox Potential (mV)	Category
>+400	Oxidised
+100 to +400	Moderately reduced
-100 to +100	Reduced
-300 to -100	Highly reduced

Redox is not reported widely in CCA leaching studies although it is an important physico-chemical feature, affecting the oxidation states and species of the leached metal(loid)s in the soil (Balasoiu *et al.*, 2001). At each sampling date, leachate volume was measured with a measuring cylinder and redox potential measured with a handheld ExStik^{TM} ORP (RE300) Waterproof Series Pen. Measurements were taken according to the manufacturer's recommendations.

Many authors argue that handheld redox probes can give unreliable results compared to their *in situ* counterparts. However, Christensen *et al.* (2000, 183) argue that obtaining quantitative redox potential measurements can be problematic in the field and 'the cost in time and equipment needs to be weighed against the potential value of the data to a particular field problem'. The advantage of using a handheld redox probe was that it proved cheaper than purchasing *in situ* probes and was more convenient. The handheld probe was deemed to be sufficient for this study as it provided a general indication of soil conditions.

The redox data was corrected for variation in pH according to Cheetham (2004). In summary, for each pH unit below 7, 59mV was subtracted from the reading. Conversely, for each pH unit above 7, 59mV was added. Because redox was measured to a resolution of two decimal places, values in between were interpolated. For example, at pH 6.82, 10.62mV was subtracted from the reading. Correction for standard hydrogen electrode (SHE) was not required as the probe was pre-calibrated (Williams, *pers. comm.*, 2009).

3.2.7 Synthetic Precipitation Leaching Procedure

A laboratory based synthetic precipitation leaching procedure (SPLP) was used to determine the potential for CCA metal(loid)s to leach out of freshly treated and weathered CCA wood. Townsend *et al.* (2003a), Townsend *et al.* (2004), Townsend *et al.* (2005) and Dagan *et al.* (2006) have used this technique to represent leaching and metal(loid) mobility of CCA components in field conditions on exposure to rain water.

The method used is based on the United States Environmental Protection Agency Method 1312 (Environmental Protection Agency, 1994a) which is used to assess the risk of leaching from contaminated soils to groundwater (Townsend *et al.,* 2004). Deionised water (equivalent to 20 times the weight of the woodchips) was acidified to pH 4.2 ± 0.05 using sulphuric and nitric acids (3:2). The woodchip samples were then immersed in a plastic container and shaken for 18 ± 2hr on a shaker (Stuart Scientific SF1^{TM}). The mixture was then filtered and the filtrate was digested in a microwave. The resultant digestates were analysed by ICP-OES.

The results from this procedure can greatly overestimate the loss of metal(loid)s particularly from freshly treated wood. However in this situation it was only used as an indication of levels of metal(loid) loss from the wood prior to setting up the lysimeters. It also allowed a comparison of the leaching characteristics of freshly treated and weathered CCA wood.

3.2.8 Total Elemental Analysis

Levels of As, Cr and Cu were measured in soil, woodchip, leachate and DGT samples to determine the leaching characteristics of the CCA preservative from wood and preservative behaviour in the soil. There are two principal methods for analysing elements, either direct analysis of the solid (for example using x-ray fluorescence spectroscopy) or by digesting the samples and releasing the elements (Dean, 2003). Samples collected during fieldwork were prepared and digested prior to analytical measurement.

3.2.8.1 Preparation of Samples

All samples had to undergo treatment prior to sample extraction and digestion. Tests were made with both oven dried and field moist soil samples and it was found that field moist soil was more appropriate to use as volatilisation of arsenic during oven drying could result in underestimation. Field moist soil was kept refrigerated until required.

Woodchips were air dried in the lab and then milled down using a Retsch SM100^{TM} cutting mill (Model APP 020) at the Geography Department, University of Leeds. The milled wood was passed through a 2mm bottom sieve. All untreated wood was processed first followed by treated wood to prevent cross contamination. The instrument components were cleaned with compressed air and vacuumed in between samples to remove any wood residue. Leachate samples were kept frozen until required for analysis.

3.2.8.2 Sample Extraction

There are a number of techniques available for sample extraction. A simple form of decomposing solid sample matrices is dry ashing which involves heating the sample in a furnace at 400-800°C. The limitations of this method include loss from volatilisation (a problem for As), resistance of some materials to ashing, difficult dissolution of ashed materials and high risk of contamination (Dean, 2003). This technique is now largely replaced by acid digestion. Acid digestion can be carried out using either a hot plate or multiple-sample digester. However these methods take longer and pose health and safety risks to the user (Environmental Protection Agency, 1994a). The use of a commercial closed system is beneficial in terms of minimising loss of volatiles, speed of digestion due to high temperatures (200°C), capability of digesting multiple samples simultaneously, automatic monitoring of pressure and temperature sensors and safeguard measures to protect the user.

All samples were acid digested using a pressurised microwave to extract elements in the samples (Figure 3-3). The method used extracts pseudo-total elements as the acid does not break down silica within the sample. However, for the purpose of this study the extraction will be termed total element extraction as the remaining silica does not affect final levels of elements in the acid. This technique involves the use of acids and an external heat source to decompose the sample matrix (Dean, 2003). The type of acid and amount used depends on the sample and the analysis required. Methods used for the different sample types were taken from recommended CEM methods (CEM, 2004a, b & c) for aqueous, woodchip and soil samples (outlined in Table 3-4, Table 3-5 and Table 3-6).

Figure 3-3: Microwave Digestion

Leachate samples were measured out w/w and diluted with 70% concentrated HNO_3 to 10% v/v concentration. This method is also described by the Environmental Protection Agency (1994b) and is commonly used for wastes that contain suspended solids. The measurement of arsenic, chromium and copper is suitable with this method. Wood chip samples were weighed to approximately 0.5g then 10ml of 70% concentrated nitric acid (HNO_3) added. Soil samples were measured out to 2g with 12ml of aqua regia (9ml HCL to 3ml HNO_3). All acids were SpA grade from Romil (Cambridge, UK). Leachate filtering was trialled on the first batch of samples and it was found to contaminate samples, alter the sample pH and was time consuming. Acid digestion with a settling period was sufficient at solubilising colloidal particles and removing larger particles.

Samples and the corresponding acid were measured directly into the Teflon microwave vessels. For all batches, blanks and untreated samples were weighed first before treated samples to reduce the risk of contamination between samples. Weighing equipment was cleaned between each sample. Acid blanks consisting of the same matrix type were included in the process. Blanks and spikes of Certified Reference Material (SpexCertiPrep, Middlesex) for soil and wood were included in the process to ascertain spike recovery from the digestion process and cleanliness of the microwave vessels. Acid blanks were also included and were found to be consistently below the LOD indicating that the vessels were properly cleaned between digestion batches. The vessels were placed on either an XP1500 (12 place) or Mars Xpress (40 place) carousel depending on the number of samples to digest and type of sample. The highly organic soil and woodchip samples were left to soak overnight to reduce frothing and pressure build-up when sealed and microwaved. Methods were set-up in the Microwave Accelerated Reaction System (MARS^{TM}) CEM Corporation, USA. Following dissolution and cooling down of the digests, the solution was transferred to a 50ml sample tube and diluted by weight to approximately 50g using deionised water (Song, 2003).

All glassware and microwave vessels were acid washed after use. In between digesting batches of differing matrices, the vessels were acid leached with 5ml of the corresponding concentrated acid. Between each batch, the vessels were acid leached and rinsed with ultrapure water. In the small number of cases where this was not possible, vessels were rinsed with concentrated Lipsol detergent followed by ultrapure water and left to air dry.

Table 3-4: Microwave Digestion Conditions for Aqueous Samples

Sample amount	Acid amount	Stage	Max Power	% Power	Ramp (min)	Pressure	Temperature (°C)	Hold (min)
45ml leachate	5ml Nitric acid (70% concentration)	1	1600W	80	10:00	-	160	0:00
		2	1600W	80	10:00	-	170	0:00

Table 3-5: Microwave Digestion Conditions for Milled Wood Samples

Sample amount	Acid amount	Stage	Max Power	% Power	Ramp (min)	Pressure	Temperature (°C)	Hold (min)
0.5g milled wood	10ml Nitric acid (70% concentration)	1	1600W	80	15:00	-	200	15:00

Table 3-6: Microwave Digestion Conditions for Soil Samples

Sample amount	Acid amount	Stage	Max Power	% Power	Ramp (min)	Pressure	Temperature (°C)	Hold (min)
2g fresh soil	12ml Aqua Regia acid (3:1 $HCl:HNO_3$)	1	1600W	80	15:00	-	200	15:00

3.2.8.3 Sample Dilutions and Standards

Samples were diluted with ultrapure water down to 2 - 10% acid concentration to prevent deterioration of the sample introduction equipment of the ICP-OES. Mixed standards containing As, Cr and Cu were created by diluting 1000ppm single element standard stock solutions (99.9% pure or greater: PrimAg Xtra, Romil^{TM}, Cambridge). As the preliminary samples were of unknown values, the range used for calibration depended on values determined following qualitative analysis of initial samples. This analysis involved preliminary determination of 69 single elements in mixed standards (10ppm in 2% HNO_3). Matrix matching was applied to all samples, standards and blanks (i.e. matching solvents, concentrations of acids and solutes) to help correct for spectral interference (Boss & Fredeen, 2004). Calibrations were checked against a certified reference material (CRM) for estuary sediments of known elemental concentrations. Although this study concentrates on soil, wood and leachate, the availability of the estuarine sediment CRM and use in similar soil studies confirmed its suitability for this work (Cattani *et al.*, 2009).

3.2.8.4 Measuring Total Elements in Samples

When assessing which method to use for elemental analysis, the following criteria were used (Fifield, 1995):

1. concentration
2. possible interference
3. potential for single element and multi-element operation
4. total or speciation analysis
5. complexity
6. ease of operation
7. cost of equipment and operation
8. availability of equipment

There are a number of techniques that can be used to measure total elements in samples. Flame and Furnace Atomic Absorption Spectrometries (FAAS) can measure single elements with detection limits comparable to ICP-OES. They also have the advantage of being relatively cheap to purchase (Boss & Fredeen, 2004). Graphite Furnace Atomic Absorption Spectrometry (GFAAS) is very sensitive and can achieve low detection limits. It is also capable of analysing small amounts of sample (µl). However, it is very costly and time consuming to run and is only capable of analysing single elements at a time. Atomic Absorption spectrometry has been used successfully in CCA leaching studies (Suzuki & Sonobe, 1993; Hudson & Murphy, 1997; Chirenje *et al.*, 2003; Kartal, 2003; Townsend *et al.*, 2003a; Shibata *et al.*, 2005) however it also only measures single elements. Analysis for elements in solid material can be carried out using X-ray Fluorescence (XRF) spectroscopy. This technique provides similar results to acid digestion and FAAS with a faster processing time (Dean, 2003). However when analysing CCA contaminated soils, Mäkinen *et al.* (2006) reported that there is more variation with *in situ* studies than laboratory studies and as such confirmation needs to be undertaken. Despite the potential drawbacks, XRF has also been used in CCA studies by Plackett (1984), Wang *et al.* (1998), Cooper *et al.* (2000), Cooper *et al.* (2001) and Crawford *et al.* (2002). Anodic stripping voltammetry (ASV) can be used for looking at trace elements in solution, although it is a lengthy process.

Inductively coupled plasma - optical emission spectrometry (ICP-OES) (also referred to as inductively coupled plasma atomic emission spectrometry – ICP-AES), is useful for determining major, minor and trace elements in soil and water (Boss & Fredeen, 2004). It is also the method of choice in many CCA-treated wood studies for identification of CCA components in wood (Peylo & Peek, 1998; Lin & Hse, 2002; Kartal *et al.*, 2005), soil (Balasoiu *et al.*, 2001; Lebow & Foster, 2005; Dagan *et al.*, 2006) and leachate samples (Yamamoto *et al.*, 1999; Townsend *et al.* 2005; Yoon *et al.*, 2005; Shibata *et al.*, 2006).

ICP-OES was selected for this study as the most appropriate method for measuring total elements. It allows rapid determination of multiple elements at concentrations as low as $1mgl^{-1}$ (Boss & Fredeen, 2004). In this study LOD were 8.9ppb for arsenic, 2.8ppb for chromium and 1.3ppb for copper (n=8). Furthermore it allows for a better ionisation process and elimination of chemical interferences than (FAAS) and has been found to be more accurate and precise (Walley *et al.*, 1995). This is due to the high temperature reached within the plasma and the long residency time of the analyte in the centre of the plasma, compared to other electrical discharge emission sources (Fifield, 1995; Boss & Fredeen, 2004). Where analyte levels were below the limit of detection (LOD) achievable with an ICP-OES, an ICP-MS was used.

3.2.8.5 Inductively Coupled Plasma - Optical Emission Spectrometry

The ICP-OES unit is made up of the ICP and optical spectrometer (Figure 3-4). The ICP consists of a torch with 3 concentric quartz tubes and a copper load coil connected to a radio frequency (RF) generator (Figure 3-5) (Boss & Fredeen, 2004). Argon gas at 6 Bar pressure is led to the torch and when the torch is ignited, the application of RF induction causes the ionisation of the argon gas and creates a plasma at a temperature of 10,000K (Fifield, 1995). This plasma is known as an inductively coupled plasma (ICP) (Boss & Fredeen, 2004). The plasma is sustained by the continued application of RF energy. Liquid samples are taken up by an autosampler and peristaltic pump for nebulisation into an aerosol within a vortex spray chamber (Figure 3-6). The aerosol is then directed to the centre of the plasma by the argon gas flow where it goes through a process of desolvation, vaporisation, atomisation and finally ionisation (Boss & Fredeen, 2004). During desolvation, the solvent is removed leaving microscopic salt particles. These are then vaporised into a gas of molecules which are then dissociated into atoms (atomisation). The atoms undergo excitation and ionisation whereby one of the valence electrons is promoted to a higher energy causing it to emit characteristic wavelengths when it returns to the stable ground state (Boss & Fredeen, 2004).

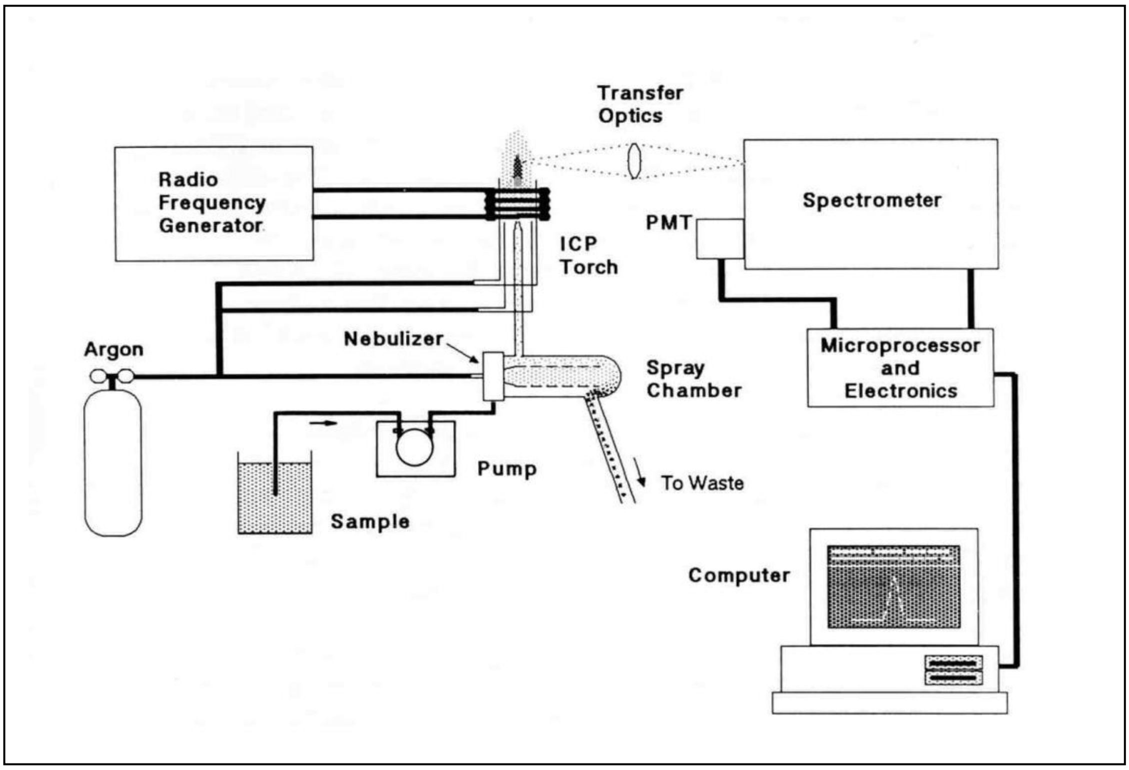

Figure 3-4: Major Components and Layout of an ICP-OES (taken from Boss & Fredeen, 2004)

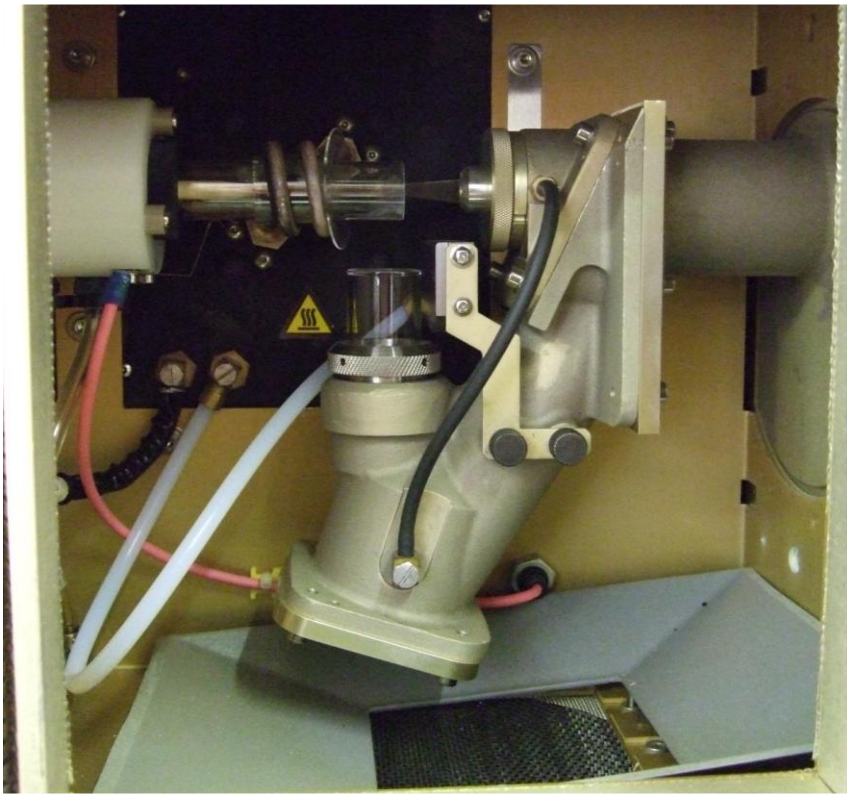

Figure 3-5: Inside the ICP instrument torch box (courtesy of Bob Knight, 2007)

Figure 3-6: Nebuliser and Vortexing Spray Chamber (courtesy of Bob Knight, 2007)

The emission spectra from the samples are monitored by photosensitive devices and sorted by wavelength in the optical emission spectrometer (Environmental Protection Agency, 1996). These are used to determine the presence of certain elements by the characteristic wavelengths for that element. At least three spectral lines were used to ensure that the emission corresponded to the element of interest. The selected wavelengths were based on the recommendations of Perkin Elmer for Optima^{TM} Series ICP-OES Spectrometers with As measured at 188.979nm, Cr at 267.716nm and Cu at 327.393nm. Quantitative determination of element concentrations is calculated using standards to create calibration curves of intensity versus concentration (Boss & Fredeen, 2004).

A certain degree of method development was required in the preliminary stages of analysis to ensure that the ICP-OES (Perkin Elmer Optima 5300DV, Connecticut, USA) was running appropriately for the samples and concentrations measured. This aided the reduction of spectral, physical, chemical and memory interferences outlined by the Environmental Protection Agency (1996). The units of measurement were selected depending on what sample type was being measured and expected levels (eg. ppm for soil and woodchips, ppb for leachate). Integration time was lengthened from 2 to 10 seconds as it allowed for stabilisation of the spectral signal by averaging the background noise over a longer time (Knight *pers comm*., 2008). The argon purge gas flow in the optics chamber was changed from normal to high to account for the wavelength at which arsenic was detected (<200nm). At this wavelength, UV light is absorbed by moisture and/or oxygen so a higher purge will displace any oxygen or moisture and enable a better light transmission (Knight *pers comm*., 2008b). Instrument optimisation was carried out regularly with 1ppm manganese. This served to align the optics and provide a maximum signal:background ratio (Environmental Protection Agency, 1996). The view was changed from radial to the more sensitive axial view for samples with lower concentrations of As, Cr and Cu. Rinse time was also increased from 60-80 seconds to ensure all elements were washed out of the system between samples. All samples were analysed with regular blank and standard checks to monitor for instrumental drift. Three replicate readings were taken for each sample and averaged.

3.2.8.5.1 Sample Selection

All wood and soil samples were digested and analysed with ICP-OES. However, due to time constraints and the large quantity of leachate collected from the long-term study, not all leachate batches from the different collection dates were analysed. Therefore, representative batches were used from the 18 collection dates covering the entire experimental period (batches 1-5, 8, 10, 12, 15, 18-20).

3.2.8.6 Inductively Coupled Plasma Mass Spectrometry

An Inductively Coupled Plasma – Mass Spectrometer (ICP-MS) (Perkin Elmer Sciex Elan DRC II, MDS, SCIEX, Ontario) was used in this study for rapid multi-elemental analysis of leachate and DGT samples at low concentrations (Figure 3-7). It is an elemental mass spectrometry method where the ICP is used as an ion source. The ICP-MS can reach LOD of <1ppb routinely. The analyte ions are separated according to their mass/charge ratios (m/e) and quantified with a channel electron multiplier (Environmental Protection Agency, 1994c).

Figure 3-7: ICP-MS Unit

The drawbacks of the ICP-MS are the initial costs and the severe sample matrix interferences compared to the ICP-OES. For example, Cr and As suffer from polyatomic interference from the plasma gas. Cr (Atomic Mass 52) can have interference from $^{40}Ar^{12}C^{+}$, $^{36}Ar^{16}O^{+}$ and As (atomic Mass 75) from $^{40}Ar^{35}Cl^{+}$ (Barker, 1999; Plant *et al.,* 2004). These interferences were reduced by introducing ammonia gas. The gas reacts with carbon thereby changing the chemical composition and atomic mass. Ammonia also acts as a collision gas which when combined with energy discrimination effectively reduces the polyatomic species (Knight *pers comm*., 2009). The disadvantage of using ammonia is a reduction in the sensitivity of the measurement of As at low levels.

3.2.8.7 Calculations of Total Elemental Concentrations

Processing of the ICP-OES and ICP-MS data was performed in Microsoft Excel 2007. Firstly, the LOD was determined as three standard deviations (SD) of the blanks. For each element, a good agreement between the wavelengths was required. Readings were taken from wavelengths that exceeded the LOD and the concentration in the original samples calculated using Equation 1 and Equation 2:

Equation 1: Total Elemental Concentration in Original Solid

$$\text{Elemental Concentration in original solid} = \frac{\left(\frac{(\boldsymbol{m} \times \boldsymbol{s})}{\boldsymbol{w}}\right) \times \boldsymbol{DF}}{\boldsymbol{DW}}$$

Equation 2: Total Elemental Concentration in Original Solution

$$\text{Elemental Concentration in original solution} = \boldsymbol{m} \times \boldsymbol{DF}$$

m = measured elemental concentration in solution
s = total weight of the solution
w = initial weight of the sample
DF = dilution factor
DW = dry weight (for soil calculations only)

3.2.8.8 Mass Balance Calculations

Mass balance calculations were carried out on the total arsenic, chromium and copper data taken from the soil, woodchips and leachate. Mass balances were only created for the CCA-wood and soil lysimeters and not the untreated wood and soil lysimeters or CCA wood monofills as the former were felt to be the most hazardous and had the most complete data. Shibata *et al.* (2007) took a mass balance approach to study leachable arsenic and chromium from an in-service CCA-treated structure. They highlighted the importance of this approach to quantify the release of elements from CCA-treated wood and ascertain movement within different environmental media. For the purpose of this work, the mass balance was calculated for CCA-treated wood and soil lysimeters at each sampling point in both the long and short-term studies.

In summary, the mass of arsenic, chromium and copper in the wood at each sample date was calculated from the product of the average elemental concentrations and the amount of wood applied to the lysimeters (4.5kg). The soil was calculated in a similar way with the average elemental concentrations multiplied by the amount of soil applied to the lysimeters (20kg). For the leachate, the average concentrations were multiplied by the average leachate volumes collected. As there were data missing due to two batches remaining uncollected and 6 batches not being analysed, concentration values had to be inferred from the leachate volumes collected or measured. Using the data in analysed batches, plots of concentration (ppb) against leachate generated were created. Significant linear trends were observed for all elements (As: $p < 0.05$, Cr: $p < 0.05$, Cu: $p < 0.05$) (Figure 3-8 to 3-10). The mean leachate volumes collected for the missing batches was used in the linear trend formulas, producing the expected elemental concentrations. The flux of elements was determined by calculating the differences in the mass of elements in the lysimeters at the beginning and end of each experiment.

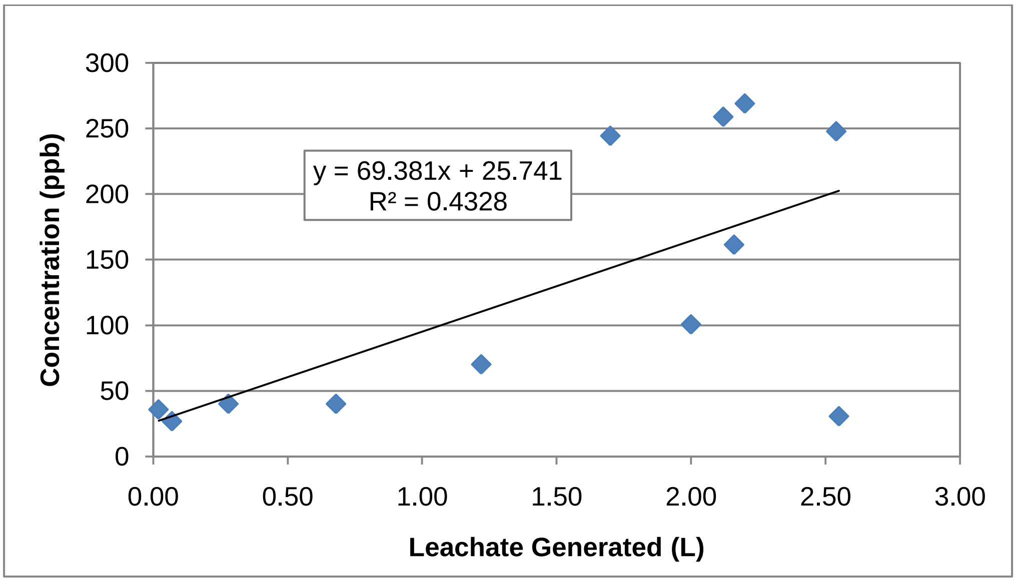

Figure 3-8: Mean Arsenic Concentration Based on Volume of Leachate Generated

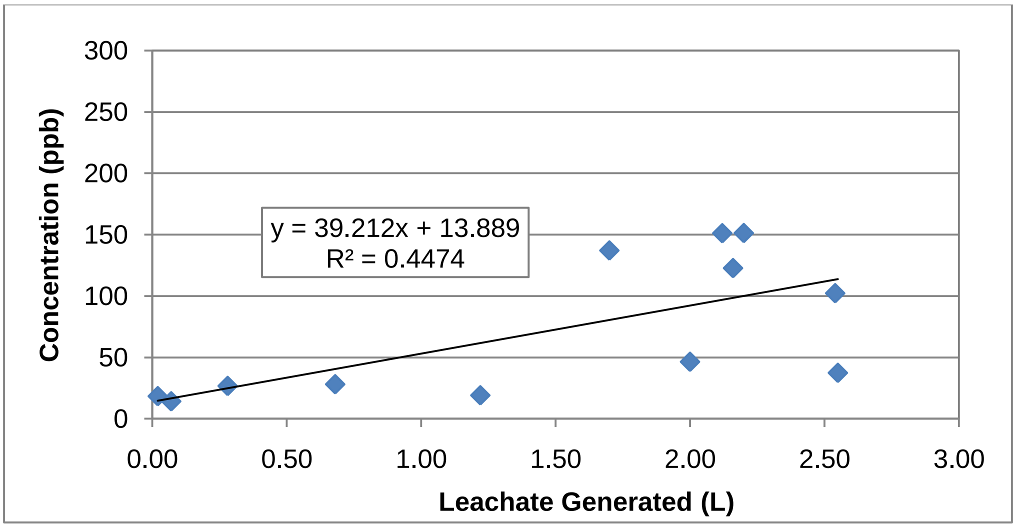

Figure 3-9: Mean Chromium Concentration Based on Volume of Leachate Generated

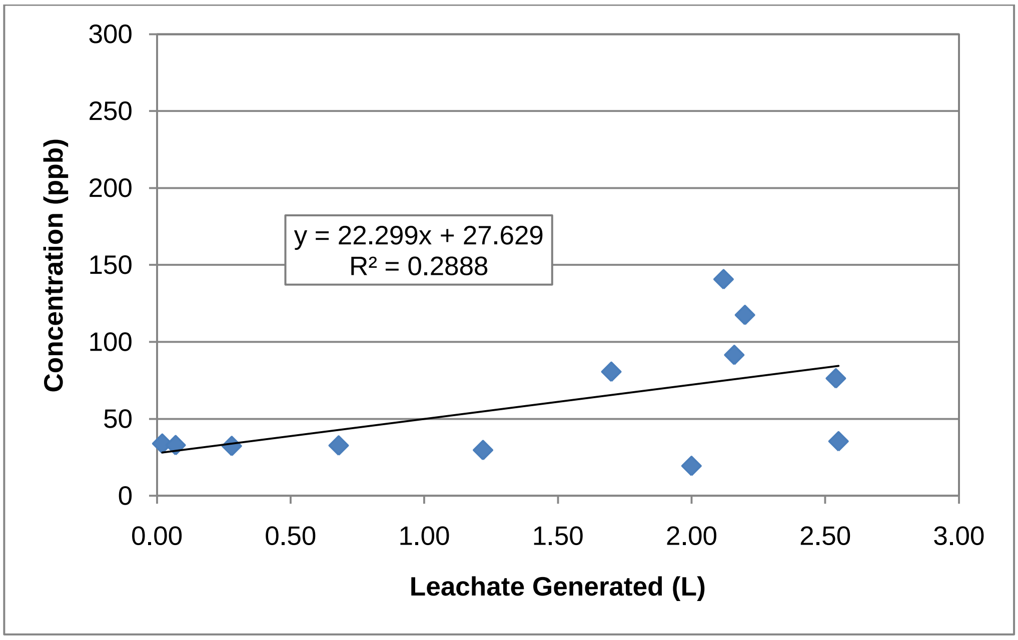

Figure 3-10: Mean Copper Concentration Based on Volume of Leachate Generated

3.2.9 Speciation Analysis

Speciation work was carried out on the initial batch of leachates with a cross section of samples representing each of the treatments. The species of an element can greatly affect its behaviour and impact on human health and the environment (Stumm & Morgan, 1981). Furthermore, once elements are released into the environment, they may alter in species and form complexes with other elements. An understanding of these transformations is important to evaluate potential impacts (Solo-Gabriele *et al.*, 2004b).

Chromium can exist in the environment as 0, +2, +3 +4 and +6 valence states (Solo-Gabriele *et al.*, 2004b). However, the main species are Cr (III) and Cr (VI). Cr (III) is not toxic to humans. Cr (VI) however is 10 to 100 times more toxic than Cr (III) (Pantsar-Kallio & Manninen, 1997; Dean, 2003; Cai *et al.*, 2006). It also tends to be more mobile in the environment (Solo-Gabriele *et al.*, 2004b; Song *et al.*, 2006). Arsenic is also present in many forms. Inorganic species usually found in the environment include As (III) and As (V) (Redman *et al.*, 2002). As (III) is the more toxic, soluble and mobile of the two (Pantsar-Kallio & Manninen, 1997; Mandal & Suzuki, 2002). The more mobile and toxic forms of arsenic and chromium pose a significant risk in soils as there is the potential for uptake into food crops and therefore entry into the food chain. These species may also be mobilised into surface and groundwater.

In previous CCA leaching studies, it was found that only inorganic forms are present in leachate (Jambeck *et al.*, 2006; Khan *et al.*, 2006a). Based on these results and the higher toxicity of the species, only the inorganic forms of arsenic and chromium were analysed.

There are a number of laboratory techniques that can be used to measure arsenic and chromium species in liquid as outlined in Goodman & Glidewell (2002), Greenway (2002), Pickering (2002) and Cai *et al.* (2006). High Performance Liquid Chromatography with Inductively Coupled Plasma Mass Spectrometry (HPLC-ICPMS) is a powerful separation and detection technique that requires only small amounts of sample whilst being highly reproducible. Khan *et al.* (2004) and Khan *et al.* (2006a) have used this method to speciate CCA leachates. The technique is less labour intensive than gas chromatography (GC) (Pearson, 2007) and has been used most commonly for arsenic and chromium speciation (Guerin, *et al.*, 1999; Pearson, 2007). Furthermore, GC works with volatile samples and is therefore not an appropriate technique.

The technique used reverse phase HPLC with a non-polar stationary phase. In summary, previously frozen non-volatile leachate samples were defrosted and 20μl injected into a with a C18 monolithic silica column non-polar stationary phase with a polar mobile phase. The column used in this study has been shown to give rapid separation with equivalent or superior peak efficiencies to traditional columns (Pearson *et al.*, 2007). The mobile phase was set-up for ion-pair chromatographic separation of arsenic and chromium species (Pearson *et al.*, 2007). Separation was achieved by ion-pair liquid chromatography where ions are paired with the additive to the mobile phase; Tetrabutylammonium Bromide (TBAB). The species are then separated in the column based on the polarity of the sample and therefore retention time in the column (Pearson, 2007) (see Table 3-7).

Table 3-7: Operating Conditions for ELAN DRCII ICP-MS and Ion-Pair HPLC (Adapted from Pearson *et al.*, 2007)

ICPMS	Speciation
RF forward power/W	1100
Plasma gas flow rate/ L min^{-1}	15
Nebuliser gas flow rate L min^{-1}	0.88
Dwell time per amu/ms	500
Sweeps per reading	1
Readings per replicate	160
Replicates	1
Time per sample	4 min
HPLC	
C18 reversed phase column	Chromolith™ RP-18e 100 x 4.6 mm id
Mobile phase	2.5mM Tetrabutylammonium Bromide (TBAB)
	10mM phosphate buffer (pH 5.6)
Flow rate	1% (v/v) methanol
Injection volume	1.0ml min^{-1}
	20µl

The HPLC was coupled with an ICP-MS for identification of species due to its speed, sensitivity and multi-element detection capabilities (Cai *et al.*, 2006; Rahman *et al.*, 2009b). Detection limits achieved, accuracy and precision of the method are available in Pearson *et al*. (2007). Limits of detection included 0.107ppb for As (III) and 0.101ppb for As (V) (n=10) (Pearson, 2007). Precision was measured as the relative standard deviation (RSD) of the peak area for As (III) (5.9%) and As(V) (5.4%) (n = 4) (Pearson, 2007). The accuracy of the method was determined by analysis of a CRM of freeze-dried human urine. The results for AsB and DMA were 66.82 ± 1.71ppb and 44.82 ± 1.53ppb respectively. The values for the equivalent species in the CRM were 69 ± 12ppb and 36 ± 9ppb. The operating conditions were similar to a previous study and are listed in (Table 3-7).

The mobile phase was freshly prepared for each batch and the ICP-MS optimised according to Pearson (2007). During optimisation it was found that the sample flow rate needed to be increased from 1.0ml min^{-1} to 2.5ml min^{-1}. Furthermore ammonia gas was added at 0.5ml min^{-1} to prevent interference of ArC^+ with Cr^+ at ratio (m/z) 52. However, the ammonia gas reduced the sensitivity of the measurement of arsenic at low levels. Oxygen would have been more appropriate to use as the reaction gas (Cai *et al.*, 2006) but this was unavailable for this study.

Most speciation methods can only measure the species of one element. A novel technique was used allowing for simultaneous determination of inorganic species of both arsenic and chromium in less than three minutes. Neubauer *et al.* (2004) managed to simultaneously speciate arsenic and chromium in environmental waters by carefully selecting chromatographic conditions. The HPLC set-up used in the current study had slightly different operating conditions from those outlined by Pearson (2007) and was found to be as effective with readings in under three minutes (Figure 3-11).

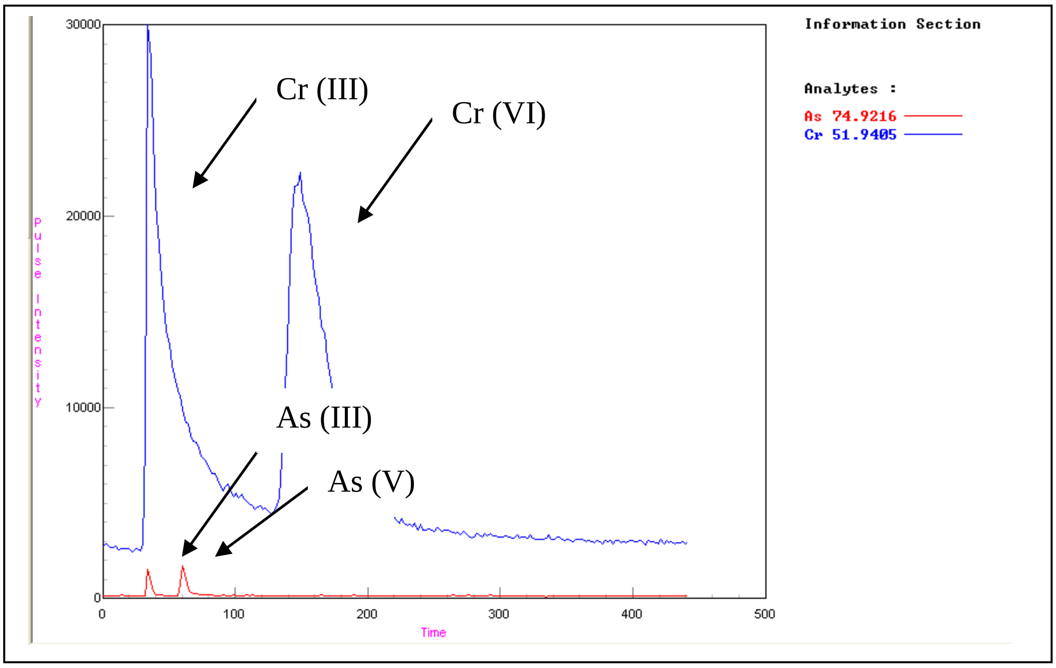

Figure 3-11: Chromatogram Demonstrating Simultaneous Speciation of Inorganic Arsenic and Chromium

3.2.10 DGT Analysis and Calculations

The eluent from the DGT samples (see section 2.5.3.2) was retrieved and diluted five times. The samples were then measured using ICP-MS against mixed arsenic and chromium standards. Blank samples were also introduced throughout. The following formulae taken from Zhang *et al.* (2004) and Fitz *et al.* (2003) were used to calculate the amount of element accumulated in the gel (Equation 3).

Equation 3: Amount of Element Accumulated on the Resin Gel

$$\boldsymbol{M = C(Vacid + Vgel)/fe}$$

M = mass of elemental accumulated in the resin gel
C = elemental concentration in elution samples
$Vacid$ = volume of acid added for elution
$Vgel$ = volume of resin gel
fe = elution factor

3.3 Statistical Analysis

Statistical analyses were performed with SPSS^{TM} (version 16) and Microsoft Excel (2007) with confidence levels of 95% or 99%. A selection of standard statistical analyses and multivariate analyses were used on the data collected from the lysimeter leaching studies.

3.3.1 Correction for Missing Values and Minimum Measurable Levels

Before any statistical analysis could be undertaken on the leachate elemental concentration data, corrections had to be applied for missing values. The leachate data had missing values due to a number of factors, including shortage of leachate sample tubes, broken or lost sample tubes and unavailability of leachate for collection from some lysimeters. Furthermore, due to the very low elemental concentrations (ppb) in some of the preliminary leachate samples, some of the samples fell below the LOD. For As, Cr and Cu, the minimum measurable levels were 8.8ppb, 2.6ppb and 3.8ppb respectively. A Limit of Measurability (LOM) experiment was performed to test for the actual concentrations that the ICP-OES was capable of measuring. Calibration standards were created between 1-10ppb for As, Cr and Cu (calibration curve r^2 for As = 0.9999; Cr = 0.9999, Cu = 0.9999). Spiked acid and equivalent matrix matched samples were created within the range of 1-8ppb to run as samples. The results of the experiment (Table 3-8) illustrate the limiting effects of sample matrix and digesting of samples on measurability of data compared with clean acid. Furthermore, the varying results for arsenic compared to copper and chromium demonstrate the problematic nature of analysing arsenic at very low levels.

Table 3-8: Limit of Measurability Results (1-8ppb)

Concentrations	**As**		**Cr**		**Cu**	
	Matrix	**Acid**	**Matrix**	**Acid**	**Matrix**	**Acid**
1ppb	-3.36	3.18	2.47	1.23	0.66	1.32
2ppb	-2.11	1.67	3.53	2.30	9.55	2.56
3ppb		3.58		3.38		3.50
4ppb	-3.22	6.77	5.41	4.41	19.01	4.72
5ppb		8.71		5.49		5.91
6ppb		7.68		6.82		6.79
7ppb		15.41		7.86		8.23
8ppb	4.59	10.86	9.38	8.52	16.42	9.01

The LOM results indicate that for elemental concentrations below 8ppb, the data are unreliable. As a result, readings below the LOD were recorded as being zero, although this may not necessarily be the case. The gaps in the data were corrected using missing value analysis and the zeros using statistical multiple imputation. For each missing concentration value, a range based on the concentration levels of the other matching lysimeters within the batch, was used to generate random numbers within the range. These numbers were used to substitute for the missing data.

Multiple imputation is a useful tool in environmental studies to deal with missing values within a known distribution. Missing values is a common problem experienced in environmental sampling. However, this technique is not a substitute for good experimental design (Finney, 1988) and was only possible due to an adequate number of replicate samples (7 CCA-treated and soil and 7 untreated wood and soil lysimeters) with which to carry out the imputations. In their work on leaching from a CCA-treated deck, Shibata *et al.* (2007) experienced similar problems with missing leachate samples. As they did not have sufficient replicates, they had to estimate leachate volume based on rainfall depth, catchment area and moisture evaporation from the soil. In the current study, corrections were only applied to leachate batches 1-15 as these had sufficient replicates. In summary, wherever there was a concentration of zero present in the data, random numbers were generated between zero and one then multiplied by the minimum measurable levels for the corresponding element. This was repeated ten times for each value before being added to the data. The ten new generated datasets were then averaged for each data point, resulting in a new imputed dataset. The imputations were carried out three times and the variances checked in SPSS. It was found that there were no significant differences between the variances ($p < 0.05$) demonstrating that the imputations did not change the original dataset significantly. The multiple imputation method is more rigorous than the estimation method adopted by Shibata *et al.* (2007) as it calculates realistic values within a range taken from replicate samples as opposed to calculations from a single sample.

3.3.2 Standard Statistical Analyses

To test for differences between two sets of data, the t-test or Mann Whitney U tests were used. Much of the leachate data violated assumptions of equal variance and/or normal distribution as proven through Levene’s Statistic for homogeneity of variances and Kolmogorov-Smirnov and Shapiro-Wilk for tests of normality respectively. As such, Mann Whitney (non-parametric test equivalent of the t-test) was used. Where neither of the assumptions had been violated the standard t-test was used.

When comparison of several means was necessary, one-way analysis of variance (ANOVA) tests were used. These were followed with Tukey *post hoc* tests to determine where the significant relationships were situated. Where assumptions of normal distribution and/or homogeneity of variance were violated, the non-parametric equivalent Kruskall-Wallis was used. This was followed up with Mann-Whitney *post hoc* comparisons to determine the positioning of significant differences between datasets. The Mann Whitney *post hoc* tests were coupled with a Bonferroni correction on the level of significance to reduce the Type I error rate (when an apparently genuine effect in the population is not real) (Field, 2005).

Two-tailed correlations were used to examine the linear relationships between variables. Where data was normally distributed, the Pearson product-moment correlation coefficient was used, which measures the strength of the relationship between two variables and the direction of the relationship (Field, 2005). Where data was non-parametric, Spearman’s rank correlation was used.

3.3.3 Multivariate Statistical Analyses

Multivariate statistics were only applied to leachate data from the long-term leaching study as there were enough replicates and a full dataset was available following correction with multiple imputations.

Principal Component Analysis (PCA) was initially conducted to examine the underlying structure of the data to identify clusters of variables (pH, redox and concentrations of arsenic, chromium and copper) and produce a plot of how the variables vary in relation to each other. PCA interpretation was improved using orthogonal factor rotation. Varimax rotation was used as recommended by Field (2005). This method loads a smaller number of variables highly onto each other whilst keeping them independent.

In order to test for differences in metal concentrations according to treatment and the effect of time, a repeat-measure ANOVA with two independent variables was used (Field, 2005). For this procedure, the two independent within-group variables were: leachate batch (time) and metal concentrations (arsenic, chromium and copper). Between-group variables related to the treatment (CCA-treated wood and soil lysimeters, untreated wood and soil lysimeters). The assumption of spherecity was tested using Mauchly’s test (where differences between each pair of scores should have equal variance) (Field, 2005).

3.4 Summary

This chapter has discussed the methods of physico-chemical laboratory analysis used on samples collected from fieldwork discussed in Chapter 2. The laboratory methods were justified in light of the advantages and disadvantages of the selected method and possible alternatives. Any issues experienced using the methods and suggestions for improvements were also covered. The data generated from the laboratory analyses were converted to results using the formulae presented in Equation 1 through Equation 3. Following any necessary correction of results, standard statistical and multivariate analyses were applied where appropriate to study relationships and trends in the data.

The following three chapters will discuss the results obtained from the field and laboratory studies. Chapter 4 will present the background conditions of the fieldwork based on the physico-chemical results of the wood, soil and leachate. The concentrations of arsenic, chromium and copper in the soil and wood during the long-term and short-term leaching studies and DGT studies will be discussed in Chapter 5. Chapter 6 will present the arsenic, chromium and copper concentrations in leachate generated from all studies.

4 Physico-chemical Results

4.1 Introduction

This chapter presents the results for physico-chemical measurements made on wood, soil, leachant and leachate during the lysimeter leaching experiments. Previous studies have highlighted the major factors involved with leaching from CCA wood (Cooper, 1994; Hingston *et al.*, 2001). The amount of leachant and contact time have been shown to influence leaching of the CCA components from wood (Kartal *et al.*, 2005; Taylor & Cooper, 2005). This was related to rainfall duration and levels in the long-term study and water application in the short-term study. Temperature of the leachant and surrounding environment has also been shown to be an important factor (Cockcroft & Laidlaw, 1978; Cooper, 1994; Van Eetvelde *et al.*, 1995b; Taylor & Cooper, 2005; Moghaddam & Mulligan, 2008). Soil parameters that control leaching include moisture content (Cooper, 1994), organic matter content (Schultz *et al.*, 2002), texture (Schultz *et al.*, 2002), electrical conductivity (Lebow *et al.*, 1999), pH (Bergman, 1983; Bergholm, 1989; Cooper, 1991; Wang *et al.*, 1998; Balasoiu *et al.*, 2001; Hingston *et al.*, 2001; Cooper *et al.*, 2001; Crawford *et al.*, 2002; Townsend *et al.*, 2003a; Khan, 2004; WRAP, 2004; Solo-Gabriele *et al.*, 2005) and redox (McLaughlin *et al.*, 2000). The extent of leaching will also depend on the initial levels of arsenic, chromium and copper in the wood, soil and leachant (McLaughlin *et al.*, 2000; Crawford *et al.*, 2002), along with specific concentrations of certain other interrelated elements in the soil such as aluminium, calcium, iron and manganese.

The physico-chemical data obtained from the lysimeter studies are presented as scatterplot graphs over time. The leachant and temperature conditions for the long-term leaching study are presented in section 4.2 and for the short-term leaching study in section 4.3. Section 4.4 presents the physico-chemical results of the soil and leachate. The initial levels of arsenic, chromium and copper in the wood, soil and leachant are covered in section 4.5. Section 4.6 presents the concentrations of common elements of interest in the soil and leachate. Section 4.7 is a discussion of the physico-chemical results and the final section, 4.8 will summarise the chapter.

4.2 Leachant and Temperature Results: Long-Term Leaching Study

Rainfall and ambient temperature were recorded throughout the outdoor long-term leaching study (as outlined in section 2.3.5). There was 522.7mm of rainfall over the 147 days of the experiment (Figure 4-1), with much of it occurring in a two week period.

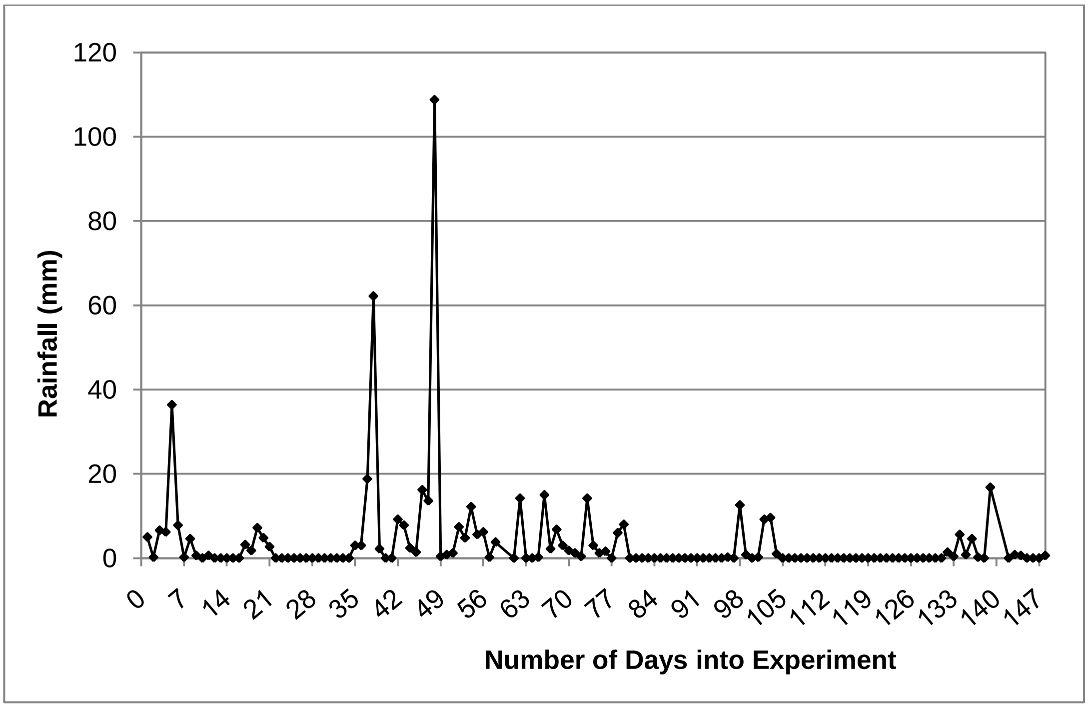

Figure 4-1: Long-Term Study Rainfall Data

Exceptional amounts of rainfall were experienced across the region and included an estimated 1 in 150 year rainfall event in June 2007 (Coulthard *et al.*, 2007). The rainfall measured by the weather station during the experimental period was higher than that recorded by the Environment Agency for the equivalent period in each of the previous 4 years (Table 4-1). Many of the lysimeters became waterlogged and leachate was lost as a result. This intense rainfall caused increased levels of leaching but also produced a greater dilution effect.

Table 4-1: Total Rainfall Between 9th May and 3rd October for the Years 2002-2007

Year	**Total Rainfall (mm)**
2002	199.1
2003	269.0
2004	320.4
2005	234.6
2006	335.0
2007	522.7

Ambient temperatures were measured hourly and 24-hour averages are given in Figure 4-2. The average temperature over the entire experimental period was 14.34°C. Soil temperature was also measured in two of the lysimeters with buried Tiny Tag™ probes at 7.5 cm (Tiny Tag 1, average temperature measured 16.00°C) and 11cm depth (Tiny Tag 2 average temperature measured 17.05°C). The ambient air temperature increased significantly over the experiment ($p < 0.05$) whilst that in the soil at -7.5cm decreased significantly from the introduction of the temperature probe at day 40. The deeper probe at -11cm did not show any significant trends over time.

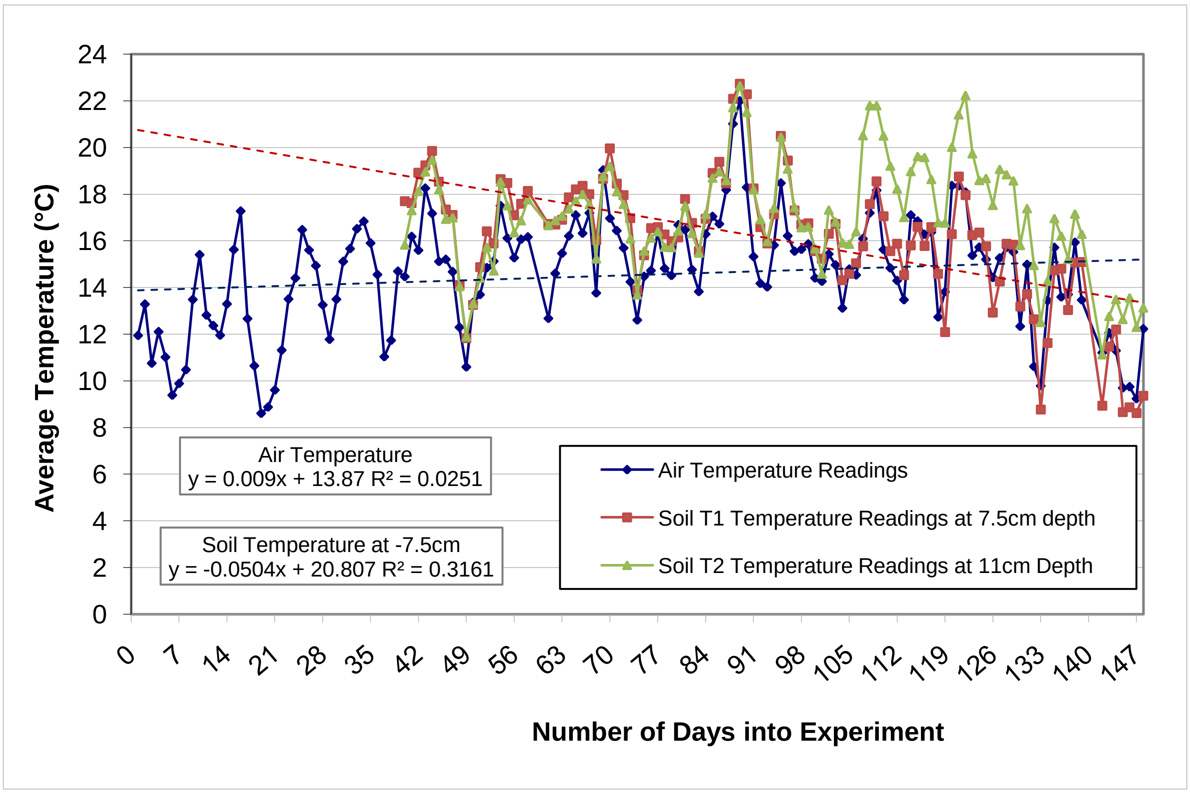

Figure 4-2: Long-Term Study Average Temperature Data

Ambient air temperatures and those recorded at different depths by the different instruments were co-variant but with significant differences ($H(2) = 36.37$, $p < 0.01$). Using Mann-Whitney tests with a Bonferroni correction (0.0167 level of significance) it was found that the weather station recorded significantly lower temperatures (*Mdn* = 15.27) than either of the Tiny Tag probes (Tiny Tag 1 *Mdn* = 16.41; $U = 3917$, $p < 0.0167$) (Tiny Tag 2 *Mdn* = 17.07; $U = 2778.5$, $p < 0.0167$). Watts (1975) studied differences between air and soil temperature in shallow pots within a controlled environment and found considerable variation. In exposed soil, temperatures measured were consistently higher than ambient air temperatures. Adding a mulch layer would intensify this effect (Ramakrishna *et al.*, 2006). This difference demonstrates the importance of measuring soil rather than air temperatures in this type of study. However, many leaching studies looking at soil do not measure this. The two Tiny Tag probes were added at day 49. The probes measured significantly different temperatures over the course of deployment ($H(2) = 36.37$, $p < 0.01$) ($U = 4325$, $p < 0.0167$). This may be due to the different depths they were placed at with the probe at -11cm recording higher temperatures than the probe at the soil/mulch interface. The difference may also be attributed to the proximity of the lysimeters with Tiny Tag 2 to the surrounding buildings and therefore higher temperatures experienced during the autumn months.

4.3 Leachant and Temperature Results: Short-Term Leaching Study

The short-term lysimeter leaching study was set up in a greenhouse in order to control watering and evaluate the possible effects of the unnaturally high rainfall experienced in the long-term leaching study. The summer and winter average rainfall for the previous five years was applied to the lysimeters in such a way as to simulate different weather patterns (see Section 3.4). Leachate was generated on one occasion from the lysimeters receiving water in single monthly quantities. Lysimeters receiving water weekly, generated leachate consistently throughout the study, whilst those receiving the same amount of water but in daily doses generated no leachate.

The average soil temperature at 7.5cm depth over the four weeks was 12.48°C (Figure 4-3), approximately 2°C less than the average for the long-term leaching study. Values also decreased significantly over time ($p < 0.01$). The big dip was related to a cold spell in the second half of the month.

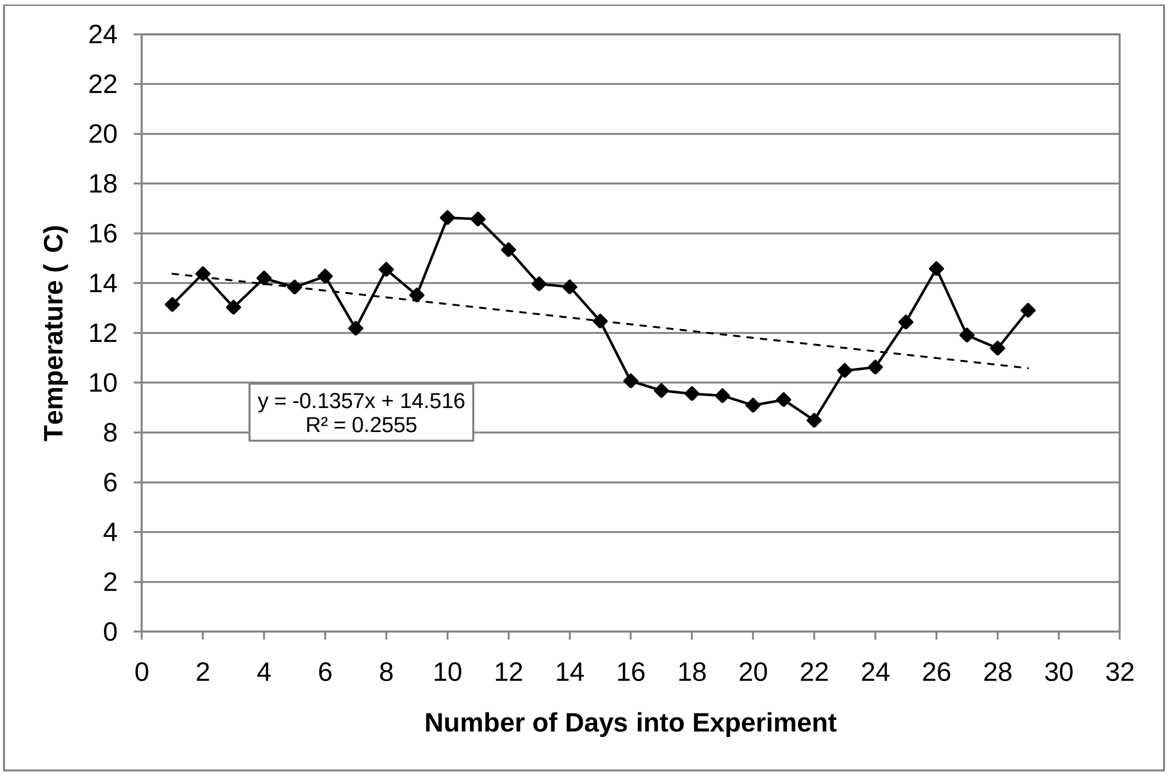

Figure 4-3: Greenhouse Study Soil Temperature

4.4 Physico-Chemical Results

4.4.1 Soil Moisture Content: Long-Term Leaching Study

Soil moisture content (MC) was measured according to the method outlined in section 3.2.1 on samples collected from the lysimeters (section 2.3.6 for the long-term and section 2.4 for the short-term leaching experiment). The values in the long-term study were high over the experimental period (Figure 4-4) reflecting the heavy rainfall (Figure 4-1). The trends observed also appear to be influenced by rainfall patterns with higher soil MC occurring on days 42 and 84 during the period of heavy rain and lower soil MC occurring on days 63 and 126 during days of no rainfall. There is also a lag effect where soil MC is high on days following heavy rain, for example day 84.

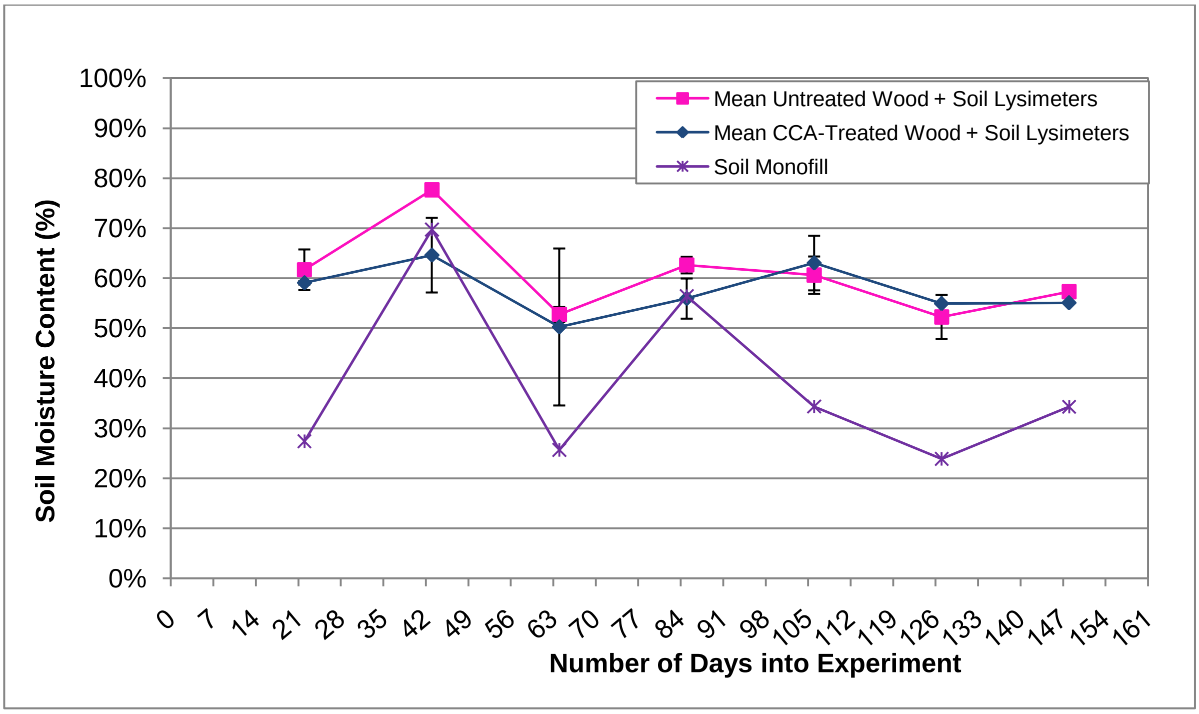

Figure 4-4: Long-Term Study Soil Moisture Content (± 1 standard deviation)

Significant differences were observed between those lysimeters containing CCA wood, those containing untreated wood and the soil monofill ($H(2) = 6.968$, $p < 0.05$). The MC of the soil in the monofill was found to be significantly lower (*Mdn* = 34.31%) than the soil in the lysimeters containing untreated (*Mdn* = 58.83%) and CCA-treated wood (*Mdn* = 58.86%) ($U = 15.00$, $p < 0.05$ and $U = 17.00$, $p < 0.05$ respectively). Soil MC between the lysimeters containing untreated wood and CCA-treated wood were not significantly different.

The soil lysimeter fluctuated more than the lysimeters containing soil and wood. The results are to be expected since in the absence of a mulch layer, soil loses more moisture at a faster rate during dry periods (Othieno, 1980). Conversely, this soil wets up faster during wet periods. Therefore, in the wood-containing lysimeters, excess water was trapped within the soil following the periods of heavy rainfall and only escaped by slow percolation at the base of the lysimeter as evaporation at the surface was inhibited by the mulch. As such, MC levels in the lysimeters containing soil and wood remained high and fairly constant until the end of the study. This effect was observed in the experiment where wood-containing lysimeters remained waterlogged throughout (see section 2.4).

4.4.2 Soil Moisture Content: Short-Term Leaching Study

During the short-term leaching study, the average soil MC in the wood and soil lysimeters increased steadily and significantly ($p < 0.05$) over time. This increase is indicative of moisture accumulation in the soil, resulting from mulch addition. Watering regime had an impact on MC (Figure 4-5), with lower soil MC for the daily and higher soil MC for the weekly and monthly water applications. During the study it was noted that when water was applied daily, much of it was retained in the mulch layer and only small amounts filtered down into the soil. Conversely, weekly and monthly applications exceeded the moisture retaining limit of the mulch, thereby resulting in infiltration into the soil.

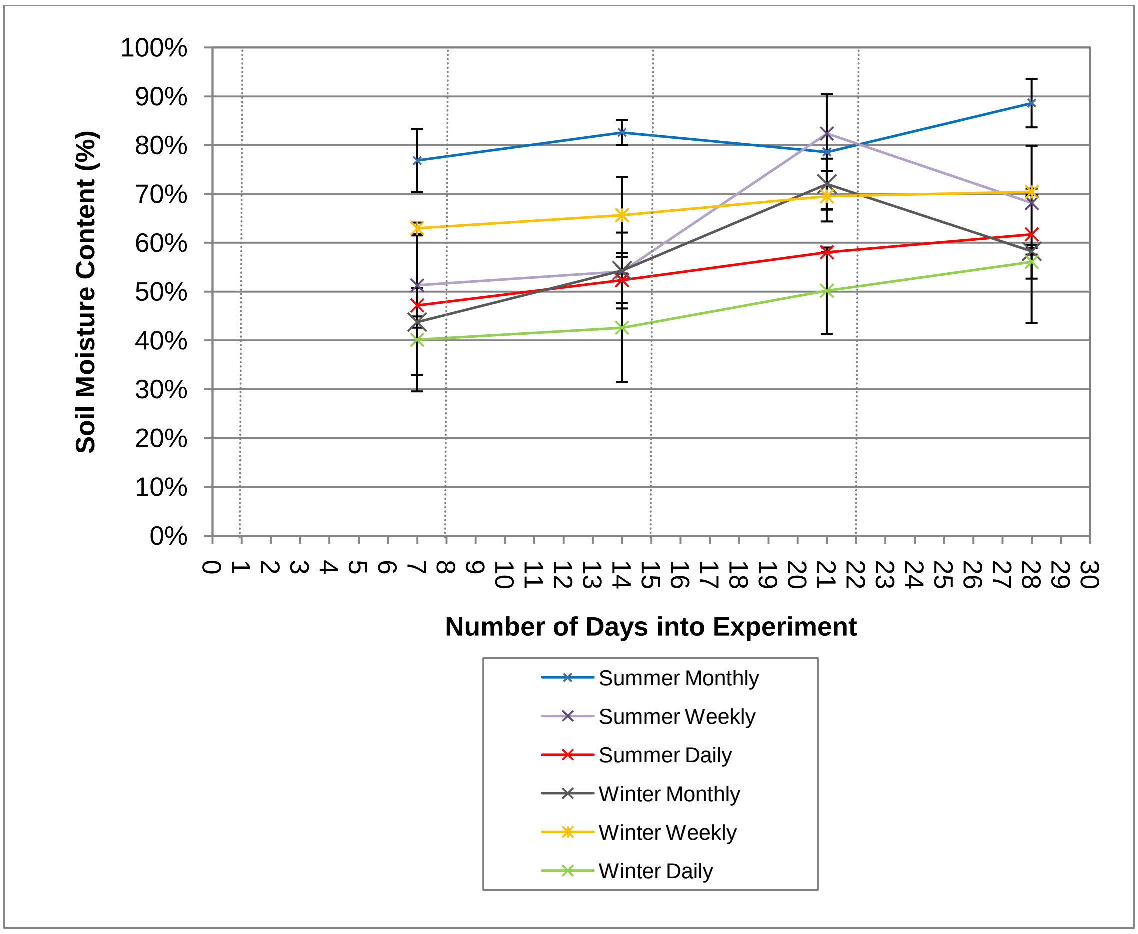

Figure 4-5: Short-Term Study Average Soil Moisture Content According to Watering Regime (± 1 standard deviation). Grey dashed lines denote weekly watering events. Monthly watering took place on Day 1

4.4.3 Soil Organic Matter: Long-Term Leaching Study

Measurements of soil organic matter (OM) were carried out on samples according to the method outlined in section 3.2.2. OM levels were found to range between 12% and 20% (Figure 4-6) with significant differences between the treatments ($F(2,30) = 8.659$, $p < 0.01$). The soil monofill ($M = 14\%$) had significantly lower soil OM levels than the lysimeters containing wood and soil (untreated wood and soil lysimeters, $M = 17.62\%$; CCA-treated wood + soil lysimeters, $M = 17.54\%$) ($p < 0.01$). There was no obvious or significant trend in soil organic matter content over time.

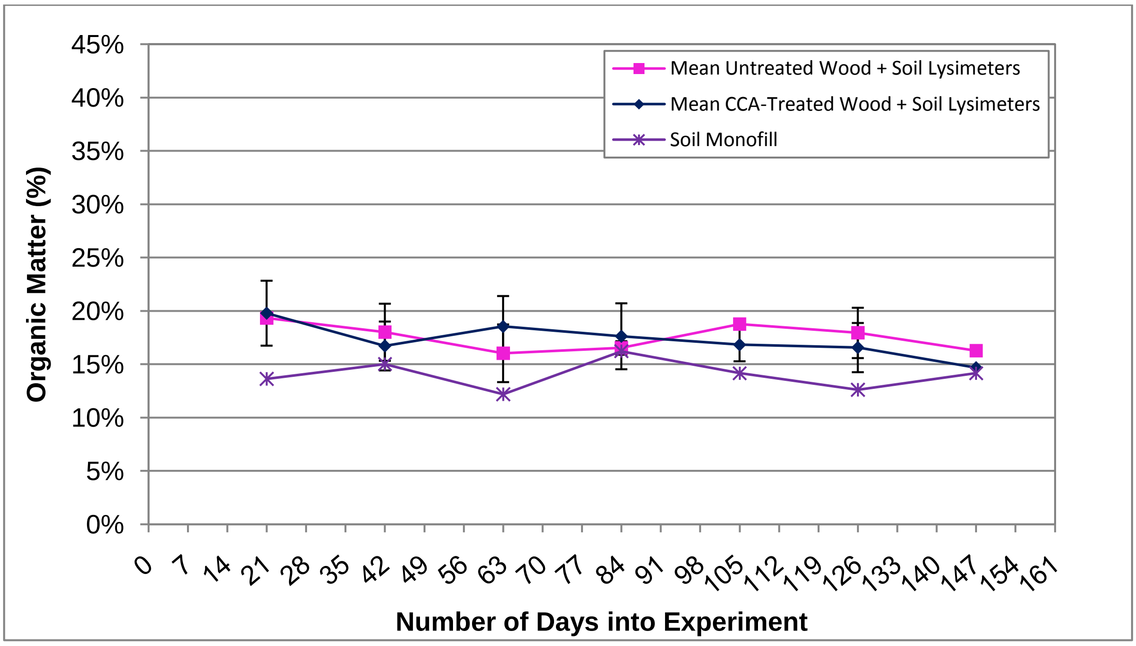

Figure 4-6: Long-Term Study Soil Organic Matter Content (± 1 standard deviation)

The soil OM levels for the short-term leaching study were higher than those in the long-term study (Figure 4-7). It is not clear why this is the case as the same amounts of soil and woodchip were measured into the lysimeters in both studies. The difference may be related to the LOI method used for measuring soil OM. The method required only 5g of oven-dried soil to carry out the analysis. With such a small amount of sample it is easy for the results to be biased. For example, if pieces of organic material such as small twigs, roots or part of a woodchip were inadvertently included in the procedure, they have the potential to significantly increase the soil OM result. Replicate soil samples were analysed in an attempt to overcome this potential bias, however the large error bars in Figure 4-7 suggest that there was still a problem with heterogeneity of sample.

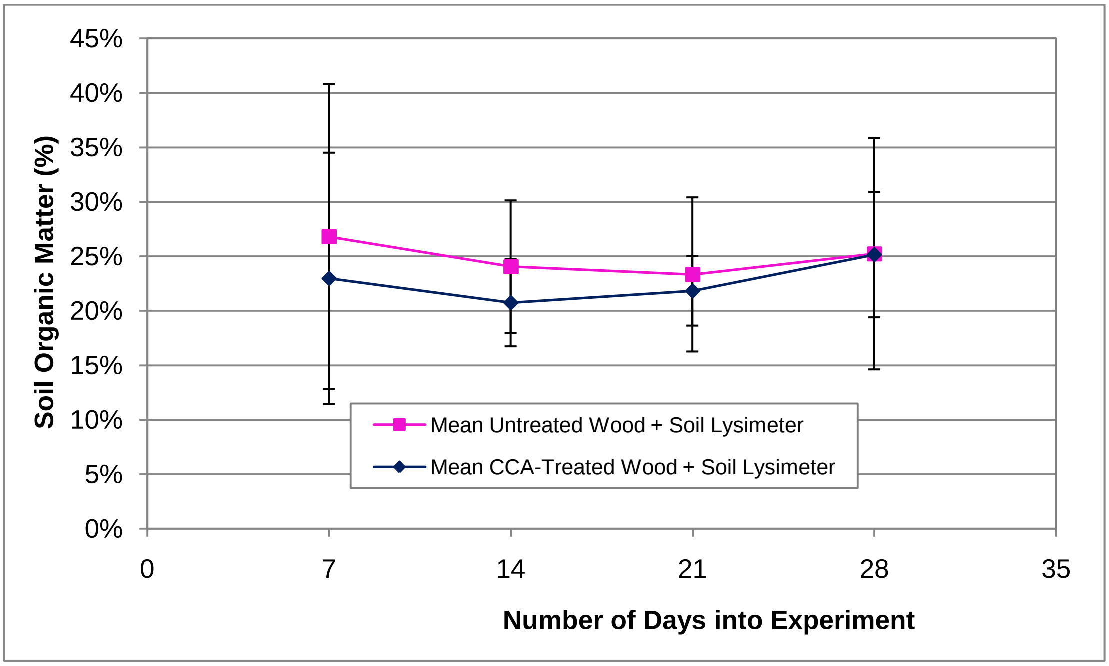

Figure 4-7: Short-Term Study Soil Organic Matter Content (± 1 standard deviation)

4.4.4 Soil Texture

The topsoil texture was characterised prior to the lysimeter experiments using the method described in section 3.2.3 on five representative subsamples. The soil was found to be a sandy loam (76.75% ± 1.95% sand, 13.39% ± 0.98% silt and 9.86% ± 0.92% clay).

4.4.5 Soil Electrical Conductivity: Long-Term Leaching Study

Soil electrical conductivity (EC) in the long-term study generally increased up to day 85 then sharply decreased and levelled from day 106 for the soil monofill and untreated wood and soil lysimeters (Figure 4-8). The CCA-treated wood and soil lysimeter EC values remained high (between 600 and 725ppm) from the start of the experiment up to day 85 and then decreased in all lysimeters. This trend may be a dilution effect resulting from the heavy rainfall up to day 84.

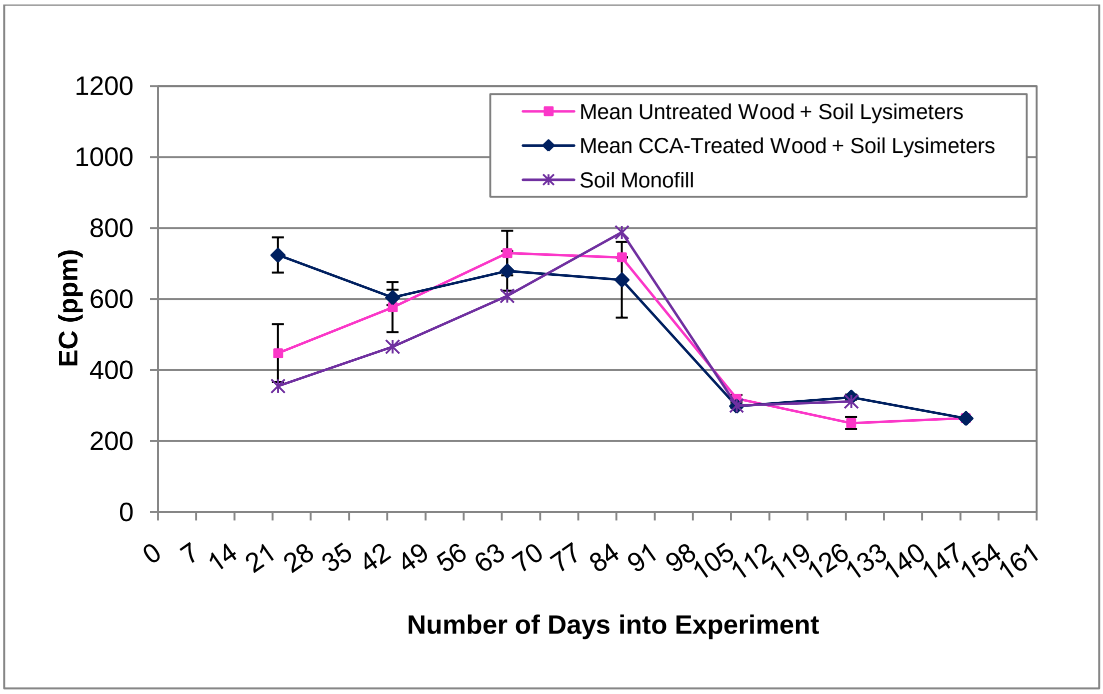

Figure 4-8: Long-Term Study Soil Electrical Conductivity (± 1 standard deviation)

4.4.6 Soil Electrical Conductivity: Short-Term Leaching Study

In the short-term leaching study, soil EC measurements were found to increase over time although in only the untreated wood and soil lysimeters were these trends significant ($p < 0.05$) (Figure 4-9). This trend is similar to that experienced in the first half of the long-term leaching study.

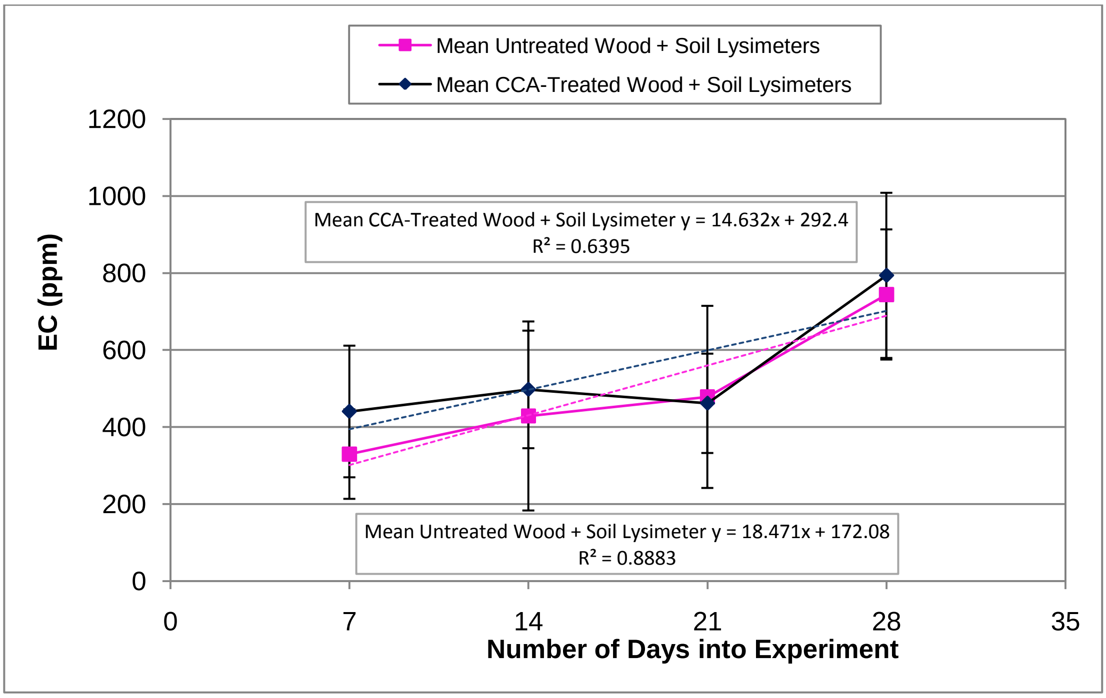

Figure 4-9: Short-Term Study Soil Electrical Conductivity (± 1 standard deviation). Dotted lines denote linear trends

4.4.7 Soil Redox: Long-Term Leaching Study

The measurement of soil redox is outlined in sections 2.3.6 and 3.2.6. Redox levels generally decreased over time (all correlations significant $p < 0.05$) (Figure 4-10). During the period of heavy rainfall between day 1 and day 85, conditions in the soil of all lysimeters was moderately reducing (between +100mV to +400mV). Following this, the condition in the lysimeters containing the wood mulch became reducing (-100mV to +100mV) (Patrick & Mahapatra, 1968). This is explained by waterlogging following heavy rainfall (Figure 4-1). The conditions in the soil monofill lysimeters remained moderately reducing, supporting the assumption that the soil monofill lost more moisture at a faster rate than soil in the mixed lysimeters (refer to section 4.4.1 for further explanation).

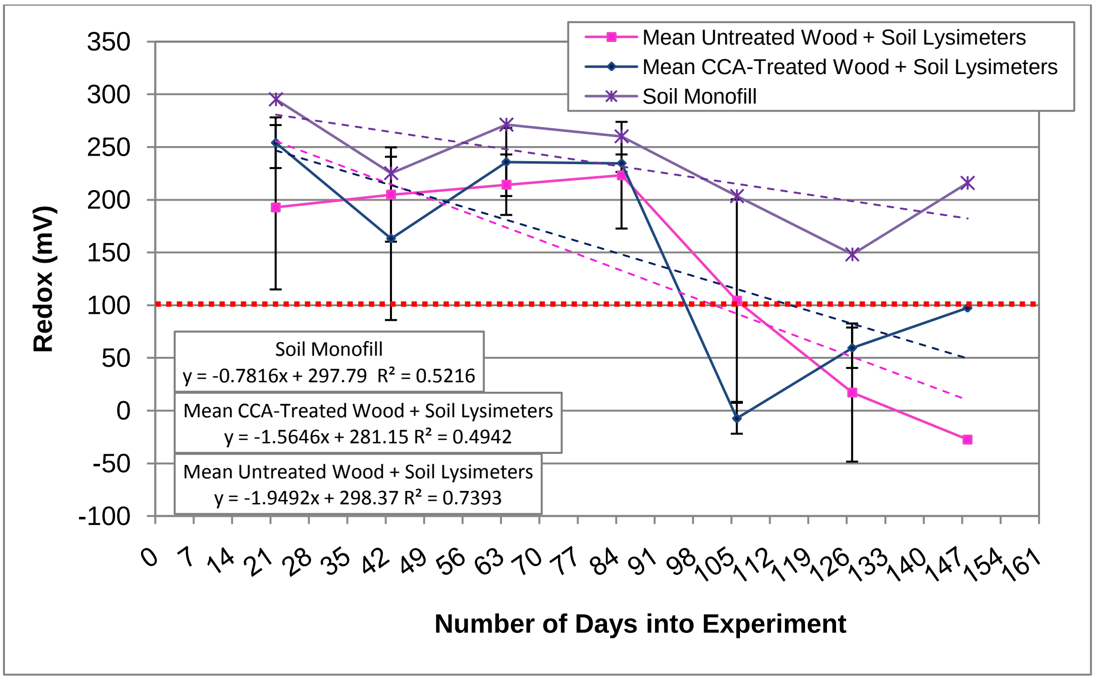

Figure 4-10: Long-Term Study Soil Redox (± 1 standard deviation). Red dotted line denotes redox class boundary (< +100 are reducing conditions, +100 upwards are moderately reducing conditions). Coloured dotted lines denote linear trend of corresponding coloured data series

4.4.8 Soil Redox: Short-Term Leaching Study

The redox of the soil in the short-term leaching study demonstrates a decreasing though non-significant trend (Figure 4-11) as seen in the long-term study (refer to section 4.4.7). In both cases, the mulch containing lysimeters started off with Eh values around the +200 to +250 range, moderately reducing conditions. In the long-term study the wood-containing lysimeters became increasingly reduced (Figure 4-10). The short-term study lysimeters may have followed a similar trend if the study had run on for longer. In the short-term leaching study, Eh was found to have an inverse relationship to soil MC (refer to Figure 4-5). The retention of water as shown by the increasing soil MC results would result in reducing conditions (Staunton & Wang, 2005).

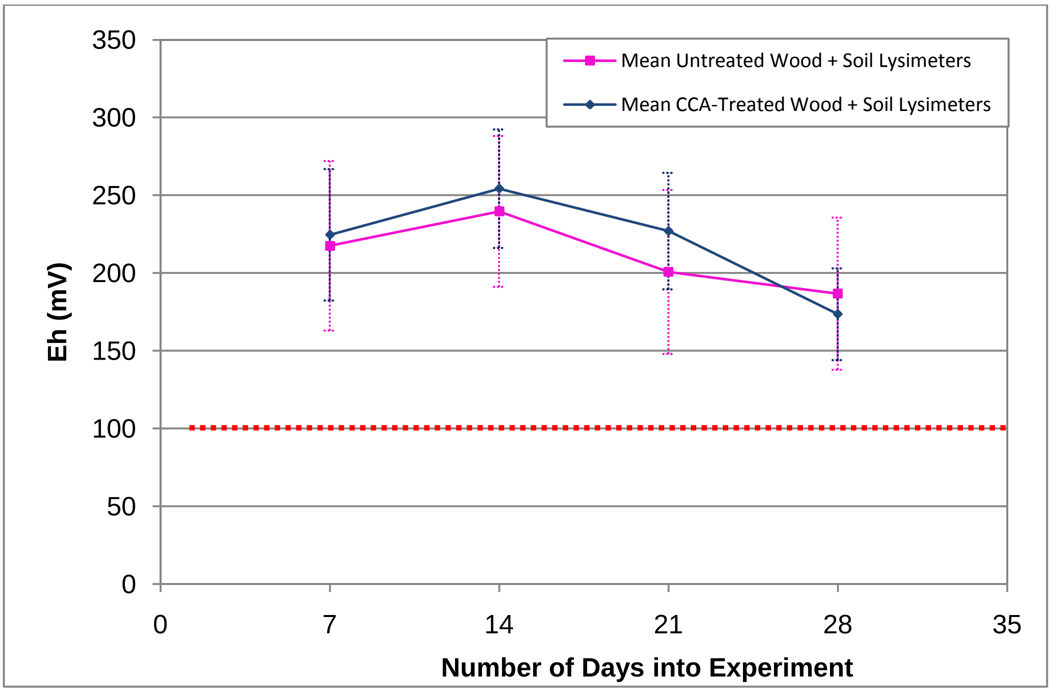

Figure 4-11: Short-Term Study Soil Redox (± 1 standard deviation). Red dotted lines denote redox class boundaries (-100 to +100 represent reducing conditions, +100 upwards represent moderately reducing conditions)

4.4.9 Soil pH: Long-Term Leaching Study

Soil pH was measured using the method outlined in section 3.2.4. In the long-term study the pH condition of the soil remained neutral (Figure 4-12) although increased significantly over time in the soil monofill and CCA-treated wood and soil lysimeters ($p < 0.01$).

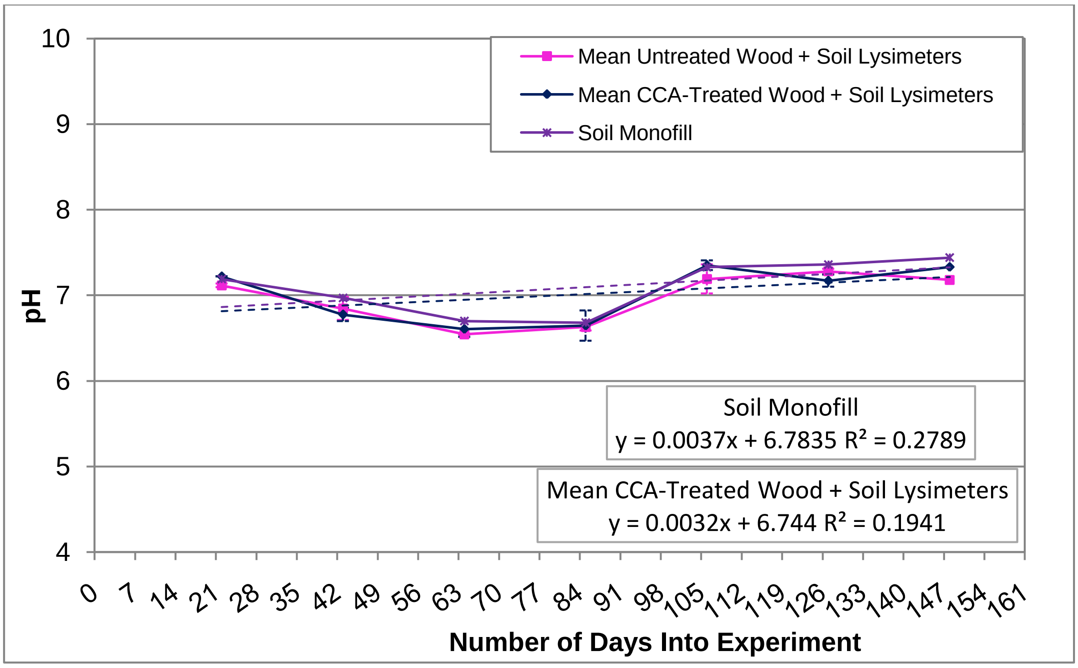

Figure 4-12: Long-Term Study Mean Soil pH (±1 standard deviation)

4.4.10 Soil pH: Short-Term Leaching Study

Soil pH in the short-term leaching study decreased over time (significantly for the untreated wood and soil lysimeters, $p < 0.05$) but remained in the near-neutral range (Figure 4-13). Only the untreated wood and soil lysimeter trend was significant. The trend mirrors the trends in the first half of the long-term study (Figure 4-12).

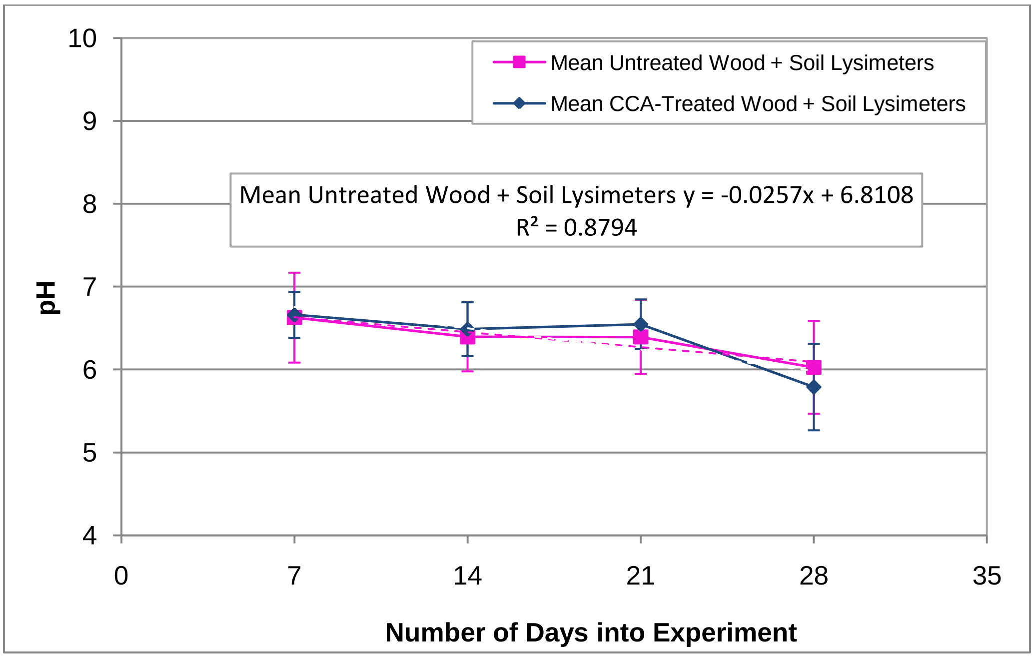

Figure 4-13: Short-Term Study Mean Soil pH (± 1 standard deviation). Coloured dotted line denotes linear trend of corresponding coloured data series

4.4.11 Leachate Redox

The measurement of leachate redox is outlined in section 2.3.6. The results from the long-term study show that the conditions remained moderately reducing (between +100 to +400 mV) over the entire experimental period (Figure 4-14). This was also the case for the greenhouse study leachate where values ranged from 180.53mV and 290.00mV. There was an increasing but non-significant trend over time (Figure 4-15). Significant differences in ORP readings were observed in the long-term study (F(4,71) = 9.47, $p < 0.01$). The untreated wood monofill gave significantly lower results compared to the CCA-treated and untreated wood lysimeters ($p < 0.01$ in both cases). Both wood monofills gave significantly lower ORP readings than the soil monofill ($p < 0.01$ in both cases). These results suggest that topsoil has a buffering effect on the ORP of the leachate passing through to the collection container.

Under normal summer conditions and with the shallow soil depths in this study, it is expected that the conditions should be oxidising (>400mV). However, as with the long-term study, the observed ORP of the leachate is somewhat lower than expected due to the anaerobic conditions in the soil.

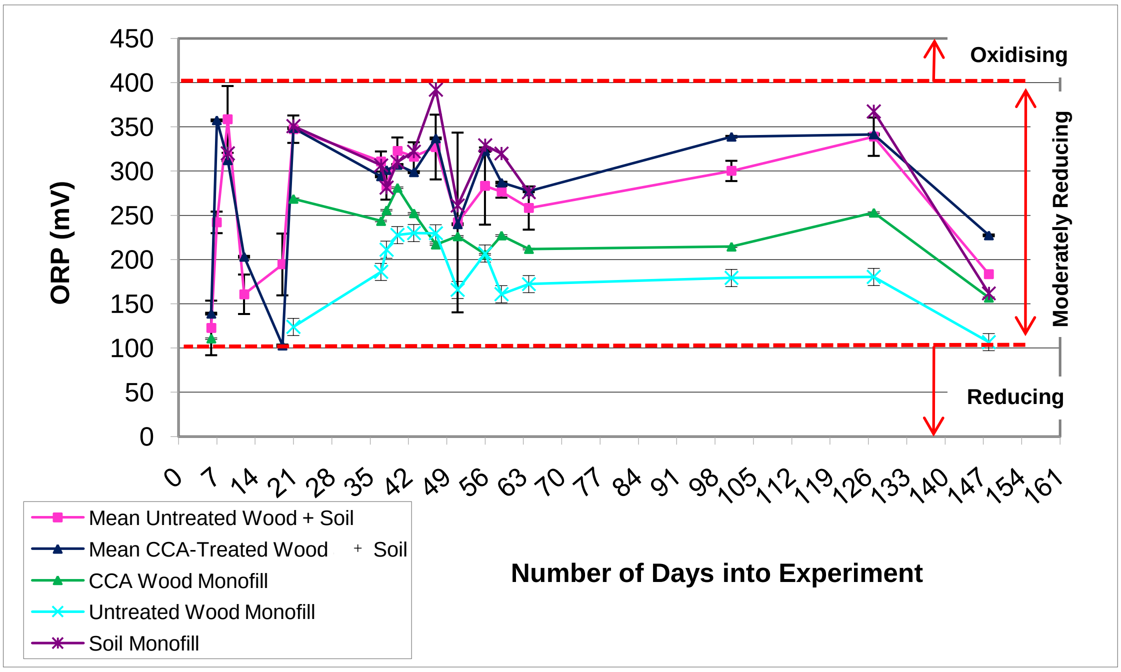

Figure 4-14: Long-Term Study Leachate Redox. Red dotted lines denote redox class boundaries (± 1 standard deviation)

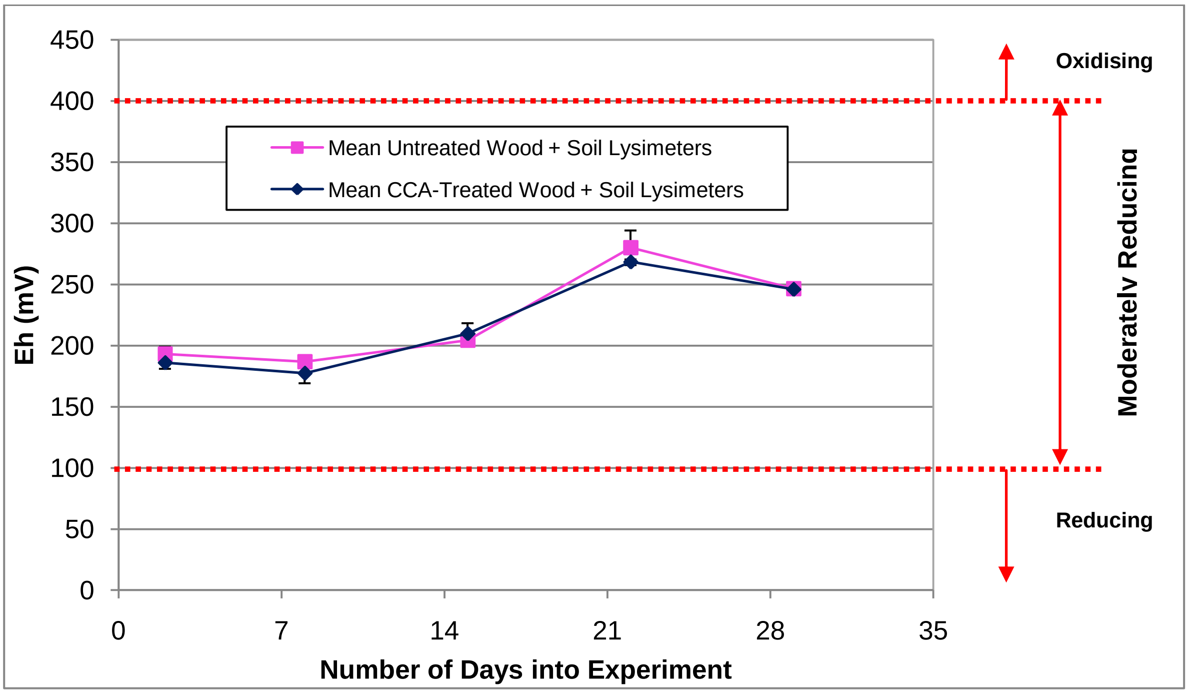

Figure 4-15: Short-Term Study Leachate Redox. Red dotted lines denote redox class boundaries (± 1 standard deviation). Coloured dotted lines denote linear trend of corresponding coloured data series

4.4.12 Leachate pH: Long-Term Leaching Study

Leachate pH was measured in the lab according to the method described in section 3.2.4. The pH of the CCA-treated wood monofill and blank wood monofill leachates were significantly lower than those of lysimeters containing soil (Tukey *post hoc* comparisons: CCA wood monofill (M = 6.4) against treated (M = 7.58) and untreated (M = 7.5) lysimeters $p < 0.01$; untreated wood monofill (M = 5.5) against CCA wood monofill, treated and untreated lysimeters $p < 0.01$) (Figure 4-16).

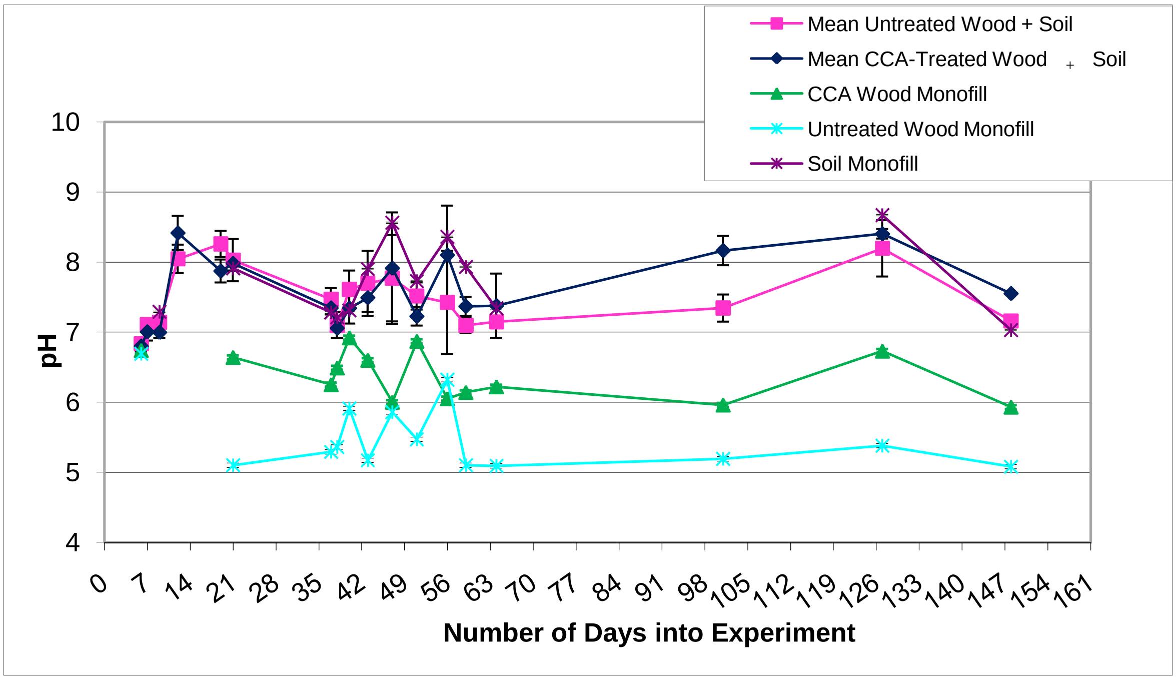

Figure 4-16: Long-Term Study Mean Leachate pH (± 1 standard deviation)

Values were fairly constant over the experimental period with leachate from the soil-containing lysimeters remaining between pH 6.8 and 8.67, that from the CCA wood monofill remaining between pH 6 and 7 whilst that from the untreated wood lysimeter was significantly lower at pH 5 to 6.7. Fluctuations within the ranges described above (particularly between days 35 and 63 appear to coincide with periods of heavy rainfall (Figure 4-1).

4.4.13 Leachate pH: Short-Term Leaching Study

Average pH values of leachate from untreated wood and soil lysimeters and CCA-treated wood and soil lysimeters in the short-term leaching study ranged between 5.56 and 7.00 with an average of 6.24 ± 0.46. The pH increased over time (Figure 4-17), although the trend was not significant.

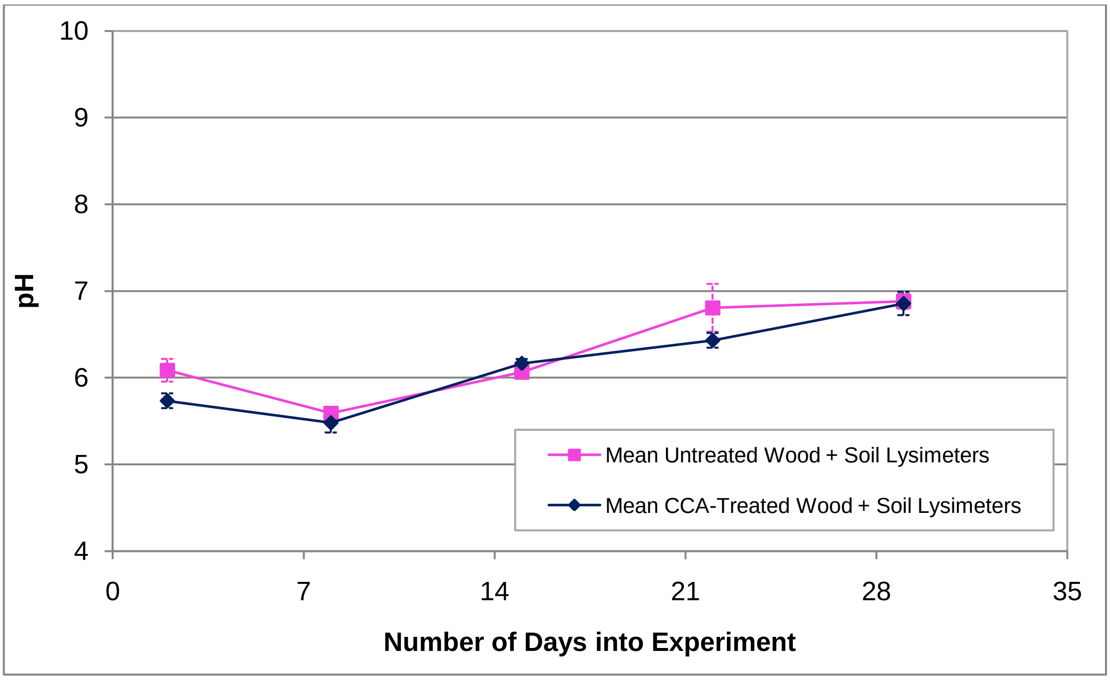

Figure 4-17: Short-Term Greenhouse Study Mean Leachate pH (± 1 standard deviation)

4.5 Initial Concentrations of Arsenic, Chromium and Copper

Initial levels of arsenic, chromium and copper were measured in wood, soil and leachant prior to experiment set-up (methods outlined in section 3.2.8). These measurements were important to gauge background levels in the study and for understanding the potential leaching properties of the wood, the fate of the elements within the soil and the influence of the leachant used.

4.5.1 Fresh CCA-treated Wood and CCA Waste Wood

Arsenic, chromium and copper analyses were carried out on freshly treated CCA wood and CCA waste wood (Table 4-2).

Table 4-2: Total Elemental Concentrations in the Wood Samples (± 1 standard deviation)

	Freshly Treated Wood	**CCA-treated Waste Wood**
Arsenic	2063.79 ± 215.94 ppm	5429.74 ± 1343.55 ppm
Chromium	3310.96 ± 413.25 ppm	10647.95 ± 3345.23 ppm
Copper	2110.15 ± 461.90 ppm	2920.74 ± 968.19 ppm

Although the weathered wood had been in service for 15 years, levels of all metal(loid)s were higher than for the freshly treated wood (1.4 times higher for copper, 2.6 times higher for arsenic and 3.2 times higher for chromium). This may be related to the industrial application of the wood and therefore higher initial loading values (Jambeck *et al.,* 2006). The higher retentions in the weathered CCA wood observed in this study suggest that most of the CCA preservative remains fixed in the wood whilst in-service, a similar result to that of Cooper *et al.* (2001) who also found that residual levels in CCA-treated poles remain high once service life ends. The proportions of the three elements in the wood also reflect the original preservative formulation with chromium in highest concentrations followed by copper then arsenic (refer to Table 2-2). However, in the weathered wood, arsenic values were higher than copper, suggesting that the elements may have leached out differentially whilst in-service.

4.5.2 Soil and Leachant

Initial concentrations of arsenic, chromium and copper in the soil were 3.10 ± 0.7ppm, 10.76 ± 2.31ppm and 24.24 ± 0.82ppm respectively. The ultrapure water used in the SPLP and short-term leaching study did not have detectable levels of arsenic, chromium of copper. The rain water in the long-term leaching study was sampled on two occasions and was also found to be free of detectable arsenic, chromium and copper.

4.6 Concentrations of Common Elements

Topsoil and leachate were analysed for concentrations of common elements and those shown to influence leaching of CCA in previous CCA leaching studies (Kennedy & Collins, 2001; Cao & Ma, 2004; Lebow & Foster, 2005; Dagan, *et al.*, 2006) (Table 4-3 for soil concentrations and Table 4-4 for leachate concentrations).

The leachate from the untreated wood and soil lysimeters and CCA-treated wood and soil lysimeters had similar concentrations of all elements. In most cases (Ca, K, Mg, Na, Ni and S), concentrations were highest in the soil monofill. Concentrations in the CCA wood monofill were much lower than in the lysimeters containing soil. The untreated wood monofill had negligible amounts of any of the elements analysed. These results suggest that the higher concentrations of elements in the untreated and treated lysimeters are sourced from the topsoil. Results from the CCA monofill leachate suggest industrial contamination of the wood whilst in-service or during storage as the untreated wood equivalent was relatively free of the elements measured.

Table 4-3: Elemental Concentrations in the Soil

Soil Element	Concentration (ppm)
Al	6284.35
Ba	72.20
Ca	8980.35
Fe	7155.82
K	2409.62
Mg	1461.86
Mn	150.43
Na	178.10
Ni	7.31
P	626.10
S	592.28
Zn	44.56

Table 4-4: Elemental Concentrations in Lysimeter Leachates (ppm)

	Untreated Wood and Soil Lysimeter Leachate Average	CCA-Treated Wood and Soil Lysimeter Leachate Average	CCA Monofill Leachate	Untreated Wood Monofill Leachate	Soil Monofill Leachate
Al	2.70 ± 2.32	1.36 ± 0.83	0.20	0.00	0.81
Ba	0.38 ± 0.01	0.36 ± 0.02	0.04	0.00	0.56
Ca	971.36 ± 24.07	970.28 ± 55.10	107.34	0.00	1598.72
Fe	2.75 ± 2.47	1.25 ±0.90	0.15	0.00	1.77
K	2123.69 ± 52.16	2135.82 ± 155.23	9.99	0.11	2259.67
Mg	203.37 ± 4.56	207.70 ± 8.48	4.05	0.00	332.02
Mn	0.09 ± 0.02	0.06 ± 0.00	0.04	0.00	0.09
Na	252.67 ± 5.44	258.22 ±12.66	53.25	0.00	345.39
Ni	0.06 ± 0.00	0.06 ± 0.00	0.00	0.00	0.56
P	4.14 ± 0.66	3.47 ± 0.75	5.38	0.00	2.70
S	319.53 ± 0.05	363.32 ±5.34	82.09	0.00	594.22
Zn	0.11 ± 0.02	0.09 ± 0.00	0.05	0.00	0.11

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4.7 Discussion of Physico-chemical Results

There are a number of interesting trends in the data. This section evaluates the results in light of the related literature in an attempt to understand how the physico-chemical conditions identified during the leaching studies may influence the leaching of arsenic, chromium and copper from treated wood.

4.7.1 Influence of Leachant Quantity and Application

The pattern and method of water application to the surface may be important factors in the leaching of CCA components from treated wood. The degree of contact and soaking of the wood controls solubility and transport of the elements from the wood (Kartal *et al.,* 2005; Taylor & Cooper, 2005).

Cooper (1994) and Lebow & Foster (2005) reported that higher leaching losses are expected from CCA wood exposed to intense rainfall conditions as opposed to wood kept in drier conditions. Furthermore, greater leaching is observed with continuous light rainfall as opposed to heavy showers (Cockcroft & Laidlaw, 1978; Lebow *et al.,* 2004; Khan *et al.,* 2006a; Cooper & Ung, 2009). This is because the water remains in contact with the wood for longer (Taylor & Cooper, 2005), allowing infiltration into the interior and therefore mobilising additional leachable species (Kennedy & Collins, 2001). Immersion in the leachant for prolonged periods (as in the SPLP) has also been shown to increase leaching from CCA-treated wood (Townsend *et al.,* 2004; Taylor & Cooper, 2005).

The above findings suggest that in the long-term study, the high rainfall and longer duration rainfall events should result in higher leaching rates and levels. This would be exacerbated by the waterlogging observed in those lysimeters containing CCA-treated wood and soil. In contrast, the water application to lysimeters in the short-term leaching study was rapid (applied in one go with a watering can). This may result in diminished leaching as the leachant had less contact time with the wood. Furthermore, there was no evidence of waterlogging in the soil. However, the high levels of rainfall and therefore high liquid to solid ratio may also result in a lowering of concentrations of CCA elements in leachate due to a dilution effect (Jambeck *et al.,* 2006).

4.7.2 Influence of Temperature

Temperatures in the soil and of the surrounding environment can have a significant effect on the leaching of arsenic, chromium and copper from CCA-treated wood (Cockcroft & Laidlaw, 1978; Cooper 1994; Van Eetvelde *et al.,* 1995b; Taylor & Cooper, 2005; Moghaddam & Mulligan, 2008, Cooper & Ung, 2009). Susceptibility of the metal(loid)s to leaching increases with increased temperatures. This is because higher temperatures provide more energy to increase the rate of diffusion and dissociation reactions of the metal(loid)s (Taylor & Cooper, 2005).

In the long-term study, soil temperatures were higher than ambient air temperatures. Furthermore, temperatures increased with depth in the soil profile. At the soil/mulch interface where the leaching process takes place, temperatures averaged 16°C over the study period. At this temperature the amount and rate of leaching may increase, although previous work suggests higher temperatures between 20°C and 35°C will have more of an effect (Van Eetvelde *et al.* 1995a; Moghaddam & Mulligan, 2008). Temperatures in the current study only exceeded 20°C on four occasions between days 88 and 95.

The short-term study soil temperatures were variable but averaged 2°C less than those in the long-term study temperatures, suggesting that leaching would be inhibited. This was particularly the case between 16 and 22 days where temperatures dropped to below 10°C. Furthermore, temperature decreased significantly over time.

4.7.3 Influence of Soil Physico-Chemical Conditions

The soil moisture contents in both the long and short-term leaching studies were closely related to the amount of leachant added to the lysimeters. Those lysimeters containing mulch were found to conserve soil moisture (Figure 4-4). This was amplified in the long-term study by the greater volume of rainfall received than in the short-term leaching study. CCA-treated wood in contact with wet soil loses more preservative than wood exposed to drier soil or to water alone. (Cooper, 1994; Wang *et al.*, 1998). Therefore, those CCA wood and soil containing lysimeters with higher soil moisture contents over longer periods (as seen in the long-term leaching study) were more conducive to leaching of CCA components due to prolonged leachant and wood contact.

Soils with higher levels of organic matter and therefore organic acids have been shown to increase leaching of elements from CCA-treated wood (Balasoiu *et al.*, 2001; Redman *et al.*, 2002; Schultz *et al.*, 2002; Kartal *et al.*, 2007; Cooper & Ung, 2008). Humic and fulvic acids have been shown to be more effective leaching agents than inorganic acids and are highly effective at only 1% concentration (Crawford *et al.*, 2002; Kartal *et al.*, 2005). These acids alongside organic ligands found in soil can react with the CCA elements (in particular copper and chromium) to form chelate complexes (Warner & Solomon, 1990; Wang *et al.*, 1998, Lebow & Foster, 2005). This causes retention of Cr and Cu in the soil (Comfort, 1993; Mäkinen *et al.*, 2005). Arsenic mobility tends to increase with high organic matter content due to the high levels of dissolved organic compounds limiting its sorption onto soil (Redman *et al.,* 2002; Dobran & Zagury, 2006).

The soil OM values found in the long and short-term studies were between 12% and 28%. These levels are high compared to other CCA leaching studies (Gifford *et al.,* 1997; Crawford *et al.,* 2002; Lebow *et al.,* 2006). At levels of only 5%, organic matter is an important predictor for loss of metal(loid)s (Crawford *et al.,* 2002). Therefore, at much higher levels, leaching from wood will be facilitated and chromium and copper metals will be retained as complexes in the soil. Arsenic will become increasingly mobile. As such, arsenic concentrations in leachate are expected to be higher than chromium and copper.

Soil texture affects the rate of drainage of the soil (Schultz *et al.,* 2002) and adsorption or mobilisation of the elements released from the CCA-treated wood. The soil used in all the lysimeter leaching studies in this research was a sandy loam with a high proportion of sand (approx. 77%). Similar soils with high sand contents have been used in leaching studies resulting in a lower retention (Chirenje *et al.,* 2003; Lebow & Foster, 2005; Cooper & Ung, 2008) and increased transport and bioavailability of metal(loid)s in the soil profile (Dagan *et al.,* 2006), compared to other soil types.

Although the OM content in the soil would result in complexation of Cr and Cu, the texture of the soil would facilitate the mobility of the elements, in particular arsenic. This lower retention would mean that higher levels of metal(loid)s are released from the CCA wood due to a concentration gradient created in the soil as they move down the soil profile.

Salinity has been shown to increase the leaching of CCA compounds (Cooper, 1994; Lebow *et al.,* 1999), particularly arsenic and copper (Kartal *et al.,* 2005). The increase in solubility relates to the formation of complexes between the salts in solution and the leached elements (Kartal, *et al.,* 2005). However, this usually occurs at ionic concentrations in the region of 34 parts per thousand and higher, well above levels found in this study (Table 4-3). In the short-term study, EC levels increased significantly over time for all lysimeters, reaching maxima of just under 800ppm by the end of the study. At these levels, EC is not anticipated to be a major factor in leaching.

4.7.4 Influence of Soil and Leachate Redox

Soil redox plays a major role in metal sorption and mobility. Generally, as conditions in the soil become more reducing, mobility of arsenic, chromium and copper increases (Reddy & Patrick Jr., 1977; Masscheleyn *et al.*, 1991a; Guo *et al.*, 1997; Maurice *et al.*, 2007). Soil redox levels in the long-term study decreased from the moderately reducing class to the reducing class in all the mulch-containing lysimeters (refer to Figure 4-10). The trends towards anaerobic conditions in the lysimeters is similar to those of Smith (2005) where redox conditions in saturated sediments became increasingly reducing over time. This was interpreted as sequential reduction where conditions become more reducing, the longer the period of saturation (Smith, 2005; Lillie & Smith, 2007; Smith & Lillie, 2007). In oxidised soil, oxygen acts as the only electron acceptor for organisms (Gregorich & Janzen, 1999). In saturated soils, the dissolved oxygen remaining in the soil is quickly depleted and other soil oxidants are used as electron acceptors by facultative anaerobes (Gregorich & Janzen, 1999). The reductions of NO_3^-, Mn^{4+}, Fe^{3+}, SO_4^{2-} and CO_2 occur sequentially causing a corresponding decrease in soil Eh (Lueders & Friedrich, 1999). At the reduced Eh values observed, it is most likely that Fe^{3+} or SO_4^{2-} reduction is taking place (Gregorich & Janzen, 1999). In the CCA wood and soil lysimeters this would cause the elements to leach from the wood and remain readily dissolvable and mobile in the soil.

The redox conditions of soil in the short-term leaching study conditions may have become more anaerobic over time as in the long-term study. However, less water was applied to the lysimeters and no waterlogging was observed. Therefore, based on the redox conditions in the study, any leached CCA elements in the soil would be more stable. The leachate redox measurements suggest that there were no significant changes in the redox of the leachate once it had passed through the soil column. However, in the long-term study soil redox was significantly lower than leachate redox ($U = 1512.00$, $p < 0.01$) suggesting that the redox conditions of the leachate became more oxidising after passing through the soil profile. This change in redox conditions may result in differences to the metal species/complexes in the soil solution compared to those in the leachate.

4.7.5 Influence of Soil and Leachate pH

Following application of water to soils (particularly with the levels in the long-term study), pH tends to fluctuate around neutrality (Sun *et al.*, 2007). The initial decrease may be related to the initial applications of slightly acidic rainwater and creation of organic acids in the soil solution resulting from wash off from the mulch layer. However, the long-term study showed that soil pH stabilises over time.

Significant differences were observed in the leachate pH taken from each lysimeter type with the monofills having lower levels than the soil-containing lysimeters (Figure 4-16). This effect was reported in the work carried out by Jambeck *et al.* (2006), who suggested that acidity as well as lignin-tanin content increased in leachate from their CCA wood monofill. This was explained by the dissolution of large organic molecules from the wood when in contact with the leachant, creating organic acids (Jambeck *et al.*, 2006). The CCA-treated wood monofill in the current study also leached out the highest concentrations of metal(loid) than other CCA wood-containing lysimeters.

The significantly lower pH in the untreated wood lysimeter leachates compared to the CCA-treated wood monofill leachate may be due to the fact that the untreated wood had not been exposed to weathering. On exposure to natural conditions, the untreated wood may have weathered at a faster rate than the CCA wood resulting in the washing off of more organic molecules, thereby creating greater quantities of organic acids in the leachate. The pH of the leachates from the untreated wood and soil lysimeters and CCA wood and soil lysimeters were not significantly different, suggesting that the soil buffers the effects of pH regardless of mulch covering.

The pH of the rainwater in this study was 6.7. The fact that the pH in the leachate of lysimeters containing soils was higher than that of rainwater, supports the suggestion that the soil has a buffering capacity for lower pH values (Murphy & Dickinson, 1990; Gifford *et al.*, 1997). Jambeck *et al.* (2006) also found that wood can have a small buffering effect by raising the pH in the leachates from the SPLP. However, in this study, the wood buffering effect was not observed as the leachant used had a higher pH than in the SPLP (~pH 4).

There is conflicting evidence as to what pH conditions promote or hinder leaching of CCA components from wood. Some authors have found that extremes of pH produce maximum leaching rates. Findings from other CCA leaching studies disagree with leaching at pH extremes and have found leaching at near-neutral pH ranges (Wang *et al.*, 1998; Warner & Solomon, 1990). Van Eetvelde *et al.* (1995a, 1995b) and Taylor & Cooper (2005) reported that chromium and arsenic reached maximum leaching levels at neutral pHs. This may be due to the presence of organic acids in the soil which have been shown to influence leaching in near-neutral pH ranges (Lebow *et al.*, 2004).

Therefore, it is possible that the near-neutral pH levels observed in the long and short-term leaching studies may cause increased leaching of arsenic and chromium.

4.7.6 Influence of Initial Concentrations of Arsenic, Chromium and Copper in Wood, Soil and Leachant

The levels of arsenic, chromium and copper in the weathered wood suggest a high loading value due to the industrial application of the wood. There have been conflicting results on the influence of the retention levels of CCA components on leachability with some studies showing no influence (Cooper, 1994) and others showing increased leachability with higher loading values (Cooper, 1994; Hingston *et al.,* 2001; Kartal *et al.,* 2007). Hingston *et al.* (2001) suggest that it is the preservative composition that influences leaching of CCA with decreased leaching from As-rich formulations and increased leaching from Cr-rich formulations. The freshly treated and weathered CCA wood used in the current leaching studies had higher values of chromium relative to arsenic and copper. This will most likely cause increased leaching when exposed to a leachant.

The initial levels of arsenic, chromium and copper in the soil can affect leaching and behaviour of the elementals in the soil. If initial levels of metal(loid)s are high, there will be increased competition for binding sites (McLaughlin *et al.,* 2000). Usually, the adsorption sites which are first occupied (i.e. by metals already in the soil) have a higher bonding strength (McBride, 2000) so metal(loid)s leached out from CCA-treated wood will not be bound as strongly to the soil. Furthermore, the concentration gradient and therefore flux between the elements in the wood and soil are affected by background levels of the metal(oid)s (Crawford *et al.,* 2002; Schultz *et al.,* 2002). At lower levels, a larger concentration gradient and therefore diffusion potential results in greater movement of metal(loid)s from the CCA-treated wood into the soil. The opposite would be true at higher initial levels and the flux of CCA components and metal sorption will be inhibited.

The concentration of metals in the soil used in the leaching studies (arsenic at 3.10 ± 0.7ppm, chromium at 10.76 ± 2.31ppm and copper at 24.24 ± 0.82ppm) were within the range of naturally occurring levels (Ma *et al.,* 1997; Lebow & Foster, 2005; Girouard & Zagury, 2009). Background levels taken from previous studies have usually averaged between 1 and 20ppm for arsenic, 3 to 200ppm for chromium and 8 to 300ppm for copper (Wang *et al.*, 1998; Cooper *et al.*, 2005; Lebow & Foster, 2005; Townsend *et al.*, 2003b). As the initial levels were within the lower range of average background levels, it is probable that this will result in more rapid leaching from CCA-treated wood to the soil.

The initial concentrations in the leachant may influence the levels of CCA metal(loid)s in both the soil and the leachate. Both the ultrapure and rain water used were free of detectable arsenic, chromium and copper and as such did not pose a contamination risk to the soil and leachate samples collected.

4.7.7 Influence of Elemental Concentrations in the Soil

Soil aluminium, calcium, iron and manganese contents have been found to correlate with soil arsenic retention (Balasoiu *et al.*, 2001; Redman *et al.*, 2002; Dagan *et al.*, 2006). Arsenic and chromium have anionic sorption behaviours and form bonds primarily with oxides of the above elements in soil (Hartley *et al.*, 2004).

Levels of elements in the soil in the form of exchangeable cations can also influence the leaching potential of CCA-treated wood waste. Soils with high concentrations of calcium, magnesium, potassium, sodium, aluminium and phosphorus will present a greater leaching hazard as they bind strongly with metallic cations (Plackett, 1984; Wang *et al.*, 1998). Kennedy & Collins (2001) found levels up to 616ppm for calcium, 470ppm for magnesium, 137ppm for sodium and 120ppm for potassium did not cause any detectable increases over background levels. In the current study the values are much higher (refer to Table 4-3) and may affect the leaching of the metal(loid)s. Levels of phosphorus as phosphate will also affect leaching of arsenic from CCA-treated wood. Phosphate is chemically similar to arsenate and at high levels can enhance arsenic release via competitive exchange (Cao & Ma, 2004).

4.8 Summary

This chapter has presented the background conditions and physico-chemical results of the lysimeter leaching experiments. The potential influence of the physico-chemical conditions on leaching were also discussed in light of relevant literature. The physico-chemical results that were used to characterise the wood, soil, leachant and leachate are outlined below:

1. The intense and long duration of rainfall events experienced in the long-term study facilitated leaching due to prolonged contact between the leachant and wood. In contrast, less water was applied to the lysimeters in the short-term study and at a faster rate. This inhibited leaching.

2. Soil temperatures were higher than ambient air temperatures and increased with depth. Levels measured in the short-term study averaged 2°C less than the long-term study. The temperatures measured in both studies were not high enough to promote leaching.

3. The soil MC was a direct consequence of the leachant addition to the lysimeters. Those lysimeters containing mulch conserved more soil moisture than those without. This was exacerbated in the long-term leaching study where there was water logging.

4. The levels of soil organic matter were high, promoting leaching from the wood and retention of some of the copper and chromium in the soil.

5. The soil used in the study was a sandy loam. This type of soil has a lower retention capacity for arsenic, chromium and copper and increased the mobility of arsenic in the soil. The resulting lower retention will result in increased leaching from the CCA wood waste due to concentration gradients created in the soil.

6. The soil electrical conductivity values (indicative of soil salinity) were not high enough to contribute to leaching of components from CCA-treated wood waste.

7. Soil redox in mulch-containing lysimeters fell over time in the long-term study. The progressive change to reducing conditions was due to sequential reduction. This will increase the solubility and mobility of arsenic, chromium and copper in the soil. Levels in the short-term study and in all leaching samples remained moderately reducing suggesting that redox conditions of the leachate became more oxidising after passing through the soil profile.

8. Soil pH remained neutral in both leaching studies. An initial decrease was attributed to the slightly acidic rainwater and creation of organic

9. acids in the soil solution from wash off. However, the levels stabilised over time. Significant differences were observed in leachate pH with the wood monofills having significantly lower levels than soil-containing lysimeters. This was due to the creation of organic acids from mulch wash off.

10. The high loading value of arsenic, chromium and copper and the Cr-rich formulation of the CCA wood waste will cause increased leaching. Background levels in the soil were below naturally occurring levels. This will cause increased leaching of CCA due to a high concentration gradient and therefore diffusion potential between the wood and the soil. The lower background levels could also cause higher adsorption of the elements to the soil.

11. Concentrations of common elements in the soil such as aluminium, calcium, iron and manganese were high and could cause increased leaching and adsorption/mobility of arsenic, chromium and copper from the treated wood.

12. The results indicate that the background conditions and physico-chemical status of the soil and leachant were conducive to arsenic, chromium and copper leaching from CCA-treated wood waste mulch particularly in the long-term leaching study. However, the interaction and combined effects of the factors were not discussed. It is not clear how the factors will collectively impact on the adsorption or mobility of the elements once released into the soil.

The next chapter will present the arsenic, chromium and copper concentrations in the CCA-treated wood waste and in the soil of both leaching studies. This will help determine the amount of leaching from the CCA-treated wood waste mulch and potential to exceed Environment Agency Soil Guideline Values. This is particularly important as Crawford *et al.* (2002) and Schultz *et al.* (2002) claim that greater leaching usually occurs when treated wood is exposed to soil rather than water. Furthermore, the resulting leachate will be greatly influenced by the soil properties and vice versa.

5 Wood and Soil Results

5.1 Introduction

This chapter presents the elemental analysis for wood and soil samples collected from the long-term and short-term leaching studies. The levels of arsenic and chromium measured in the soil are compared against Environment Agency Soil Guideline Values (SGV). The behaviour of the metal(loid)s in the soils is investigated by *in situ* speciation of chromium and the measurements of metal(loid) concentrations of arsenic and chromium down the soil profile. This was achieved by using DGT devices.

The data is presented as scatterplot graphs over time. The results for arsenic, chromium and copper levels in the wood are presented in section 5.2 for the long-term leaching study and section 5.3 for the short-term leaching study. The arsenic, chromium and copper levels in the soil are presented in section 5.4 for the long-term leaching study and section 5.5 for the short-term leaching study. The soil Eh/pH conditions are reported in section 5.6. Section 5.7 presents the arsenic, chromium and copper levels from the DGT studies for the mulch/soil interface and soil profile. Section 5.8 is a discussion of all the results and the final section, 5.9, summarises the chapter.

5.2 Arsenic, Chromium and Copper Levels in Woodchips: Long-Term Study

The levels of elemental arsenic, chromium and copper are presented in Figure 5-1, Figure 5-2 and Figure 5-3 respectively.

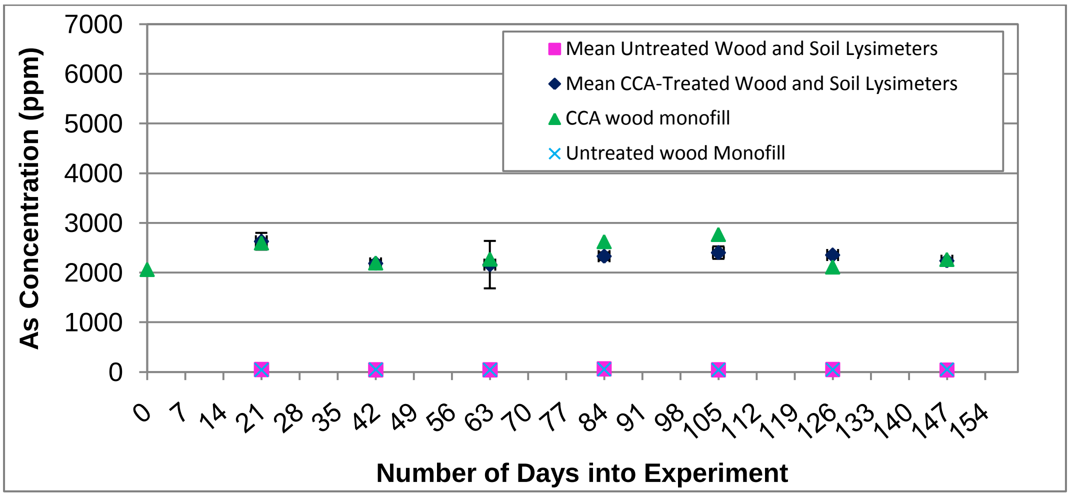


Figure 5-1: Concentration of Arsenic in Wood (± 1 standard deviation) (long-term leaching study)

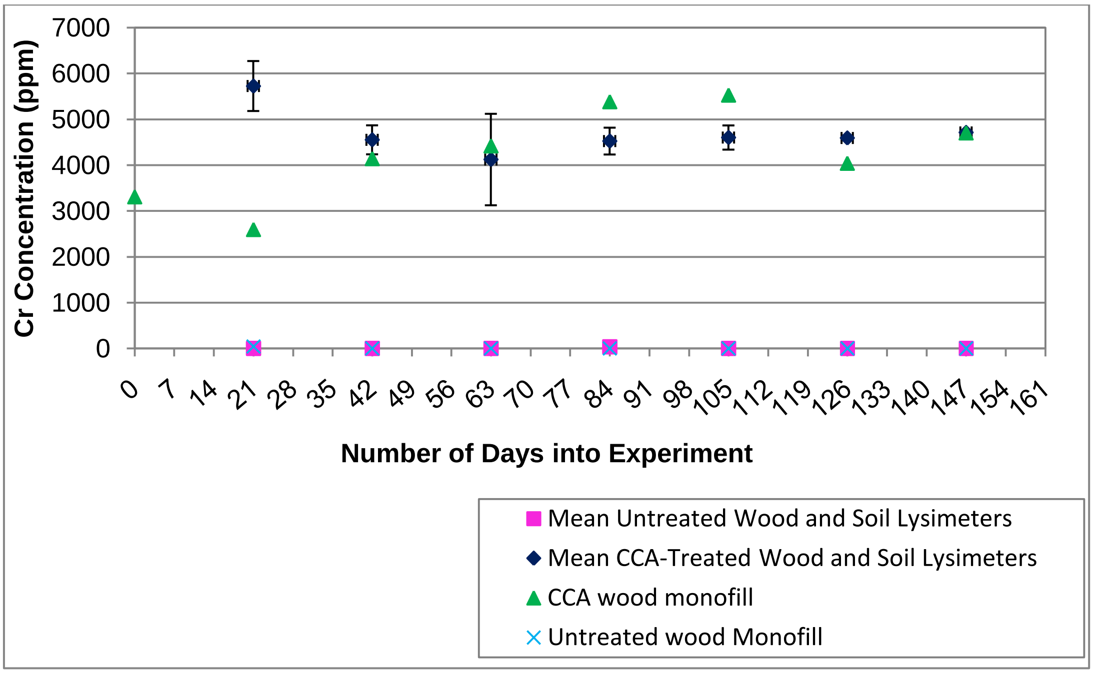


Figure 5-2: Concentration of Chromium in Wood (± 1 standard deviation) (long-term leaching study)

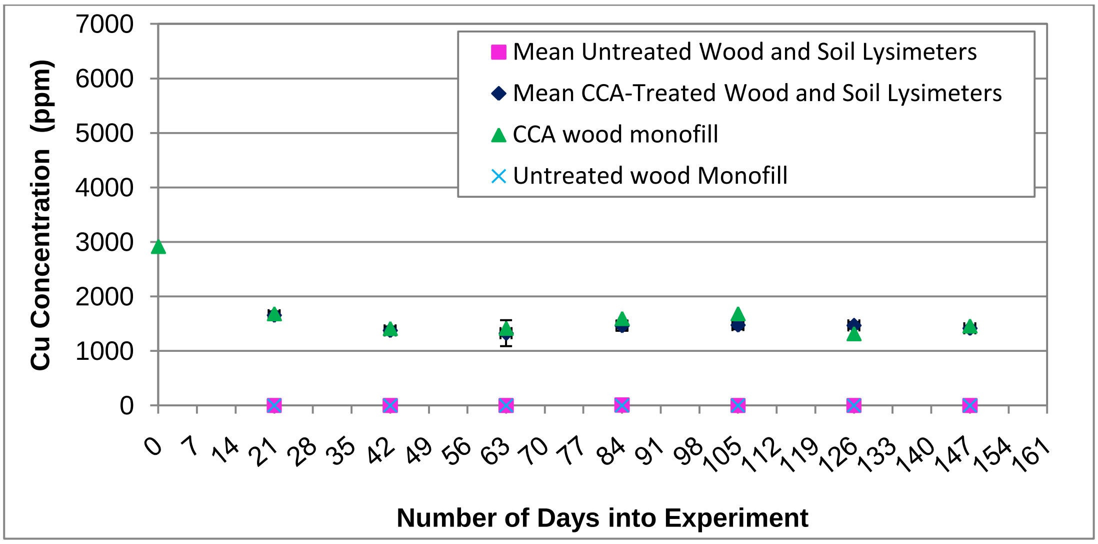


Figure 5-3: Concentration of Copper in Wood (± 1 standard deviation) (long-term leaching study)

The graphs do not necessarily reflect changes in metal(loid) levels over time as samples were taken from different lysimeters at each sampling date. They do however provide a general indication of quantities in the wood. The concentration of the elements in wood from the untreated wood monofill and mean untreated wood and soil lysimeters remained at or just above zero for all three elements throughout the experiment. In comparison, levels in the CCA wood monofill and CCA-treated wood and soil lysimeters were orders of magnitude higher. For all metal(loid)s, levels in wood taken from CCA-treated wood and soil lysimeters were significantly higher than those from untreated wood and soil lysimeters (arsenic: $t(12) = -37.584$), $p < 0.05$; chromium: $U = 0.00$, $p < 0.05$; copper: $U = 0.00$, $p < 0.05$).

The levels of metal(loid)s in the CCA-treated wood from the monofill were not significantly different to levels in the CCA-treated wood and soil lysimeters despite variability, most notably with levels of chromium (arsenic $t(13) = -1.007$, $p = 0.333$; chromium $t(13) = 1.030$, $p = 0.322$; copper $U = 15.000$, $p = 0.223$). Levels in the CCA wood ranged between 2000 to 3000ppm for arsenic, 2500 to 5500ppm for chromium and 1300 to 2930ppm for copper. The levels of each metal(loid) were not proportional in the wood, with significant differences observed ($F(2,15) = 839.05$, $p < 0.01$). Tukey *post hoc* tests revealed that levels of chromium were significantly greater than levels of both arsenic and copper ($p < 0.01$ in all cases). Levels of arsenic were also significantly greater than copper ($p < 0.01$) (Cu>As>Cr).

5.3 Arsenic, Chromium and Copper Levels in Woodchips: Short-Term Study

The mean levels of each metal(loid) in the wood collected from the lysimeters are presented in Figure 5-4 to 5-6. The concentration data from the untreated wood were below the limit of detection (LOD) and are therefore not included in the graphs. Levels in the CCA-treated wood fell within a similar range to those of the long-term leaching study with little variation over time.

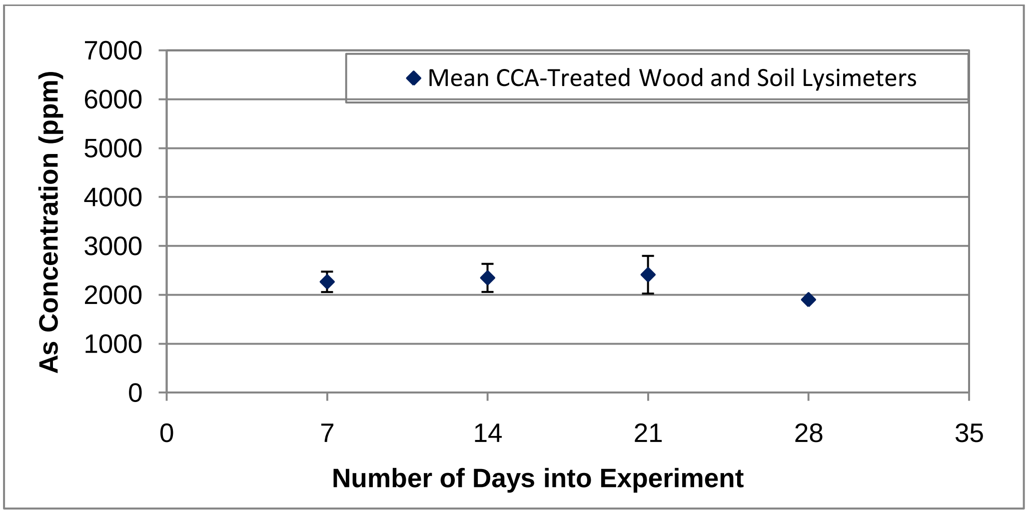


Figure 5-4: Concentration of Arsenic in Wood (± 1 standard deviation) (short-term leaching study)

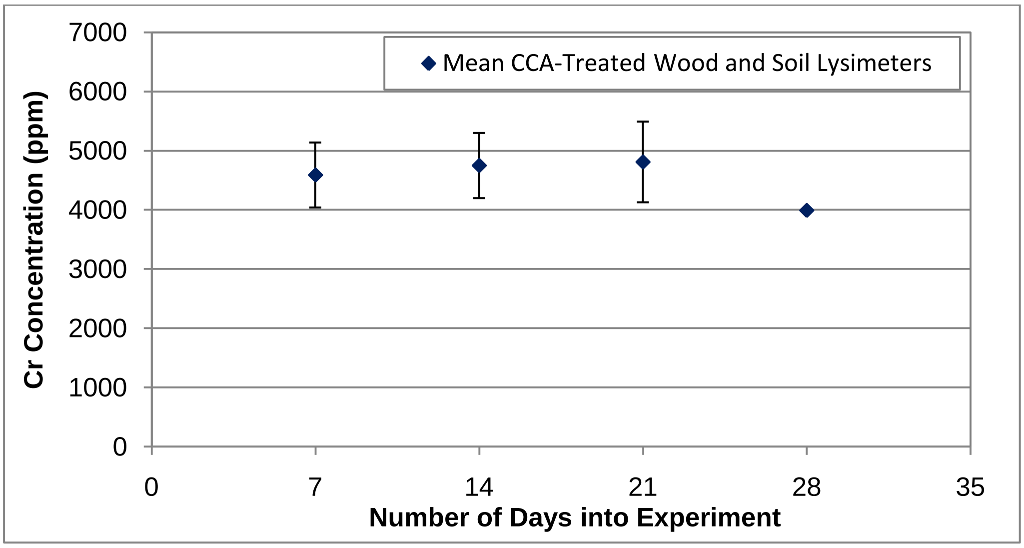


Figure 5-5: Concentration of Chromium in Wood (± 1 standard deviation) (short-term leaching study)

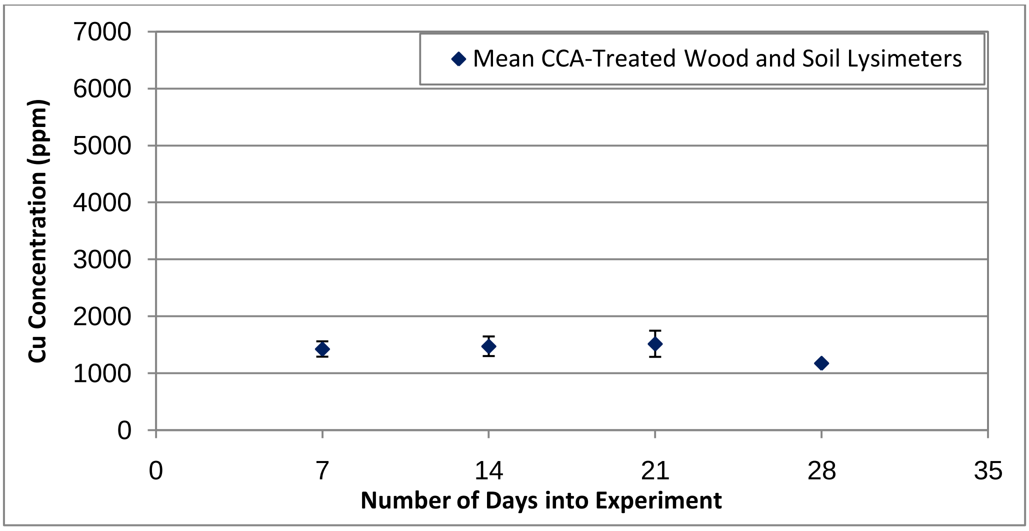


Figure 5-6: Concentration of Copper in Wood (± 1 standard deviation) (short-term leaching study)

5.4 Arsenic, Chromium and Copper Levels in Soil: Long-Term Study

The results for arsenic, chromium and copper are presented in Figure 5-7 to Figure 5-9. The levels in the soil were two orders of magnitude lower than in the wood. There was wide variation in the values in the CCA-treated wood and soil lysimeters resulting in large error bars. The variation suggests that the leaching from the CCA-treated wood may not be consistent over all the CCA-treated wood and soil lysimeters and metal(loid)s may be distributed unevenly in the soil both at the surface and with depth. Furthermore, as there were only two samples taken at each sample date, there were insufficient replicates to accurately assess variance between samples. Periods of variation also occur at times when there were high levels of rainfall.

Levels of arsenic and chromium were significantly greater from lysimeters containing CCA-treated wood than soil in lysimeters containing untreated wood (arsenic $U = 45.00$, $p < 0.05$; chromium $U = 31.50$, $p < 0.01$). However, soil guideline values for arsenic (Environment Agency, 2009) and chromium (DEFRA, 2002) were not exceeded in any of the soil samples analysed.

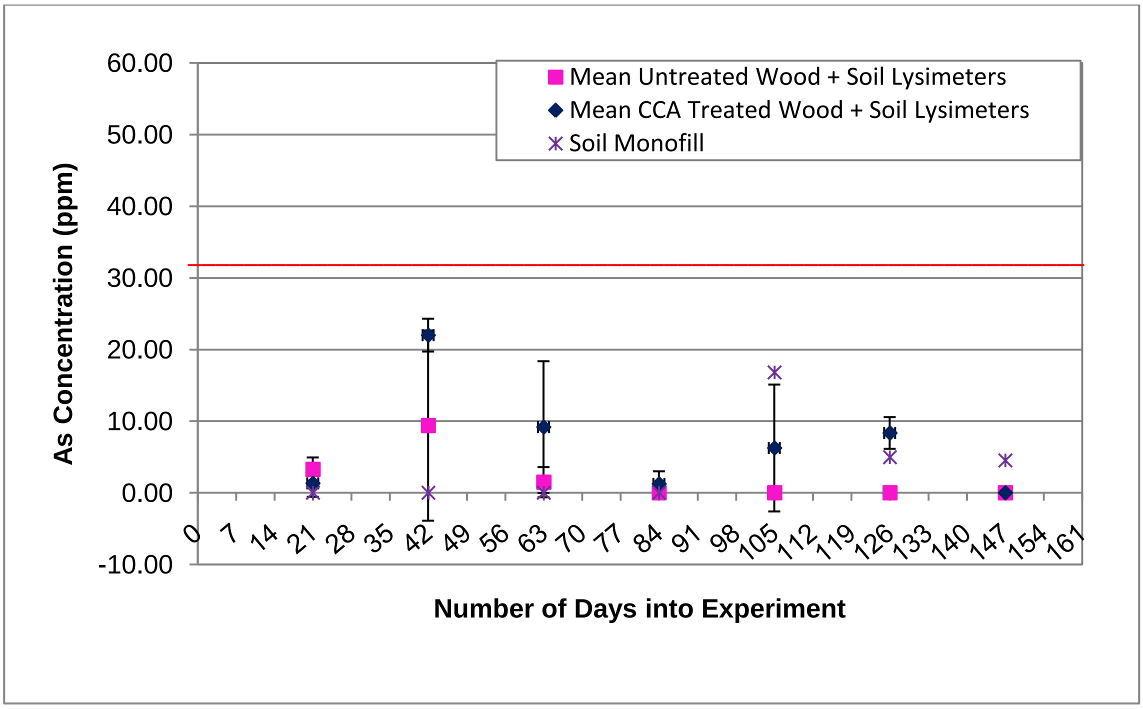


Figure 5-7: Concentration of Arsenic in Soil (long-term study). Red Dashed Line Represents Soil Guideline Value

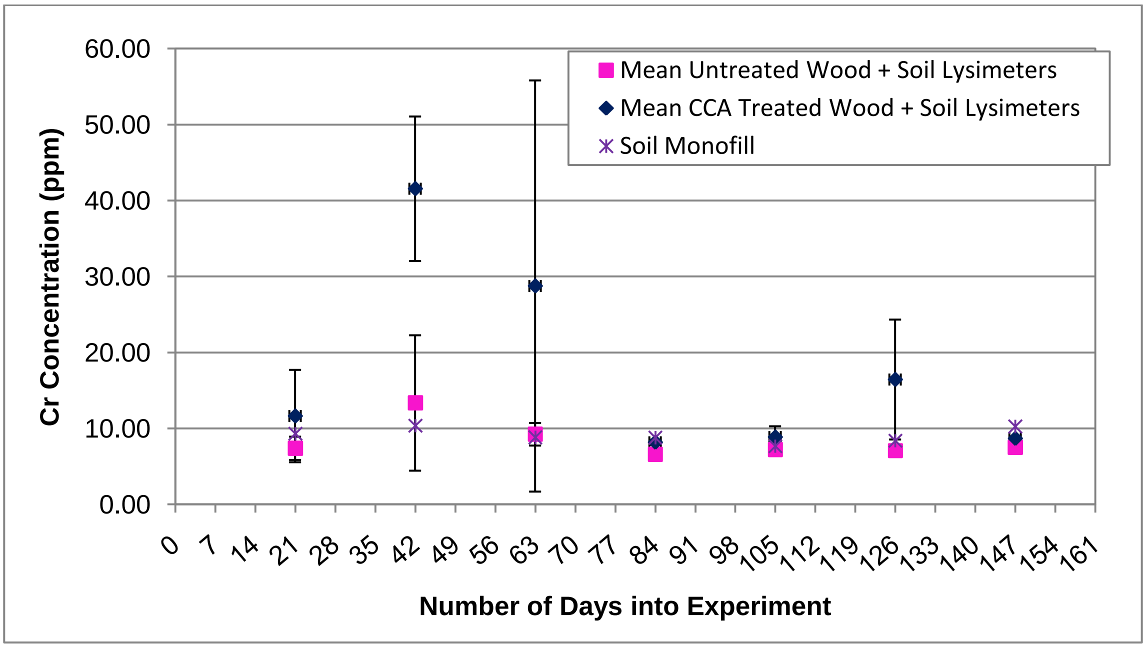


Figure 5-8: Concentration of Chromium in Soil (long-term study). Values are Well Below the Soil Guideline Value

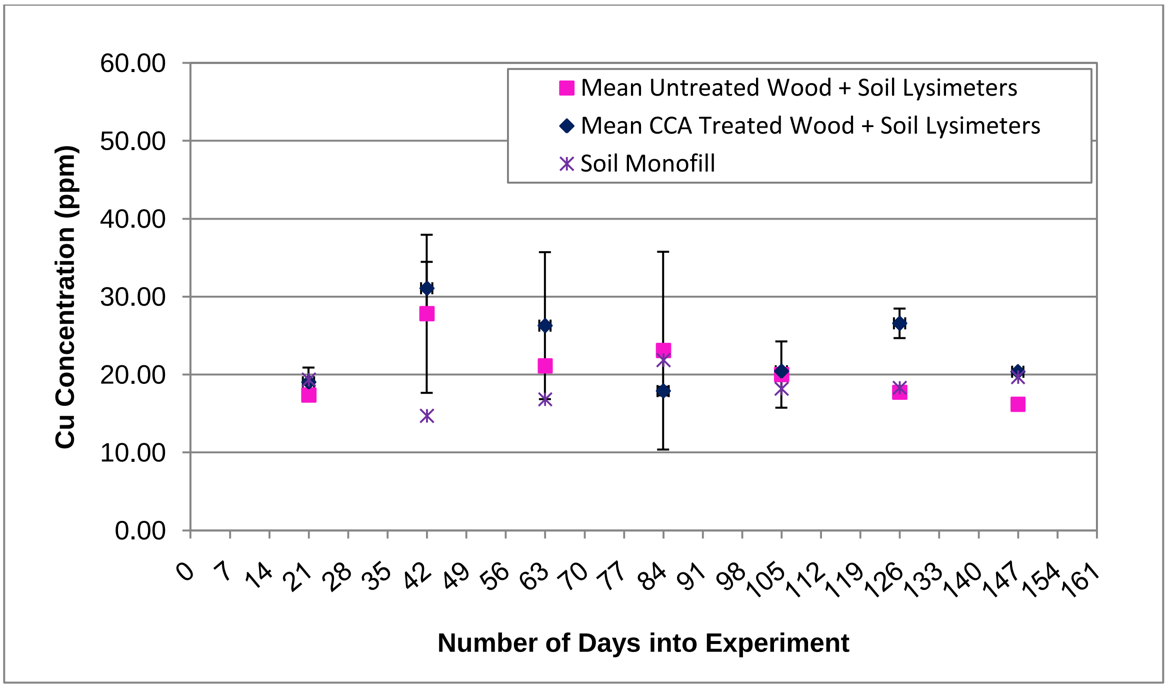


Figure 5-9: Concentration of Copper in Soil (long-term study)

When comparing the proportions of the metal(loid) levels, significant differences were observed with the lysimeters containing untreated wood ($H(2) = 22.62$, $p < 0.01$) and CCA wood ($H(2) = 10.49$, $p < 0.01$). In the lysimeters containing untreated wood, levels of copper were highest followed by chromium and arsenic (As vs. Cr: $U = 19.00$, $p < 0.0167$; As vs Cu: $U = 14.00$, $p < 0.0167$, Cr vs. Cu: $U = 18.50$, $p < 0.0167$) (As<Cr<Cu). In the lysimeters containing CCA-treated wood, arsenic levels were significantly lower than copper ($U = 23.50$, $p < 0.0167$) whilst no significant differences were observed between chromium and copper ($U = 55.50$, $p < 0.071$) or chromium and arsenic ($U = 48.00$, $p < 0.06$).

5.5 Arsenic, Chromium and Copper Levels in Soil: Short-Term Study

The results for arsenic, chromium and copper are presented in Figure 5-10 to 5-12. Again, the error bars were very big despite there being six replicates for each treatment. Concentrations of arsenic and copper were significantly greater in lysimeters containing CCA wood than those from untreated lysimeters (arsenic $U = 180.00$, $p < 0.01$; copper $U = 193.50$, $p < 0.05$). The SGV limits for arsenic and chromium were exceeded by a large margin in the first and fourth week of the experiment from soil in the CCA-treated wood and soil lysimeters. Concentrations of arsenic exceeded the SGV on three occasions: at week one (guideline value = 32ppm, exceedance values = 116.10ppm and 54.05ppm) and week four (173.62ppm). Levels of chromium also exceeded the chromium SGV in week one (guideline value = 130ppm, exceedance value =

219.97ppm) and week four (exceedance value = 422.81ppm). No significant difference was observed in the concentrations of chromium in soil from the untreated wood and CCA wood containing lysimeters. This is probably due to the leach resistance property of chromium in the wood compared to arsenic and copper resulting in no difference between the two treatments.

The effect of the watering regime (daily, monthly and weekly applications) contributed to significant differences in metal(loid) concentrations ($H(2) = 6.65$, $p < 0.05$). Weekly applications of water resulted in greater metal(loid) concentrations in soil than daily ($U = 908.00$, $p < 0.05$) or monthly ($U = 827.00$, $p < 0.01$) applications.

The three elements, were found to react differently in the soil of lysimeters containing untreated wood ($H(2) = 43.79$, $p < 0.01$) and CCA wood ($H(2) = 16.63$, $p < 0.01$). In the lysimeters containing untreated wood, concentrations of chromium were highest in the soil followed by copper and arsenic (As vs. Cr: $U = 48.00$, $p < 0.0167$; As vs Cu: $U = 0.00$, $p < 0.0167$, Cr vs. Cu: $U = 177.00$, $p < 0.0167$) (As<Cu<Cr). In the CCA-treated lysimeters arsenic concentrations were significantly lower than chromium and copper concentrations (As vs. Cr: $U = 133.00$, $p < 0.0167$; As vs. Cu: $U = 117.00$, $p < 0.0167$). Copper and chromium concentrations were not significantly different ($U = 202.00$, $p = 0.038$).

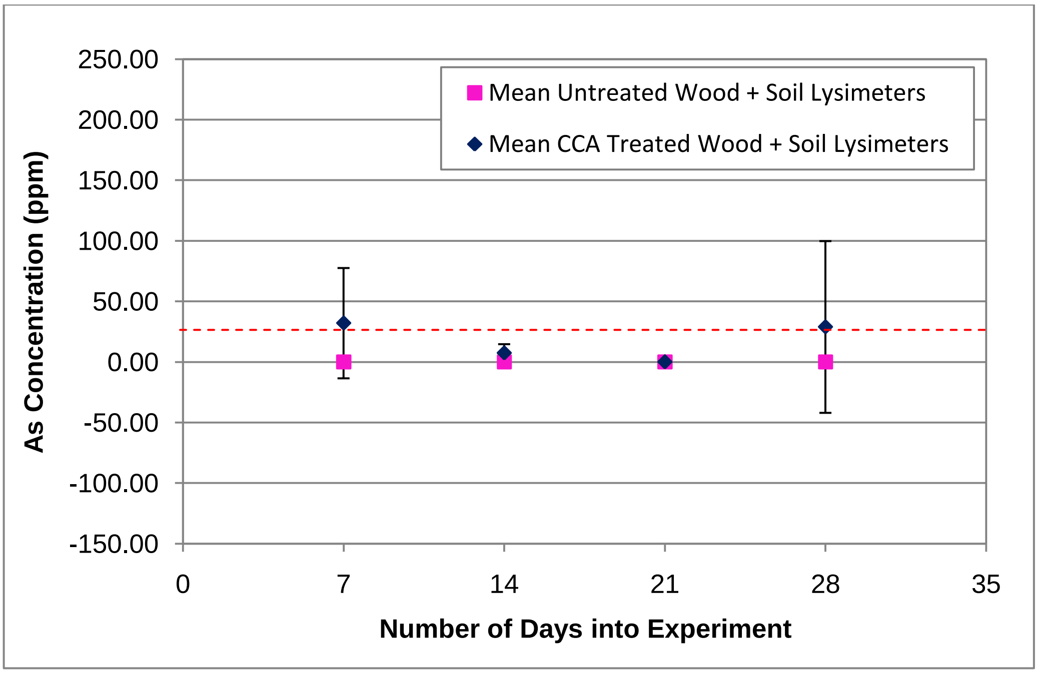


Figure 5-10: Concentration of Arsenic in Soil (short-term study). Red Dashed Line Represents Soil Guideline Value

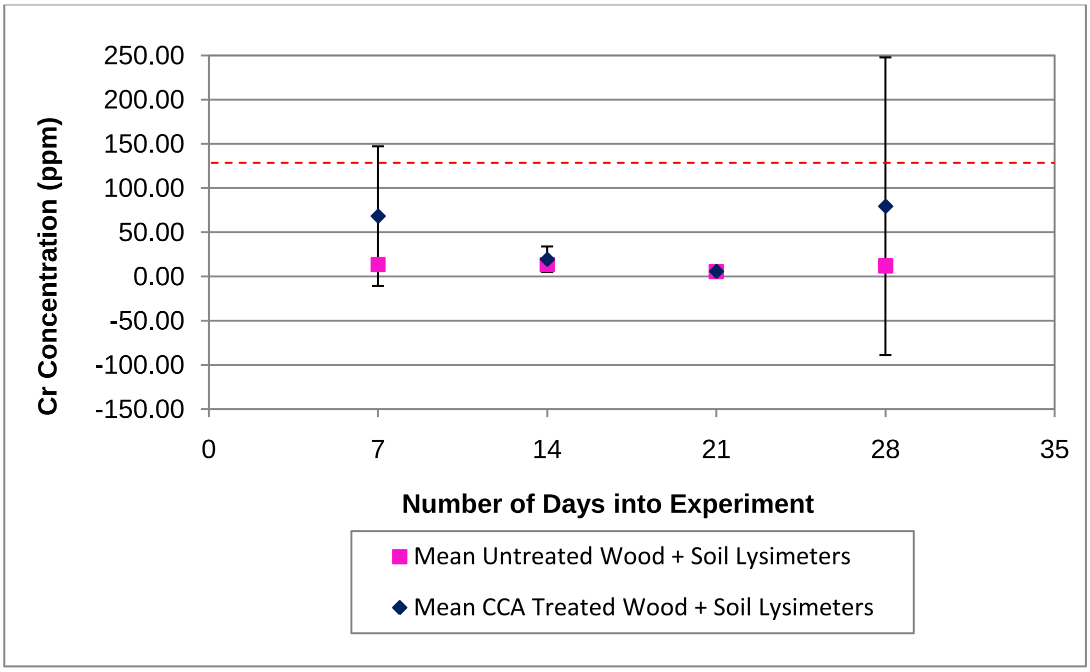


Figure 5-11: Concentration of Chromium in Soil (short-term study). Red Dashed Line Represents Soil Guideline Value

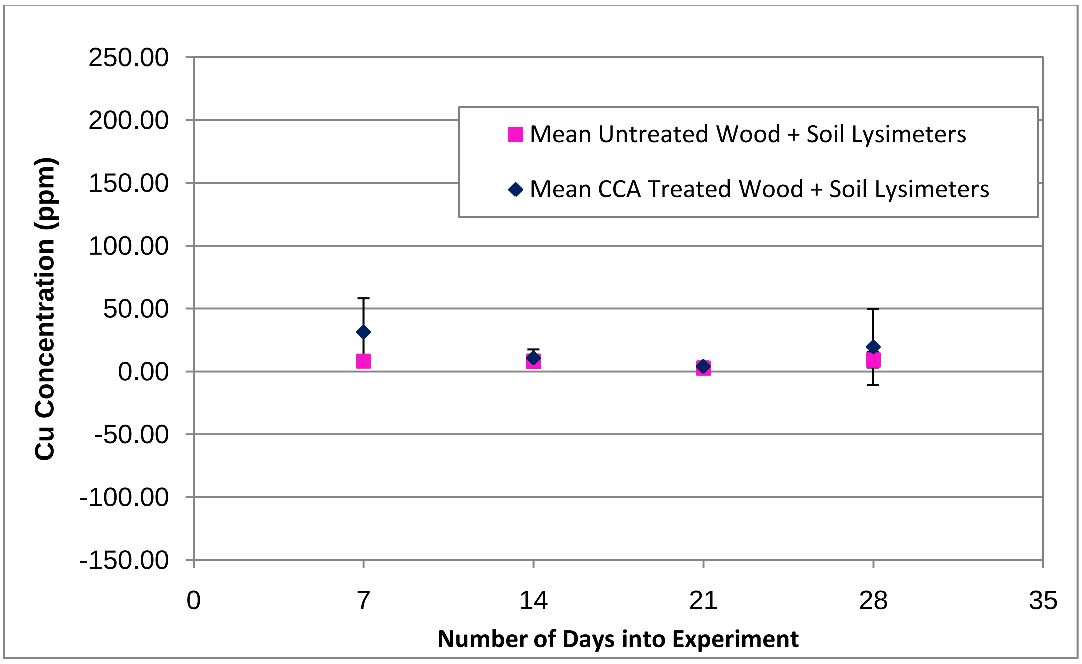


Figure 5-12: Concentration of Copper in Soil (short-term study)

5.6 Soil Eh/pH

Speciation analyses were not carried out on soil samples collected during the long and short-term leaching studies due to time constraints. However, an understanding of the transformations of metal(loid)s in the soil and resultant species is necessary to determine their toxicity, solubility, mobility and therefore potential impacts. The speciation of arsenic and chromium is affected by both redox potential and pH amongst other things (Masscheleyn, *et al.,* 1991b; Smedley & Kinniburgh, 2002) Eh/pH diagrams are used to graphically represent stability relationships of various soluble and insoluble forms of certain elements (Stumm & Morgan, 1981). They can be used to predict the species that should be present under certain Eh and pH ranges in aqueous solutions at 25°C and 1 atmosphere. However, they can only be used as a guide as most natural waters are 'in a highly dynamic state rather than in or near equilibrium' (Stumm & Morgan, 1981, 441).

The Eh/pH graphs for arsenic (Figure 5-13 and Figure 5-14) show that As (III) should dominate under reducing conditions and lower pH whilst As (V) is more stable under oxidising conditions and higher pH values. The soil Eh/pH suggests that redox and pH conditions in the soil of the long-term leaching study would promote arsenic in the pentavalent form as $H_2ASO_4^-$ and $HAsO_4^{2-}$. In the short-term leaching study the data points sit mostly within the $H_2AsO_4^-$ boundary lines. Some of the soil Eh-pH data points in both leaching studies sit near the boundary with As (III) where two species have equal activities with dominance of species occurring towards the 'interior of its domain' (Cherry *et al.,* 1979; Cullen & Reimer, 1989, 736). Therefore some of the data points near the boundary of As (V) and As (III) suggest the presence of more toxic, soluble and mobile As (III) species.

The Eh/pH for chromium in both the long-term (Figure 5-15) and short-term (Figure 5-16) studies shows that the expected species is Cr (III) ($Cr(OH)_3$ in the long-term study and $Cr(OH)_3$, $Cr(OH)_2^{+1}$ and $CrOH^{+2}$ in the short-term study). The presence of chromium (VI) in the soil environment would be unusual as it is readily reduced to Cr (III) (Nico *et al.,* 2006).

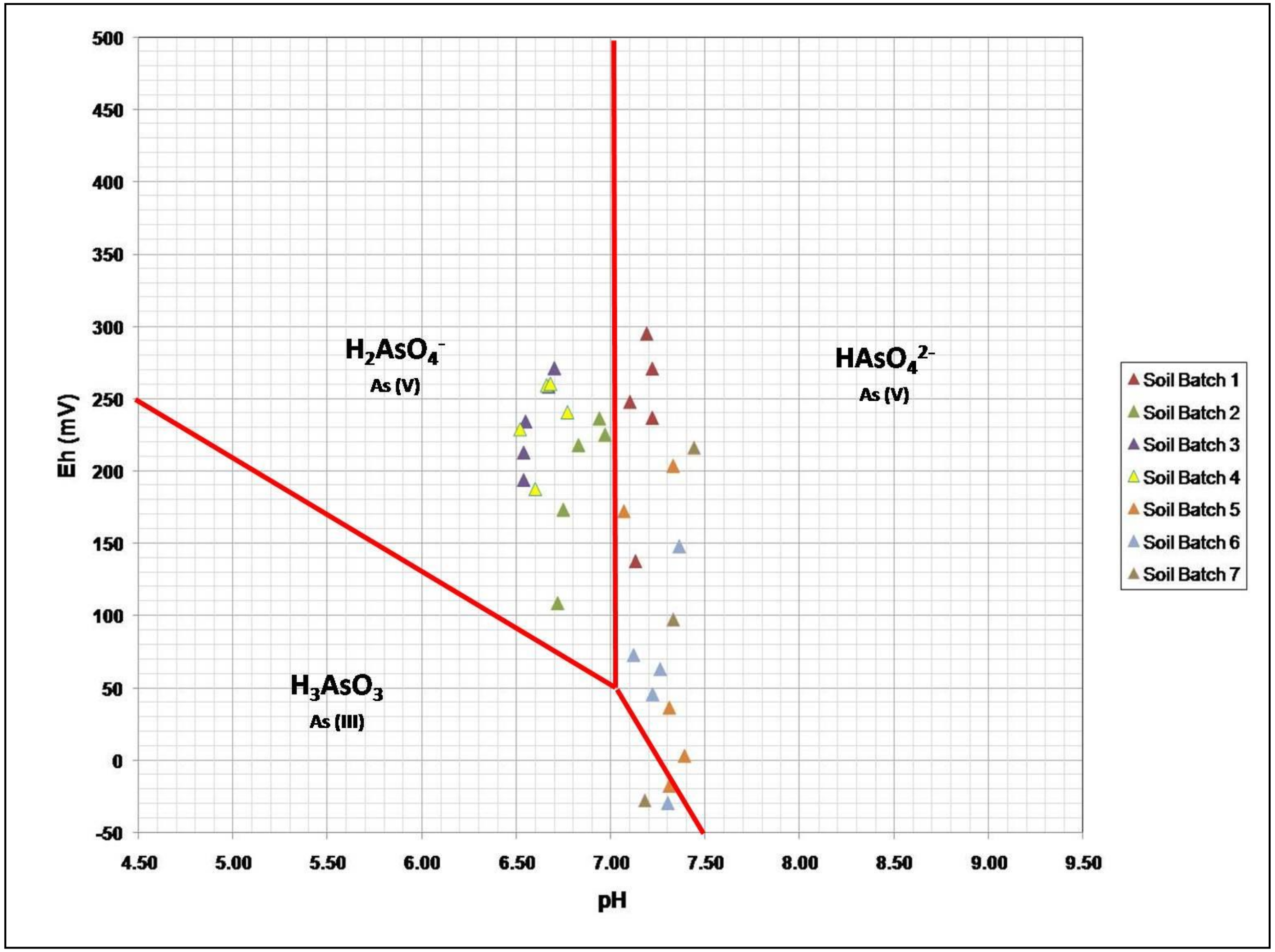


Figure 5-13: Long-Term Study Soil Arsenic Eh/pH Values (Eh/pH boundaries adapted from Solo-Gabriele *et al.*, 2004b)

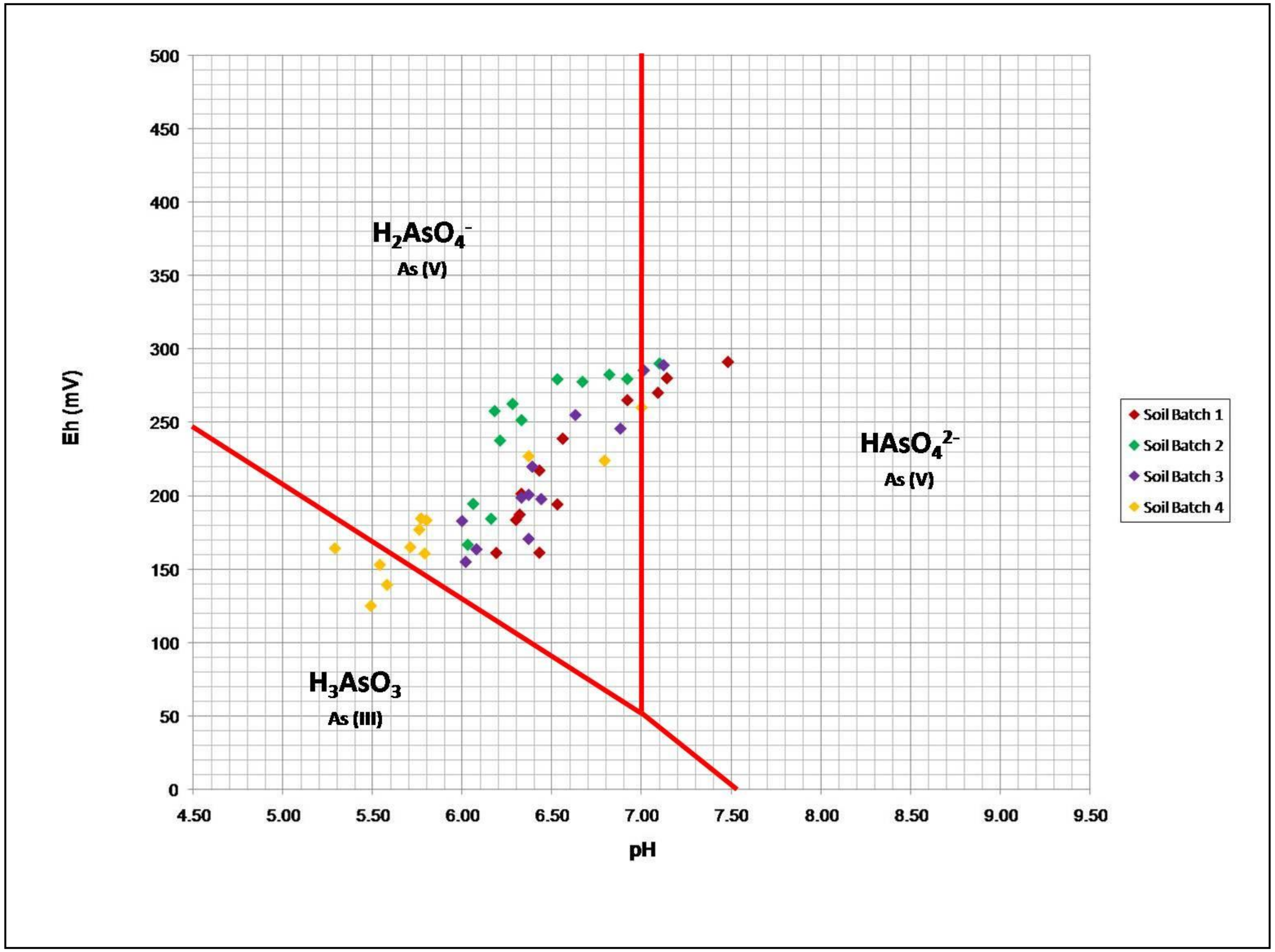


Figure 5-14: Short-Term Study Soil Arsenic Eh/pH Values (Eh/pH boundaries adapted from Solo-Gabriele *et al.*, 2004b)

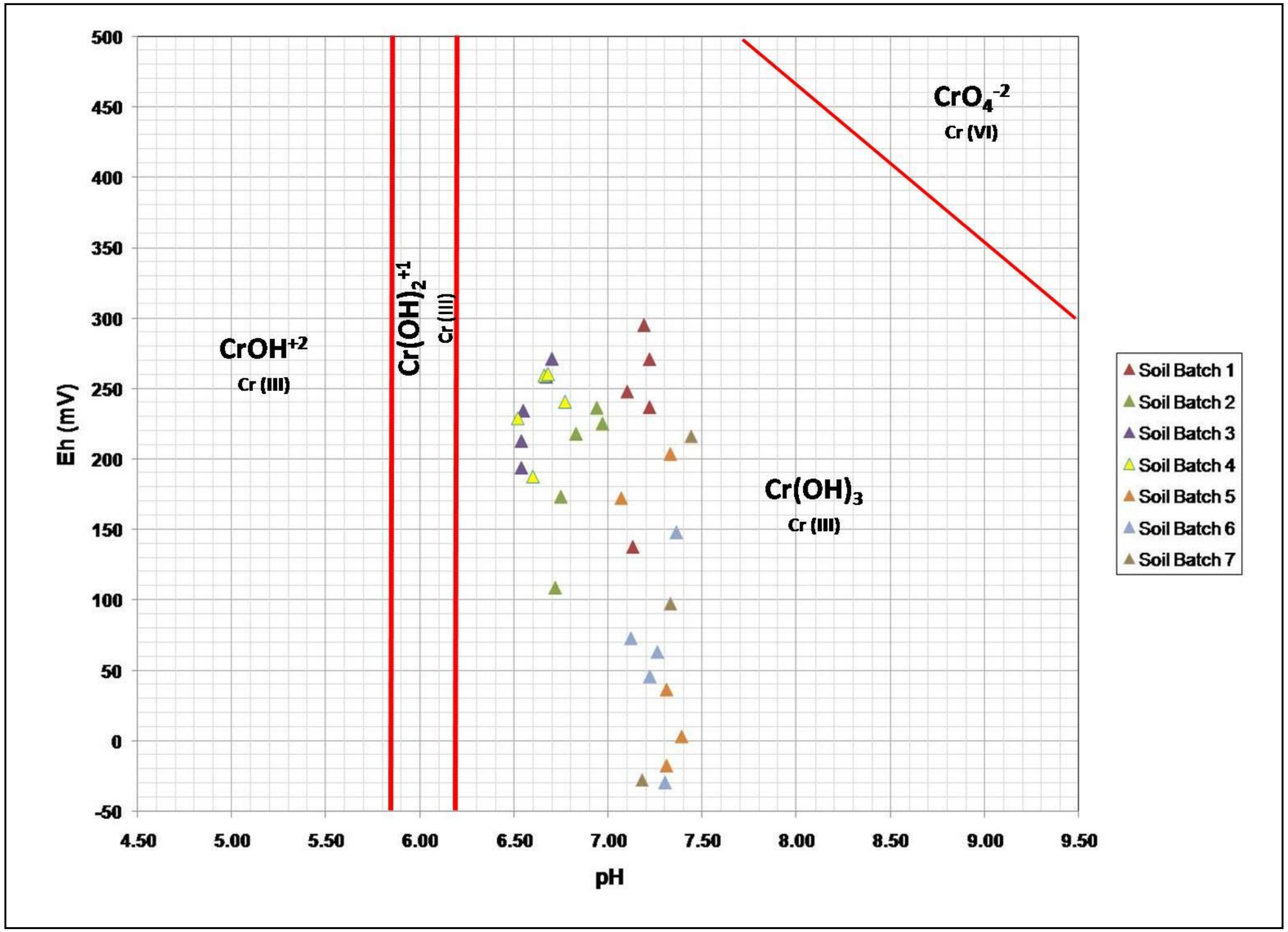


Figure 5-15: Long-Term Study Soil Chromium Eh/pH Values (Eh/pH boundaries adapted from Solo-Gabriele *et al.*, 2004b)

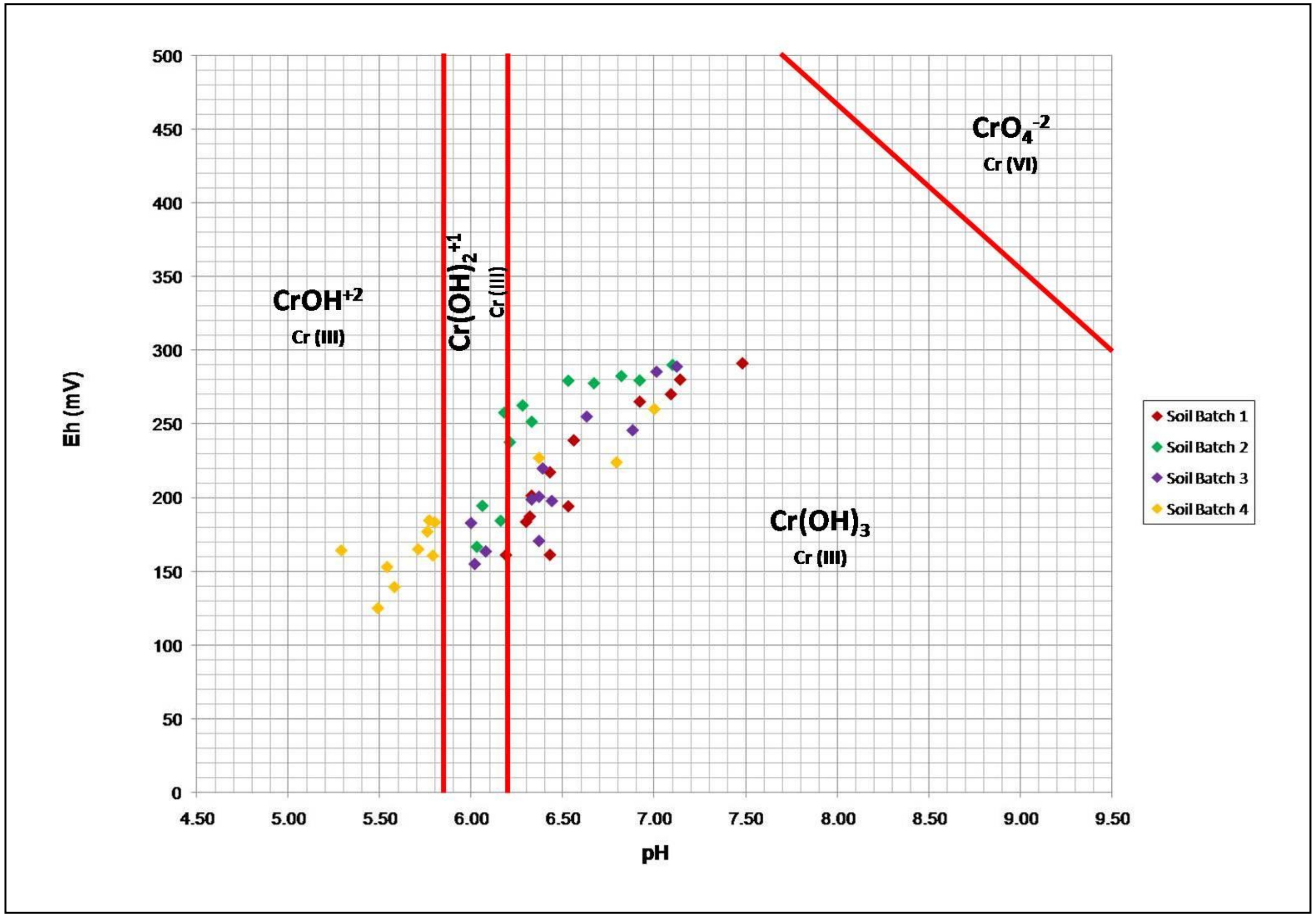


Figure 5-16: Short-Term Study Soil Chromium Eh/pH Values (Eh/pH boundaries adapted from Solo-Gabriele *et al.*, 2004b)

5.7 DGT Measurements of Arsenic, Chromium and Copper

5.7.1 Preliminary and Speciation Studies

The mass of arsenic, chromium and copper measured by the DGTs in the preliminary and speciation studies are presented in Table 5-1. The levels were very low compared to the total metal(loid) concentrations in the soil as they represent only the mobile portions (Cattani *et al.*, 2009). Arsenic was only measured in the preliminary study and so not enough data is available for statistical analysis of the results. However, it appears that there is little difference in the mass of accumulated arsenic between the untreated wood and soil and CCA-treated wood and soil lysimeters (see Table 5-1).

Table 5-1: Mass of Metal(loid)s (ng) Measured in the Preliminary and Speciation Study DGTs (untreated = untreated wood and soil, treated = CCA-treated wood and soil

	Prelim Study (24 hours) (ng)				Speciation Study (50 hours) (ng)		
	As	Cr (III)	Cr VI	Cu	Cr (III)	Cr VI	Cu
1 untreated	35.27	26.70	34.49	39.24	31.05	34.38	0.00
2 treated	33.73	46.93	66.64	43.56	32.01	35.66	0.00
3 untreated	4.80	38.81	43.71	27.47	31.35	30.32	0.00
4 treated	9.52	29.40	29.52	40.36	34.98	38.92	0.00

Within each study, the levels of Cr (VI) were not significantly different to those of Cr (III). This was also the case when comparing between studies. On the other hand, levels of copper were significantly lower in the speciation study than the preliminary study ($p < 0.05$). It is not clear why copper was undetectable in the speciation study as the DGTs had been exposed for longer and are therefore expected to accumulate more metals. It may be the case that the copper was more tightly bound to the soil in the longer study as seen in the DGT soil profile study (see Figure 5-20).

5.7.2 Soil Profile Study

The soil profile study used sediment probes as opposed to cylindrical mouldings. On retrieval, the gel moulds were divided into 2.5cm strips in order to evaluate the distribution of labile metal(loid)s in the top 15cm of soil following application of CCA-treated wood waste mulch. The mass of arsenic and chromium (III and VI) accumulated in the soil profile DGTs are presented in Figure 5-17 to Figure 5-20. Due to the low number of replicates, it was not possible to perform statistical analyses on the data.

However, all the graphs show that the mass of element accumulated in the top 5cm of the soil profile is higher for the lysimeters containing CCA-treated wood mulch before declining, with depth, to levels similar to the untreated lysimeters.

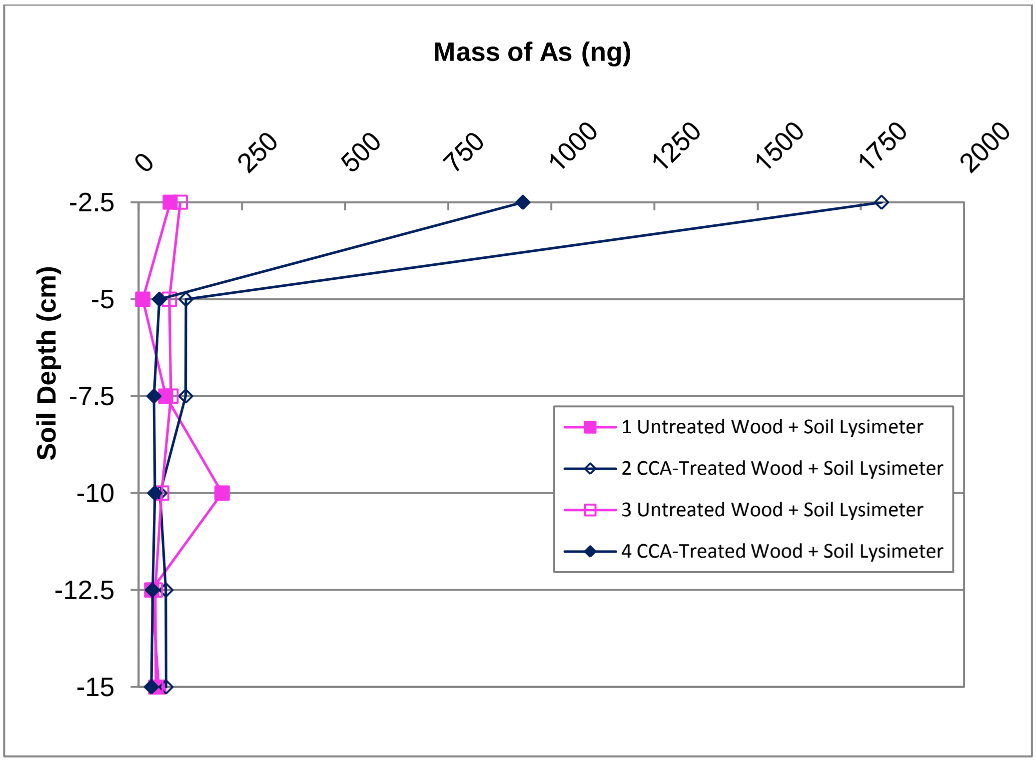


Figure 5-17: Mass of As with Soil Depth

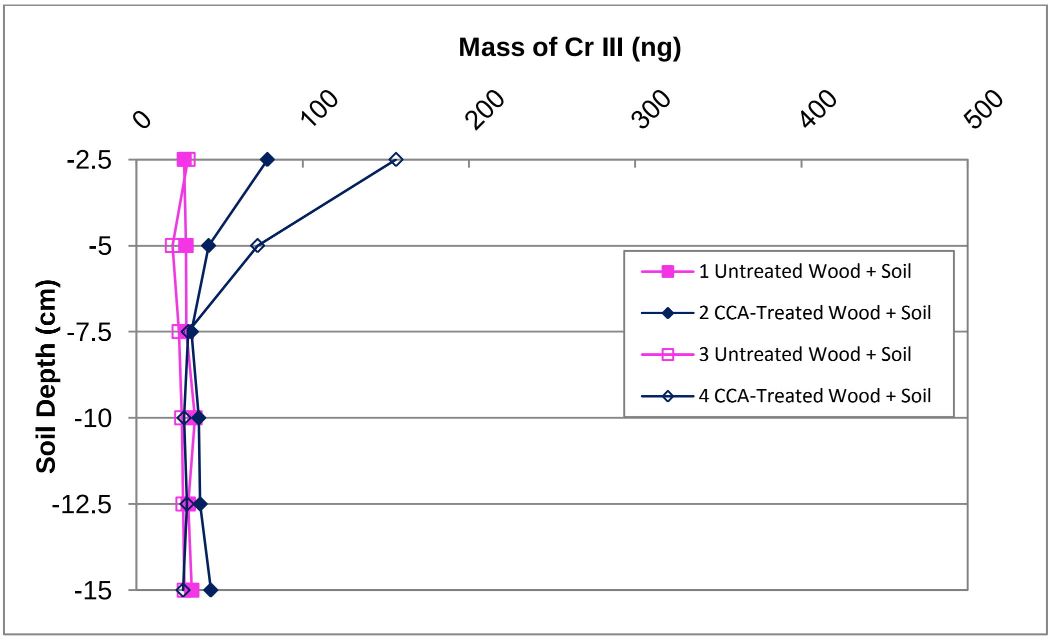


Figure 5-18: Mass of Cr (III) with Soil Depth

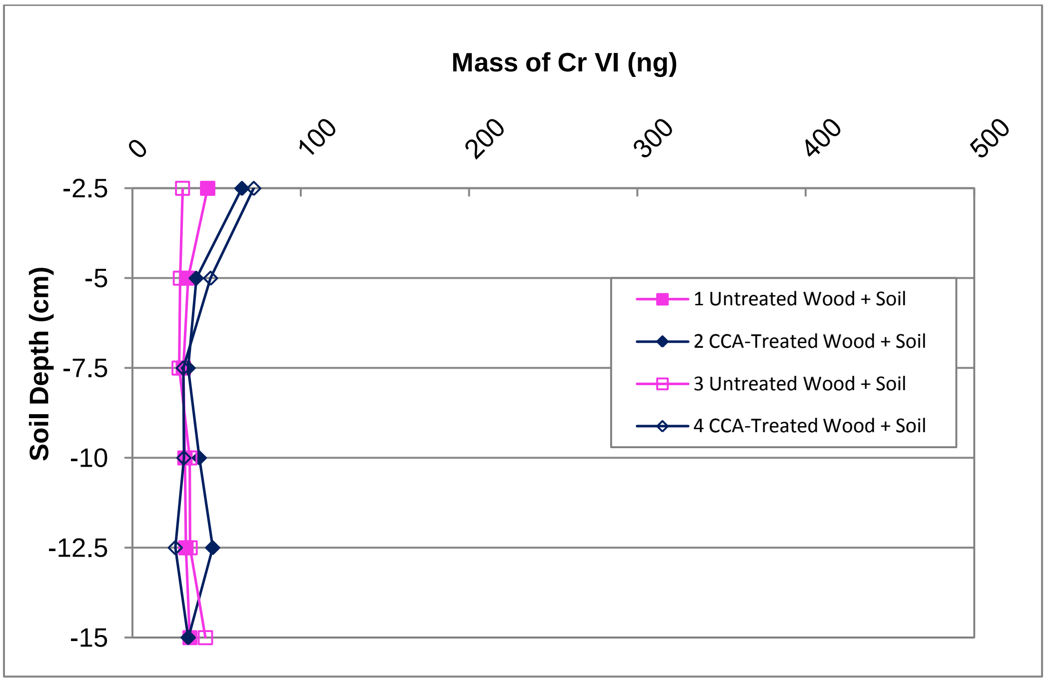


Figure 5-19: Mass of Cr (VI) with Soil Depth

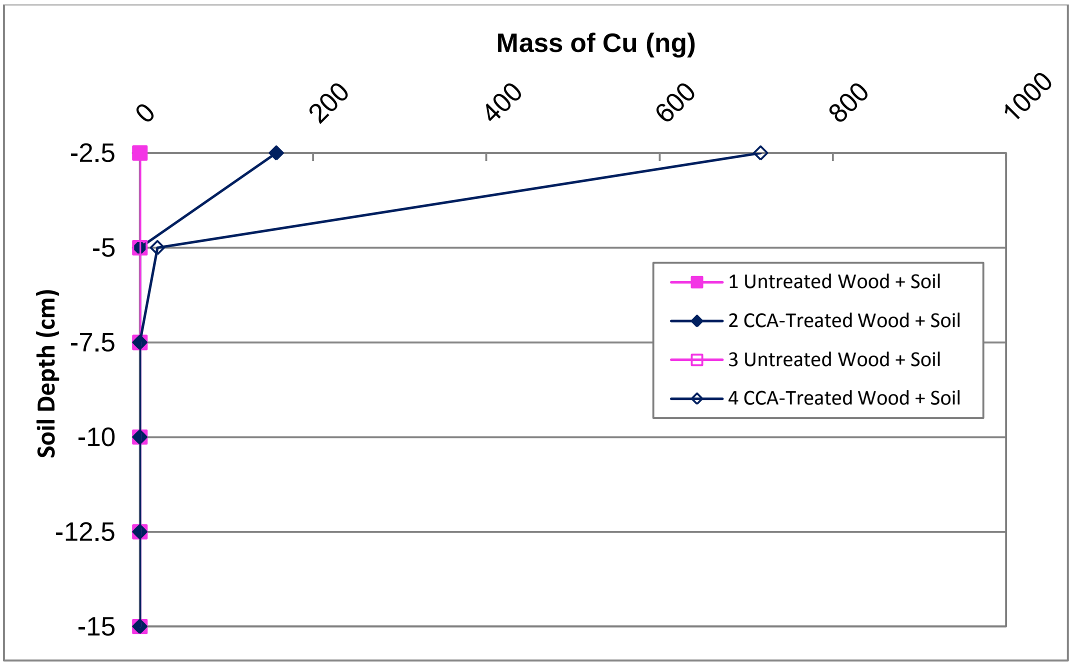


Figure 5-20: Mass of Cu with Soil Depth

The mass of As accumulated in the DGT at different soil depths is presented in Figure 5-17. The levels in the untreated lysimseters remained low through the profile apart from at -10cm in lysimeter 1. The data on the mass of Cr (III) and Cr (VI) accumulated in the soil profile DGTs are presented in Figure 5-18 and Figure 5-19. Levels for Cr (VI) are only slightly raised above the untreated lysimeter levels suggesting elevations above background levels. The mass of Cu accumulated in the DGT with depth is presented in Figure 5-20. The mass the soluble Cu species in the CCA-wood containing lysimeters declines rapidly with depth to zero values. This suggests that there is effective copper binding to the soil with depth.

5.8 Discussion of Wood and Soil Metal(loid) Levels

This section evaluates the wood and soil metal(loid) concentration results. The results highlighted some interesting patterns and processes taking place in the soil. These are examined in light of related literature in an attempt to understand how the metal(loid)s leach from the wood into the soil and how they are distributed and partitioned once there.

5.8.1 Total Metal(loid) Levels in Wood

In all studies, the elemental concentrations within the CCA wood were orders of magnitude greater than those in the untreated wood, as expected. Over the course of the experiments the concentrations of arsenic, chromium and copper in the CCA wood used in both the monofill and wood/soil lysimeters changed little. However, they were lower than those measured from the single piece of CCA wood that was analysed prior to experimental set-up. The rates of initial preservative retention and depletion during leaching can vary between samples of the same wood due to inherent differences within the wood (Schultz *et al.*, 2002). These differences can be problematic in leaching experiments but the results confirm that they can be overcome with thorough homogenisation of experimental materials and sufficient replicates. The results also suggest that the CCA-treated wood remained fairly leach resistant over time. However, due to the high preservative loading in the CCA wood waste used, only a small proportion of the preservative needs to be leached out to pose a risk to environmental and human health.

5.8.2 Total Metal(loid) Levels in Soil

The results demonstrate that exposure to CCA-treated wood causes elevated concentrations of arsenic and chromium in the soil. The ratios of the elements were similar to those in the preliminary soil samples collected prior to experiment set-up with higher amounts of chromium and copper and smaller amounts of arsenic.

There was considerable variation in the metal(loid) concentrations between the two leaching experiments and also within each experiment. This made it quite difficult to interpret the behaviour of the elements in the soil. Inter and intra-site variability in soil metal(loid) concentrations is common in this type of leaching study and has been attributed to the wide range of factors that can impact on soil metal(loid) concentrations (Stilwell & Gorny, 1997; Townsend *et al.,* 2003b). These factors can include differential exposure of the wood to wear and weather, retention levels in the wood and variations in water infiltration/runoff patterns (Stilwell & Gorny, 1997; Townsend *et al.,* 2003b). The variation suggests that the leaching from the CCA-treated wood may not be consistent over all the CCA-treated wood and soil lysimeters and metal(loid)s may be distributed unevenly in the soil both at the surface and with depth. Furthermore, periods of variation appear at times of high rainfall.

In the long-term leaching study there were some instances where concentrations of metal(loid)s were higher in the lysimeters containing untreated wood than those containing CCA-treated wood. It is unclear why this is the case as it is expected that the soil monofill and untreated wood-containing lysimeters should have values at or near soil background levels, whilst CCA wood-containing lysimeters should have higher values due to leaching from the wood. A number of factors may have contributed to these results. Firstly, in the previous chapter (4) it was shown that physico-chemical characteristics of the soil monofill were different from those that were mulched. Soil moisture (MC) was consistently lower and redox was higher, conditions that would promote the retention of arsenic, chromium and copper in the soil (Masscheleyn *et al.,* 1991a; Guo *et al.,* 1997; Maurice *et al.,* 2007). These differences may also impact on microbiological activity/processes which could also result in differences in the retention/release of metal(loid)s.

Sampling issues were also evident in this study. At each sampling date, soil samples were taken from different lysimeters in order to ensure that each lysimeter was only disturbed twice. However, this could result in inconsistent results. Furthermore, the inconsistencies may be exacerbated by the limited number of replicates (two samples of each taken at each sampling date). The problems experienced with the sampling were addressed in the short-term leaching study by using more replicates of each lysimeter and soil treatment, and with shorter time intervals between sampling, however large variations were also present in this study. The temporal point sampling nature of the regime adopted for this study may also cause variation. The leaching processes taking place in the wood and the soil are non-linear. The actual rate of release from both the wood and soil involves a complex combination of processes and as such makes analysis very challenging (Schultz *et al.,* 2002). High values may coincide with a peak in the release of CCA from the wood and retention in the soil, whilst lower values may coincide with a drop in the release of the metal(loid)s from the wood and an increased release from the soil driven by a number of factors. Therefore, the results provide a very crude description of temporal changes.

Lebow & Foster (2005) also found unexpected results in their study of arsenic, chromium and copper concentrations under a CCA-treated wetland boardwalk. They discovered large variations, with some samples having uncharacteristically low concentrations. They explained this by there being areas that 'did not encounter pockets of contamination' (Lebow & Foster, 2005, 66). This could be the case in this study.

5.8.2.1 Exceedance of Soil Guideline Values

The Soil Guideline Values are assessment criteria for evaluating human health risks from long-term and on-site exposure to chemical contamination in soil (Environment Agency, 2009b). They are limits that, if exceeded, 'may pose a possibility of significant harm to human health' (Environment Agency, 2009b, 4). SGVs are available for arsenic and chromium which specify acceptable concentrations for three different land uses; residential (with and without gardens where food may be grown), allotments and commercial/industrial (Environment Agency, 2009b). The residential land use has the lowest guideline value and as it has been found that CCA-treated wood may be inadvertently placed on the landscape mulch market, it is possible for soil contamination in this setting.

In the long-term study there were no incidents of soil metal(loid) concentrations exceeding SGVs. This may be due to the high volumes of rainwater entering the system, washing out the metal(loid)s in the soil. In the short-term study, less water was applied and this could have contributed to the binding of metal(loid)s in the soil and resulting exceedance of the guideline values. Although only a small portion of the metal(loid)s from the wood were found to infiltrate the soil, the impacts were significant. In the short-term study the SGVs were exceeded by up to 8.7 times for arsenic and 3.3 times for chromium. The maximum concentrations of arsenic and chromium were also higher than soil concentrations measured directly under in-service structures and illustrate the higher risk of leaching associated with weathered wood than in-service wood (Lebow & Foster, 2005).

5.8.3 Metal(loid) Levels Down the Soil Profile

The DGTs measured the labile fractions of arsenic, chromium and copper at the mulch/soil interface. Quantitative assessments of this fraction are particularly important as it is these forms of the metal(loid) that cause health risks (Pantsar-Kallio & Manninen, 1997). Levels of all three elements in the cylindrical deployment mould, deployed for 24 hours and 50 hours, did not show any differences between those lysimeters containing untreated wood and those containing CCA-treated wood. However, the soil profile probes that were left for a longer period do show differences that are significant. The plastic bins containing CCA-treated wood had higher concentrations of chromium and copper than the lysimeters containing untreated wood. The higher levels of the labile elements measured in the CCA wood and soil containers suggest that there is a higher risk of metal(loid) solubilisation and transportation in the soil following addition of CCA-treated wood waste mulch. Furthermore, it provides an estimation of potential uptake by plants as it measures the 'maximum potentially available concentrations of pollutants in soil water' (Cattani *et al.,* 2009, p.540).

The DGTs captured the highest levels of arsenic followed by chromium then copper. This supports the findings from other CCA leaching studies that found higher levels of total arsenic in the soil profile following contamination with CCA leachates (Stilwell & Gorny, 1997; Lebow & Foster, 2005; Dagan *et al.,* 2006). Lebow & Foster (2005) attribute this difference to the sandy loam soil used in the study which has been found to allow leached arsenic components to be relatively mobile. Copper concentrations captured in the DGT were low suggesting that it is not readily mobile in the soil. Copper is a cationic species and it binds strongly to the soil through adsorption, ion exchange, complexation with humic substances and precipitation (Dagan *et al.,* 2006). Conversely, arsenic and chromium are oxyanions which react with Fe and Al oxides forming co-ordination bonds which do not bind as strongly (Chirenje *et al.,* 2003). Furthermore, arsenic is readily mobile in water (Lebow & Foster, 2005) and is therefore more likely to move through the soil.

Most of the metal(loid)s captured by the DGT were in the top 5cm of the soil. This confirms results from other CCA leaching studies (Bergman, 1983; Bergholm, 1989; Stilwell & Gorny, 1997; Zagury, *et al.,* 2003; Chirenje *et al.,* 2005; Cooper *et al.,* 2005; Dagan *et al.,* 2006). Copper and chromium tend to decrease with depth whilst arsenic is more persistence in the soil profile due to its high mobility (Stilwell and Gorny, 1997; Zagury *et al.,* 2003). Shibata *et al.* (2007) found that in the soil beneath an in-service

CCA structure, 42.5% of arsenic was captured in the top 2.5cm and 52.5% in the deeper soils. Only 6% was recovered at the depth where they collected leachate. This was over a three year period and it is possible that over time, levels increase as the solubilised metal(loid)s are transported down the soil column. In the soil profile DGT study, at the surface, concentrations of solubilised material may be high due to the proximity of the CCA-treated wood. Furthermore, as the DGTs were only left for a week, the results may only be exhibiting the early stage of the migration of elements through the soil profile.

5.8.4 Inorganic Species of Arsenic and Chromium in the Soil

The Eh/pH conditions in both the long and short-term leaching studies favoured arsenic in the pentavalent form and chromium in the trivalent form, the less toxic and mobile of the inorganic species. The presence of Cr (VI) is somewhat surprising as the Eh/pH graphs suggest that the conditions in both the long and short-term study would favour chromium in the soil as Cr (III). The moisture conditions in the soil during the DGT studies replicated the saturated conditions in the long-term experiment. However, the DGTs only accumulate mobile species and as such do not represent total concentrations in the soil. Furthermore, as Cr (VI) is the more mobile of the two species it might be expected to accumulate in greater amounts. Nevertheless, the evidence of Cr (VI) in the surface layer highlights the potential risks due to its high toxicity and availability to plants. Cr (VI) is not very reactive with soil and moves at the same rate as groundwater (Cooper, 1994). It could therefore, contaminate groundwater.

5.9 Summary

This chapter has presented the wood and soil metal(loid) concentration results from five sets of experiments. The experiments were designed to assess the impact of CCA-treated wood waste addition to soil and evaluate the levels and behaviour of the metal(loid)s at the soil/mulch interface and down the soil profile. The main findings are summarised below:

1. The concentrations of arsenic, chromium and copper were three orders of magnitude greater in the soil and wood samples taken from CCA-treated wood and soil lysimeters than the untreated wood and soil lysimeters.

2. There was considerable variation in the soil metal(loid) concentration values measured within each leaching experiment and between the leaching experiments. Possible causes include:

    - The influence of soil physico-chemical factors including MC and redox values.
    - Differences in microbiological activity between lysimeters and treatments.
    - Temporal and spatial sampling issues associated with the leaching process.
    - Distribution of contamination in the soil underlying the CCA wood.

3. The SGVs for arsenic and chromium were not exceeded in the long-term leaching study. This may be due to the high amounts of rainwater entering the system and flushing the metal(loid)s from the soil. However, in the short-term leaching study where less water was applied to soil, the SGVs for residential areas were exceeded by up to 8.7 times for arsenic and 3.3 for chromium.

4. The DGTs measured the labile fractions of metal(loid)s in the soil solution. With a longer deployment time, differences became significant between levels in the untreated wood and soil lysimeters and CCA-treated wood and soil lysimeters. The higher levels in the CCA wood containing lysimeters suggest that there is a higher risk of metal(loid) solubilisation and transport in the soil following application of CCA wood waste.

5. The labile metal(loid) fraction from the CCA-treated wood and soil containers appeared to be primarily distributed in the top 5cm of the soil profile. Levels of all metal(loid)s were found to decrease with depth, reaching similar levels to those in the untreated wood and soil containers.

6. In the DGT study, arsenic was found to be most mobile in the soil profile followed by chromium then copper. Arsenic tends to be more mobile, whilst copper tends to bind strongly to soil.

7. The two inorganic species of chromium were successfully speciated *in situ* using both the cylindrical and sediment probe DGT devices.

8. The Eh/pH conditions in the soil and leachate of the leaching studies favour arsenic as As (V) and chromium as Cr (III).

The next chapter will present the leachate metal(loid) concentration results derived from the passage of water through the mulch and soil layers. These results will help determine if the elements leached out from CCA-treated wood waste are retained in the soil or pass through the profile. Furthermore, the concentrations in the leachate will be compared against Environmental Quality Standards for surface waters and World Health Organisation Water Drinking Guidelines to determine if they are a risk to human and environmental health.

6 Leachate Results

6.1 Introduction

This chapter presents the elemental analysis results from the leachate samples generated in the Synthetic Precipitation Leaching Procedure (SPLP) and lysimeter leaching studies. Leachate was analysed for arsenic, chromium and copper (total and inorganic species). The total levels are compared against UK Environment Agency Environmental Quality Standards for surface water and World Health Organisation Guidelines. Section 6.2 covers the results from the SPLP. Section 6.3 presents the total levels of arsenic, chromium and copper in leachate samples. Speciation results for arsenic and chromium are discussed in section 6.4. Section 6.5 is a discussion of the results and section 6.6, concludes the chapter.

6.2 Synthetic Precipitation Leaching Procedure Results

The SPLP (Method 1312; EPA, 1994a) measures the potential leachability of CCA metal(loid)s from the wood. The technique is designed to simulate field conditions exposed to rain water. This procedure was carried out to determine the leaching potential of freshly CCA-treated wood compared to both weathered CCA-treated wood and untreated wood. A detailed account of the method is available in section 3.2.7. Measurement of the extractants is described in Section 3.2.8. The results are displayed in Table 6-1.

Table 6-1: Recoverable Metal(loid) Concentrations in the SPLP Wood Sample Extracts (± 1 standard deviation)

	Freshly Treated CCA Wood	**CCA-treated Wood Waste Wood**	**Untreated Wood**
Arsenic	12.37 ± 0.38 ppm	0.38 ± 0.07 ppm	0 ppm
Chromium	4.94 ± 0.13 ppm	0.21 ± 0.01 ppm	0 ppm
Copper	9.39 ± 0.4 ppm	0.83± 0.04 ppm	0 ppm

When looking at leaching characteristics, the levels of metal(loid)s leached out of freshly treated wood were greatest for arsenic followed by copper and chromium (Cr<Cu<As). For weathered wood, copper was found at the highest levels followed by arsenic and chromium (Cr<As<Cu). Levels of all metal(loid)s leached from the freshly treated wood were orders of magnitude higher than those from weathered equivalents

(Table 6-1). There was no detectable arsenic, chromium or copper in the leachate extract from the untreated wood, confirming that the wood used for the untreated lysimeters was uncontaminated.

The concentrations of all metal(loid)s leached from freshly treated wood and weathered wood exceed the maximum Environmental Quality Standard (EQS) of the Water Framework Directive by two to three orders of magnitude (arsenic EQS: 50ppb, chromium EQS: 32ppb, copper EQS: 28ppb). These results highlight the potential risk to groundwater and surface water from leachable metal(loid)s in the wood and the need for further study to evaluate the risk of leaching from CCA-treated mulch exposed to natural conditions.

6.3 Total Arsenic, Chromium and Copper Concentrations in Lysimeter Leachate

The concentrations of total arsenic, chromium and copper were measured in leachate samples collected during the long-term (21 week) and short-term (4 week) lysimeter studies. All leachates were analysed according to the method outlined in section 3.2.8.

6.3.1 General Leaching Trends – Long-Term Leaching Study

Over the course of the long-term study, leaching trends were similar for all three elements (Figure 6-1, Figure 6-2, Figure 6-3). The highest concentrations were observed in the CCA wood monofill (Table 6-2) with arsenic, chromium and copper reaching 1.89ppm, 1.26ppm and 1.24ppm respectively. Furthermore, there was a lot of variability between different sampling dates.

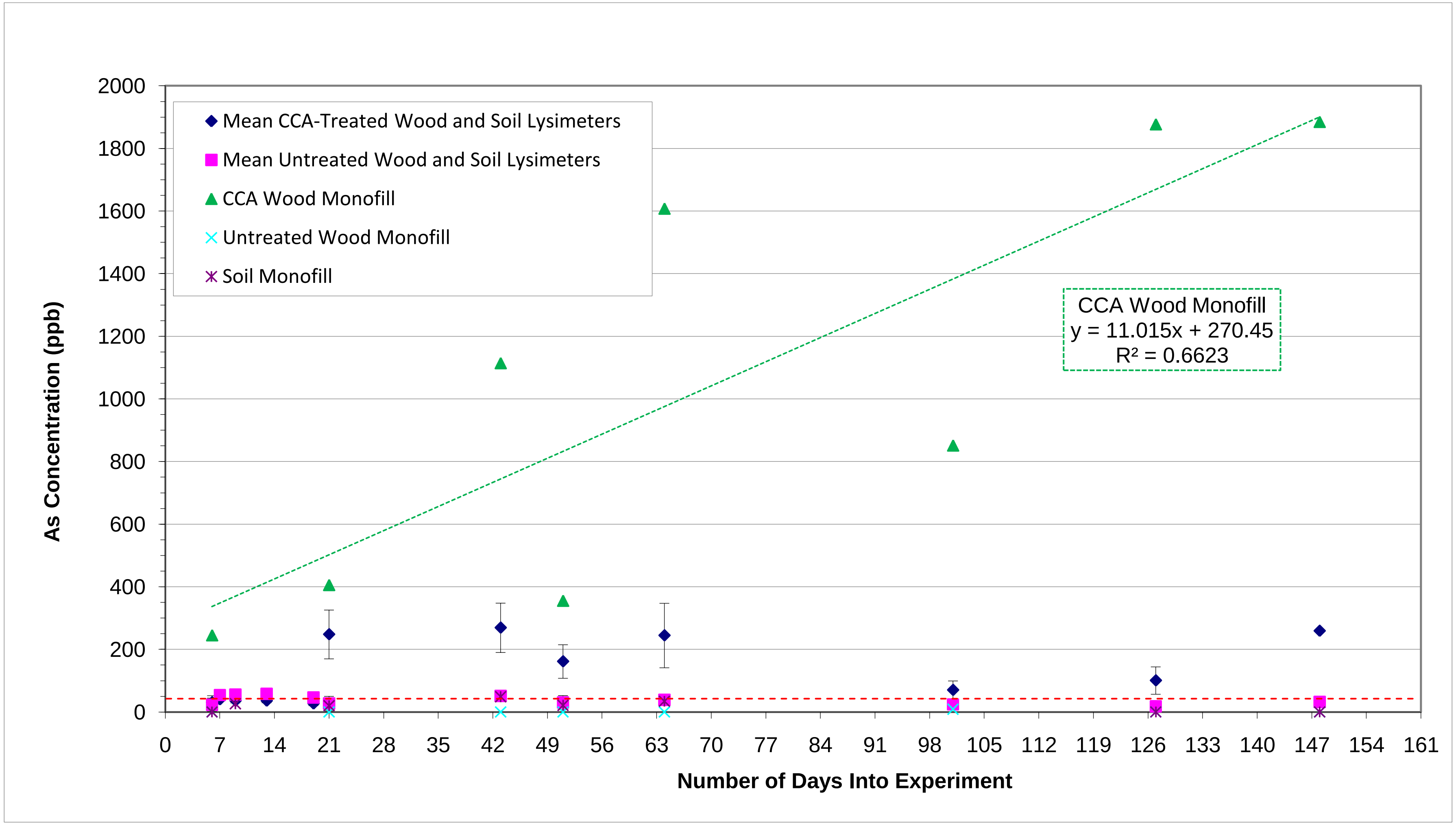


Figure 6-1: Arsenic Leaching Trends Over Time ± 1 standard deviation (dashed red line represents EQS limit)

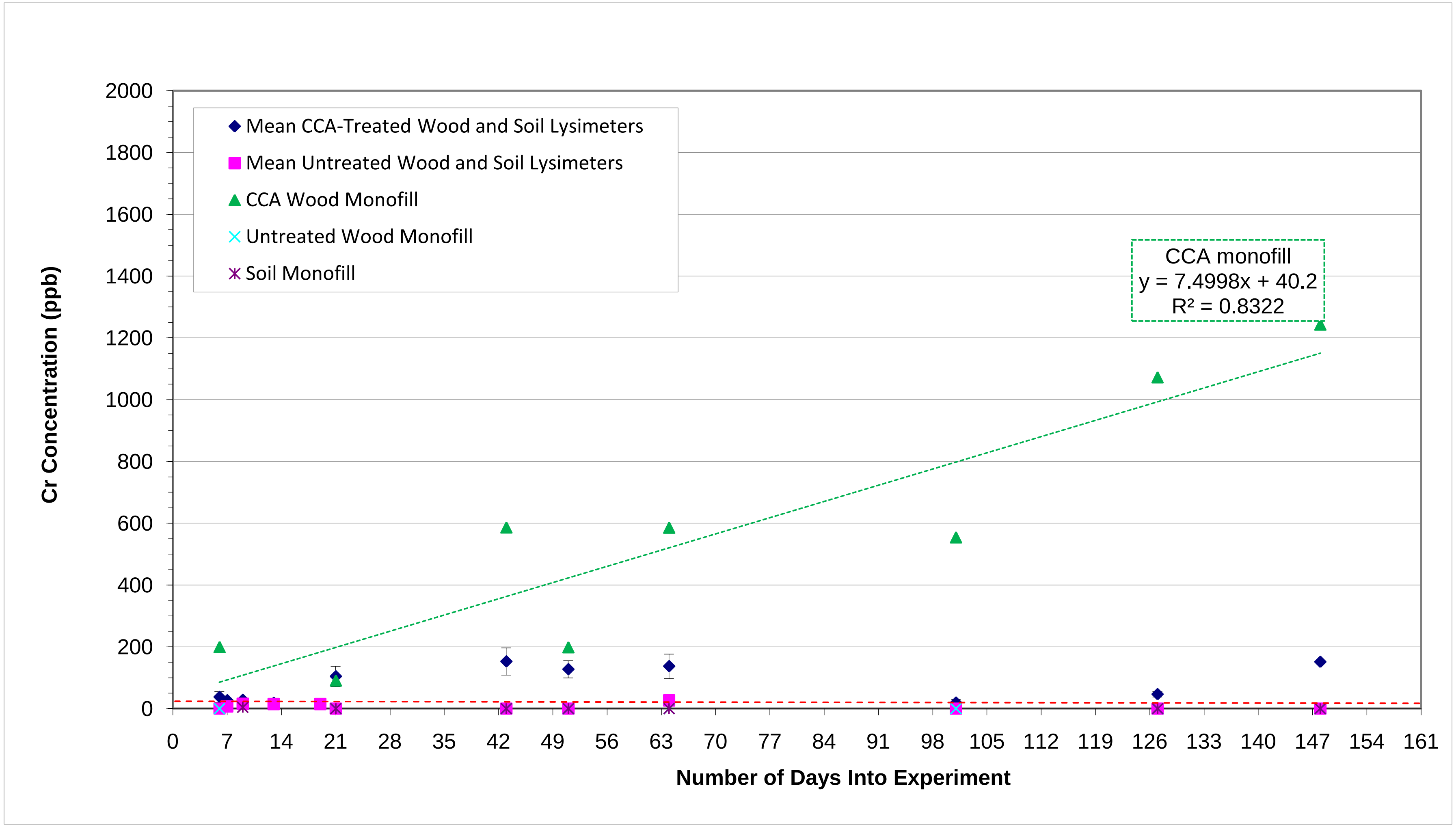


Figure 6-2 Chromium Leaching Trends Over Time ± 1 standard deviation (dashed red line represents EQS limit)

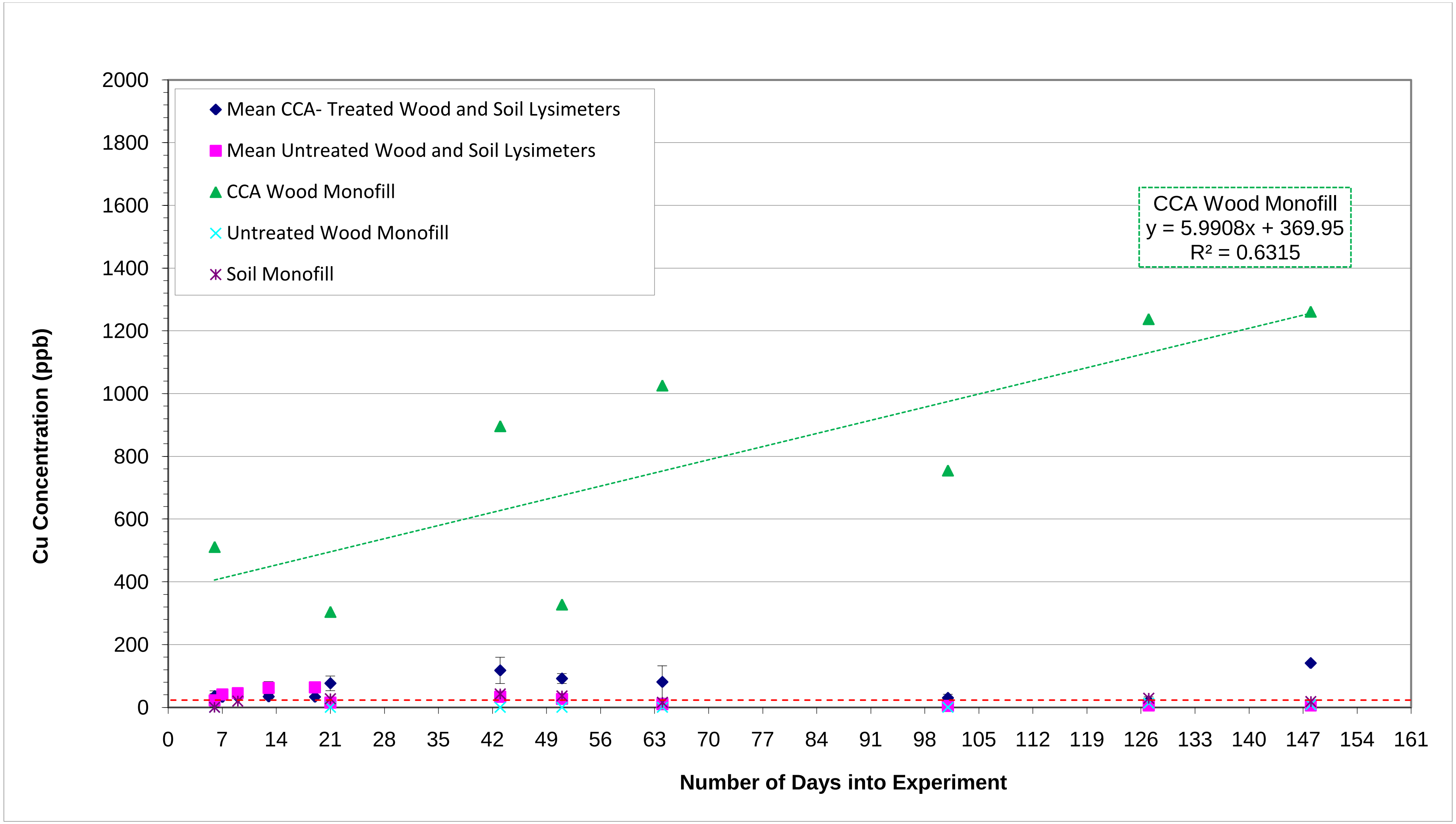


Figure 6-3: Copper Leaching Trends Over Time ± 1 standard deviation (dashed red line represents EQS limit)

Table 6-2: Mean Leaching Concentrations for Experimental Period

	Arsenic (ppb)	Chromium (ppb)	Copper (ppb)
Untreated Wood and Soil Lysimeters	38.22	6.48	28.04
CCA-treated Wood and Soil Lysimeters	126.80	71.85	60.22
CCA-treated Wood Monofill	1042.85	566.12	790.05
Untreated Wood Monofill	1.10	0.00	2.73
Blank Soil Monofill	18.85	0.59	23.71

6.3.1.1 CCA Wood Monofill

Concentrations in the CCA wood monofill leachate were found to significantly increase over time (arsenic $r^2 = 0.66$, $p < 0.01$; chromium $r^2 = 0.83$, $p < 0.01$; copper $r^2 = 0.63$, $p < 0.05$) (Figure 6-1, Figure 6-2, Figure 6-3). The CCA wood monofill can be compared directly with the SPLP as it uses the same material and similar conditions. However, the SPLP is a more severe leaching method as the element concentrations in the leachate of the long-term study were not comparable until the end of the experimental period. The SPLP leachate metal(loid) concentrations were high following only 18 ± 2 hours of immersion in the leachant.

6.3.1.2 CCA-treated Wood and Soil Lysimeters

The CCA-treated wood and soil lysimeter leachate concentrations increased over time but the trends were not significant (arsenic $r^2 = 0.18$, $p = 0.44$; chromium $r^2 = 0.14$, $p = 0.12$; copper $r^2 = 0.13$, $p = 0.12$). The leached elemental concentrations remained at or below EQS for all metal(loid)s until day 19 of the experiment. From this time onwards, concentrations of leached metal(loid)s fluctuated around the EQS thresholds, sometimes exceeding them. These results further highlight the potential environmental issues associated with leaching of metal(loid)s from CCA-treated wood waste under near-natural conditions.

6.3.1.3 Variations in Leaching Patterns

Both the CCA-treated wood monofill and the CCA-treated wood and soil lysimeters showed similar variations in leaching patterns. For all metal(loid)s, concentrations dip at days 51 and 101 and peak at days 43, 64, 127 and 148. The samples taken on day 51 were sampled three days after the 1 in 150 year rainfall event where 108.80mm of rain fell in a 24 hour period. This would greatly dilute the leachate. The samples collected on day 101 were collected after 12.60mm of rainfall. Samples from day 43 and 64 followed 7.80mm of rainfall and 14.20mm of rainfall respectively. The samples collected on day 127 resulted from draining of the waterlogged soil during a long dry spell. If more time had been available for all batches to be analysed, the leaching patterns could have shown more detailed trends. Plotting concentration against rainfall intensity reveals that higher concentrations of metal(loid)s in leachate are generally associated with lower rain intensities in the CCA wood monofill (Figure 6-4). The concentrations decrease with increasing rain intensity in an exponential fashion. On the other hand, there was no obvious relationship between rain intensity before sampling and leachate metal(loid) concentrations in the CCA wood and soil lysimeters. This is due to the buffering effect of the soil.

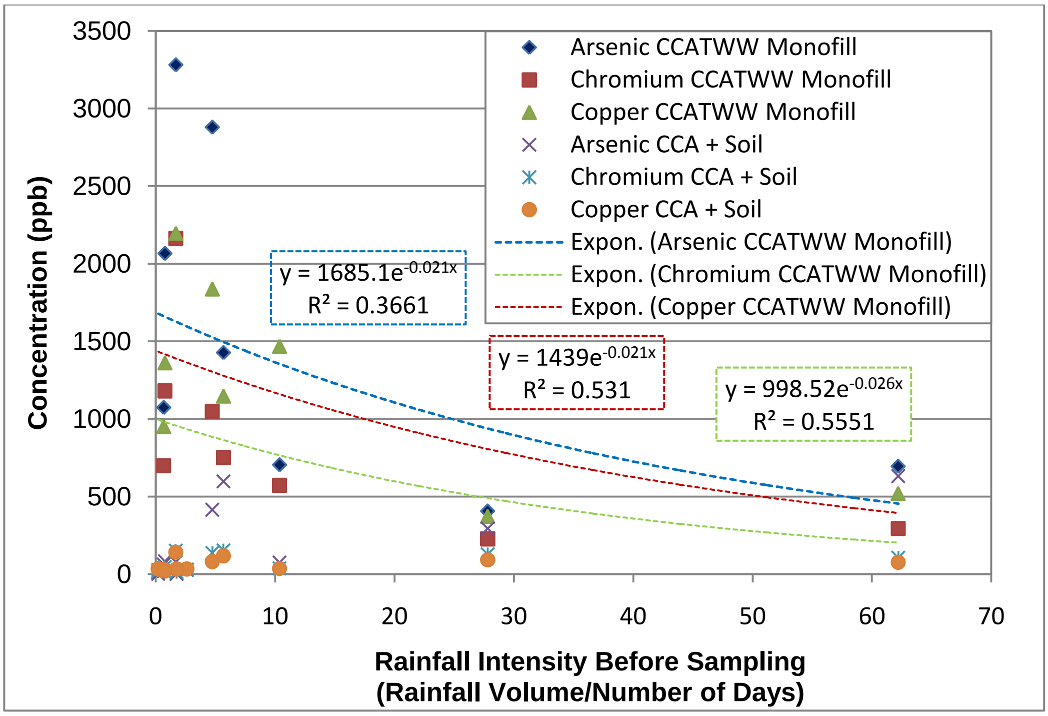


Figure 6-4: The Influence of Rain Intensity on Metal(loid) Concentration in Leachate

When pairing the concentration values of the CCA wood monofill against the mean values of the CCA-treated wood and soil lysimeters, all three metal(loid)s leached out in significantly greater amounts than in the CCA-treated wood and soil lysimeters (As: $U = 3.00$, $p < 0.001$, Cr: $U = 0.00$, $p < 0.001$, Cu: $U = 0.00$, $p < 0.001$). When comparing CCA-treated wood and soil lysimeters and untreated wood and soil lysimeters, significant differences were observed, with higher levels of all metal(loid)s found in the leachate of the CCA-treated wood and soil lysimeters (As U = 2.00; Cr U = 1.00; Cu U = 4.00; $p < 0.01$).

6.3.1.4 Untreated Wood and Soil Monofill Lysimeters

All the metal(loid) concentrations from the untreated wood and soil lysimeters, untreated wood monofill and soil monofill remained at or below the EQS for arsenic and chromium with slightly elevated levels for copper in the and untreated lysimeters between day 6 and 19. This suggests that neither the lysimeters nor the samples collected from them were contaminated during the experiment or analysis.

6.3.1.5 Proportions of Metal(loid)s Leached

When using the imputed data for the CCA-treated wood and soil lysimeters (batches 1-15), the metal(loid)s were found to leach out in significantly different amounts (H(2) = 10.78, $p < 0.01$). Using Mann-Whitney tests with a Bonferroni correction (0.0167 level of significance) it was found that arsenic leached out in significantly higher concentrations than chromium ($U = 1365$, $p < 0.0167$) and copper ($U = 1453$, $p < 0.0167$). Although copper leached out in higher concentrations than chromium (Cr<Cu<As), the results were not significantly different. The CCA-treated wood waste monofill leached in the following order Cr<Cu<As though the differences between the medians of the three elements were not significantly different. The leaching pattern observed in the CCA monofill leachate differs from that of the SPLP (Cr<As<Cu).

PCA was carried out on data from the untreated and treated lysimeters (Figure 6-5). In the untreated wood and soil lysimseters the three metals behave differently from each other with arsenic falling in component 1 and chromium and copper in component 2. pH and redox were anti-correlated. In the CCA-treated wood and soil lysimeters, the three elements are grouped very closely suggesting that they vary in the same way throughout the experiment. Redox and pH vary independently to metal concentrations. When grouping both CCA-treated wood and untreated wood data (Figure 6-5), pH and redox cluster in both studies. The elements in the leachate from CCA wood lysimeters vary consistently to each other. The elements in the leachate from the untreated lysimeters vary differently from that of the treated lysimeters and arsenic varies differently to copper and chromium. A Repeat Design ANOVA was carried out on the data to ascertain differences. Effects over time were significant ($p < 0.05$) as well as differences between the two treatments ($p < 0.05$). Furthermore, there was a significant interaction between the type of treatment and time ($p < 0.05$).

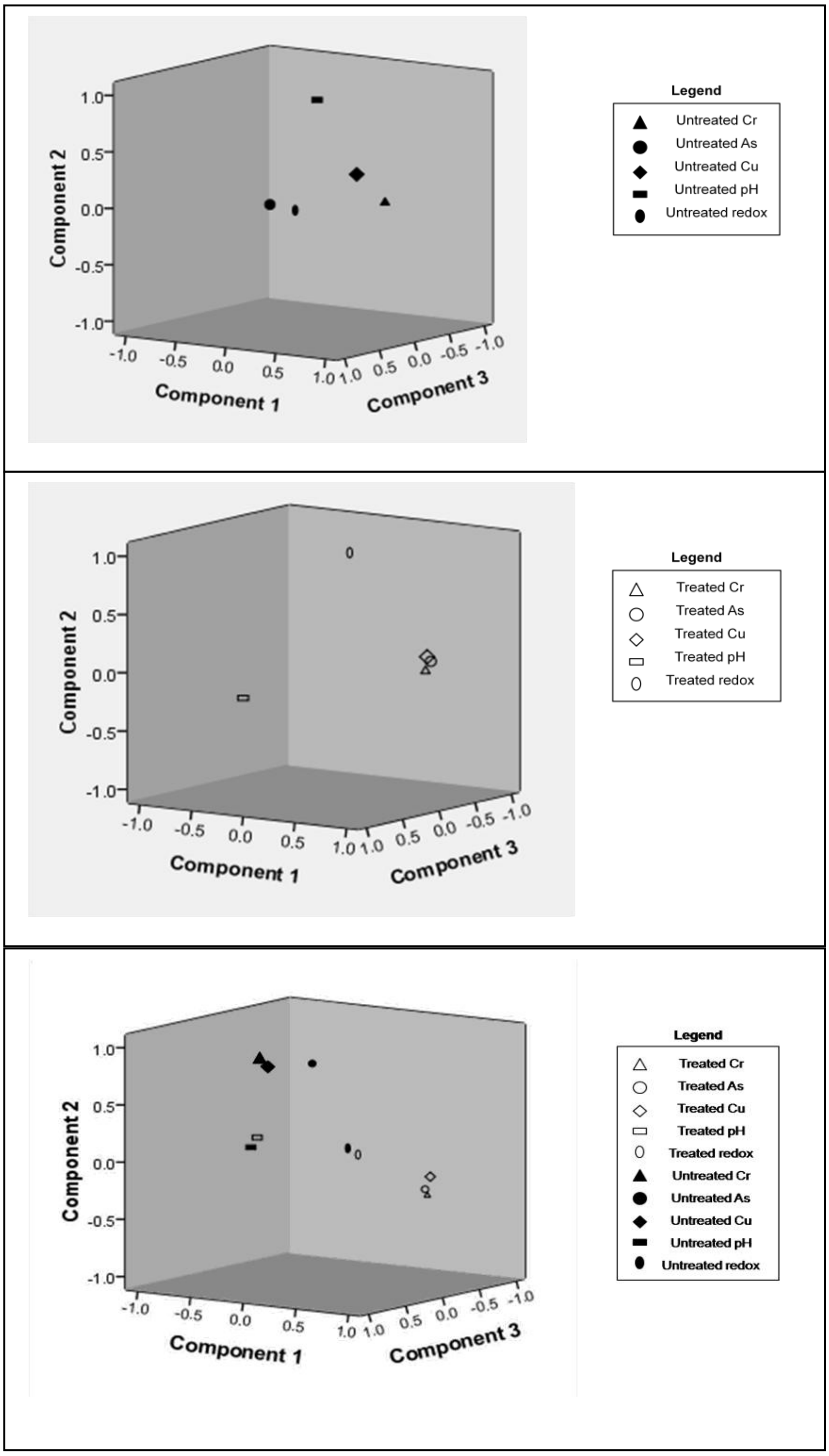


Figure 6-5: Principle Component Plots for data from untreated wood and soil lysimeters (top) and CCA treated wood and soil lysimeters (bottom)

In terms of leaching patterns, significant positive correlations were observed with the leaching of all three metal(loid)s in both the CCA-treated wood and soil lysimeters and the CCA wood monofills (Figure 6-6) (Treated lysimeters leachate As vs. Cr $r = .872$, $p < 0.01$; As vs. Cu $r = .602$, $p < 0.05$; Cr vs. Cu $r = .734$, $p < 0.01$) (CCA wood monofill leachate As vs. Cr $r = .881$, $p < 0.01$; As vs. Cu $r = .905$; $p < 0.01$; Cr vs. Cu $r = .976$, p

< 0.01). This suggests that although metal(loid)s leach in differing concentrations, they have similar overall leaching patterns.

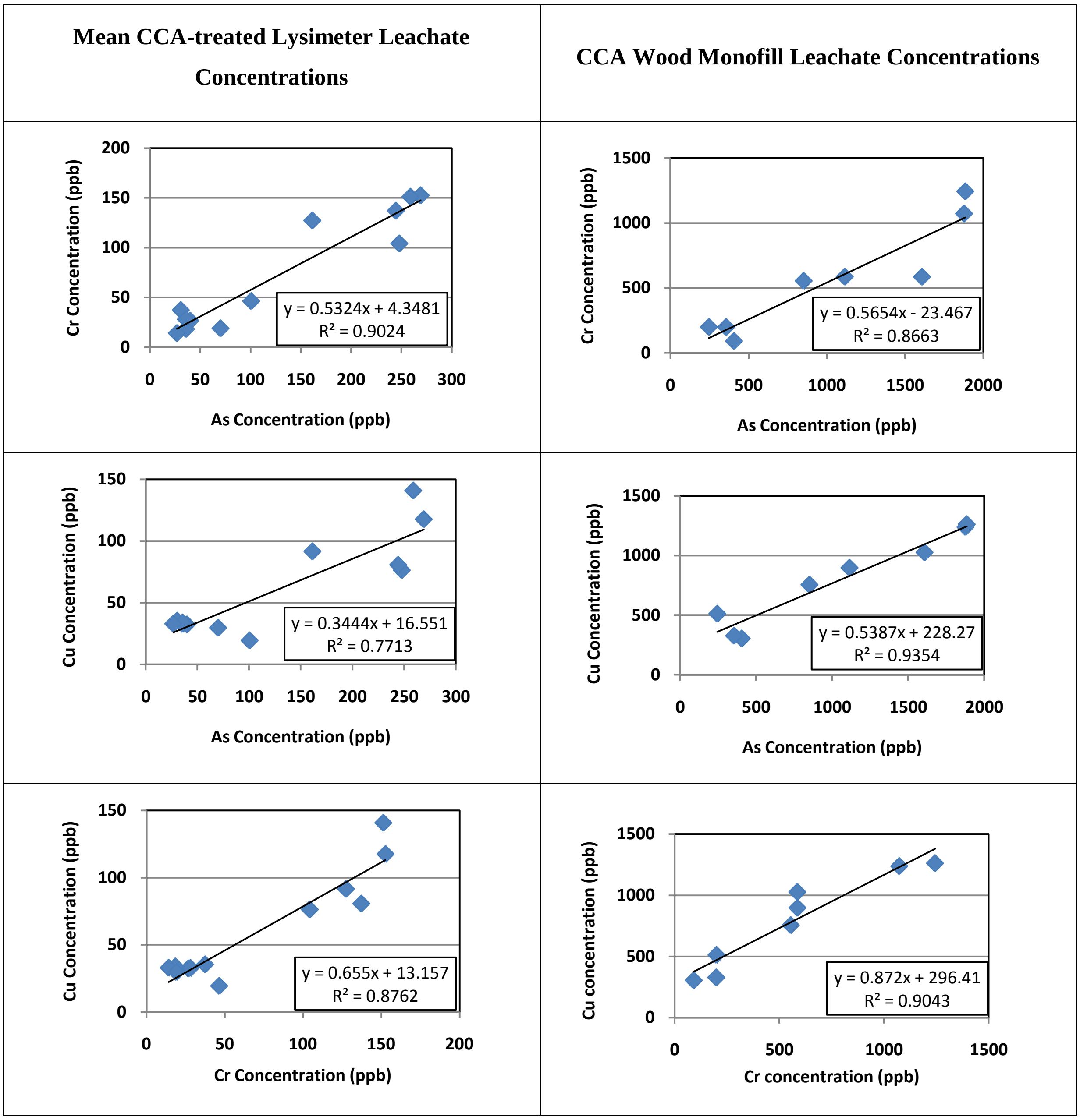


Figure 6-6: Leachate Metal(loid) Correlations

6.3.2 General Leaching Trends – Short-Term Leaching Study

Results for the metal(loid) concentrations in leachate from this study are given in Table 6-3. The controlled watering regime resulted in less leachate being generated in the lysimeters compared to the uncontrolled long-term study. Leachate was generated in the first sample collection from the lysimeters receiving both the summer and winter monthly applications of water. The untreated wood and soil lysimeters had no detectable concentrations of any of the metal(loid)s in the leachate and the levels in the CCA-treated wood and soil lysimeters remained well below the EQS.

Table 6-3: Short-Term Leaching Study Metal(loid) Levels (T = CCA-treated wood and soil, UT = untreated wood and soil). Shading denotes exceedance of EQS

						Concentration (ppb)		
Watering Regime	Sample	Date	Day	Leachate Volume	Watering (ml)	As	Cr	Cu
Summer Monthly	UT	04/10/2007	2	2720	12907.39	0.00	0.00	0.00
Summer Monthly	T		2	2640	12907.39	0.00	5.83	17.82
Summer Weekly	UT		2	70	3226.85	0.00	0.00	0.00
Summer Weekly	T		2	300	3226.85			
Summer Daily	UT		2		460.98			
Summer Daily	T		2		460.98			
Winter Monthly	UT		2	1345	14072.77	0.00	0.00	0.00
Winter Monthly	T		2	2570	14072.77	13.90	4.66	6.09
Winter Weekly	UT		2	1060	3518.19	0.00	0.00	0.00
Winter Weekly	T		2	1140	3518.19	30.03	14.83	**88.48**
Winter Daily	UT		2		473.25			
Winter Daily	T		2		473.25			
Summer Monthly	UT	11/10/2007	8		12907.39			
Summer Monthly	T		8		12907.39			
Summer Weekly	UT		8		3226.85			
Summer Weekly	T		8	280	3226.85	0.00	3.38	7.51
Summer Daily	UT		8		460.98			
Summer Daily	T		8		460.98			
Winter Monthly	UT		8		14072.77			
Winter Monthly	T		8		14072.77			
Winter Weekly	UT		8	1050	3518.19	0.00	0.00	0.00
Winter Weekly	T		8	1450	3518.19	15.28	17.82	**33.90**
Winter Daily	UT		8		473.25			
Winter Daily	T		8		473.25			
Summer Monthly	UT	18/10/2007	15		12907.39			
Summer Monthly	T		15		12907.39			
Summer Weekly	UT		15	550	3226.85	0.00	0.00	0.00
Summer Weekly	T		15	450	3226.85	0.00	0.00	5.20
Summer Daily	UT		15		460.98			
Summer Daily	T		15		460.98			
Winter Monthly	UT		15		14072.77			
Winter Monthly	T		15		14072.77			
Winter Weekly	UT		15	1270	3518.19	0.00	0.00	3.65
Winter Weekly	T		15	1070	3518.19	0.00	11.98	21.99
Winter Daily	UT		15		473.25			
Winter Daily	T		15		473.25			
Summer Monthly	UT	25/10/2007	22		12907.39			
Summer Monthly	T		22		12907.39			
Summer Weekly	UT		22	1055	3226.85	0.00	0.00	0.00
Summer Weekly	T		22	830	3226.85	20.33	10.82	20.41
Summer Daily	UT		22		460.98			
Summer Daily	T		22		460.98			
Winter Monthly	UT		22		14072.77			
Winter Monthly	T		22		14072.77			
Winter Weekly	UT		22	1320	3518.19	0.00	0.00	5.09
Winter Weekly	T		22	1210	3518.19	0.00	0.00	0.00
Winter Daily	UT		22		473.25			
Winter Daily	T		22		473.25			
Summer Monthly	UT	01/11/2007	29		12907.39			
Summer Monthly	T		29		12907.39			
Summer Weekly	UT		29	1520	3226.85	0.00	0.00	0.00
Summer Weekly	T		29	1230	3226.85	0.00	0.00	0.00
Summer Daily	UT		29		460.98			
Summer Daily	T		29		460.98			
Winter Monthly	UT		29		14072.77			
Winter Monthly	T		29		14072.77			
Winter Weekly	UT		29	1310	3518.19	0.00	0.00	5.10

Winter Weekly	**T**	29	1300	3518.19	18.34	10.52	15.48
Winter Daily	**UT**	29		473.25			
Winter Daily	**T**	29		473.25			

The lysimeters receiving a daily application of the summer and winter average rainfall did not generate leachate and it is expected that due to the small quantity applied, the water would have evaporated or remained in the soil, reflecting the high soil moisture contents observed. The weekly applications of rainfall generated leachate consistently over the entire study. In this case all the metal(loid) levels for the untreated wood and soil lysimeters remained at or below the EQS apart from higher levels of copper in weeks 3 (88.48ppb) and 4 (33.90ppb) in the lysimeters receiving the winter weekly applications of water.

6.3.3 Leachate Eh/pH

Speciation analyses were only carried out on a selection of samples from the first leachate batch of the long-term study. As such, the Eh and pH data collected from all leachate batches was used to determine conditions within the leachate and likely species of arsenic (Figure 6-7 and Figure 6-8) and chromium (Figure 6-9 and Figure 6-10). The arsenic Eh/pH data graph for the long-term study demonstrates that the leachate data ranges more widely than the soil (refer to Figure 5-15), however the conditions favour leaching of the same species of arsenic (V) as $H_2AsO_4^-$ and $HAsO_4^{2-}$. Conditions in the short-term leaching study leachate also favoured the leaching of arsenic (V) as $H_2AsO_4^-$. In both studies there is the potential for arsenic to leach out as As (III) (H_3AsO_3).

The chromium species favoured in the leachate from both long-term (Figure 6-9) and short-term (Figure 6-10) leaching studies was chromium (III) as $CrOH^{+2}$, $Cr(OH)_2^{+1}$ and $Cr(OH)_3$. In the long-term leaching study some points lay at high pH and Eh values near the theoretical boundary of the conditions that favour Cr (VI). It is therefore possible that Cr (VI) may have been present in the leachate of the long-term study.

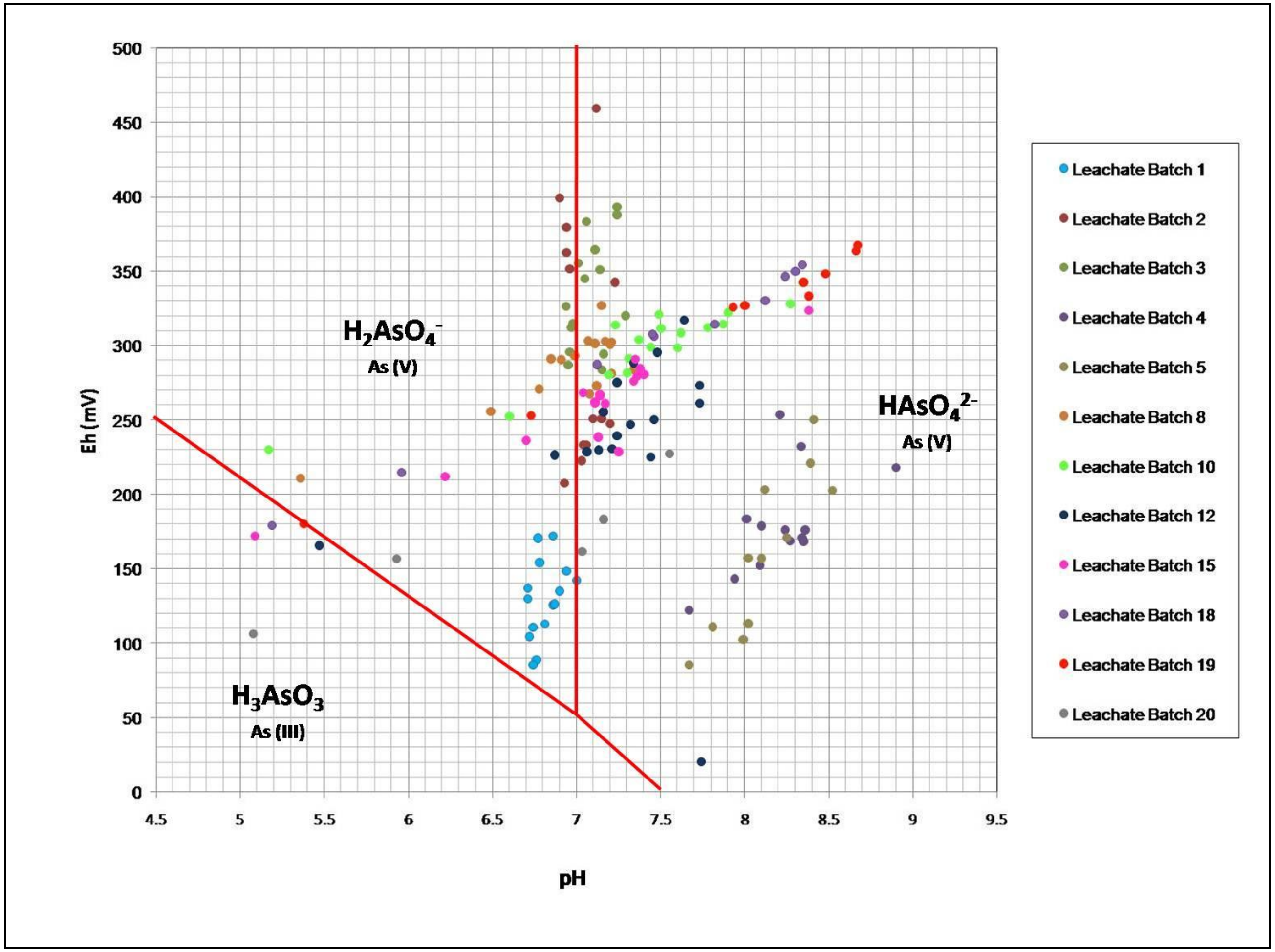


Figure 6-7: Long-Term Study Leachate Arsenic Eh/pH Values (Eh/pH boundaries adapted from Solo-Gabriele *et al.*, 2004b)

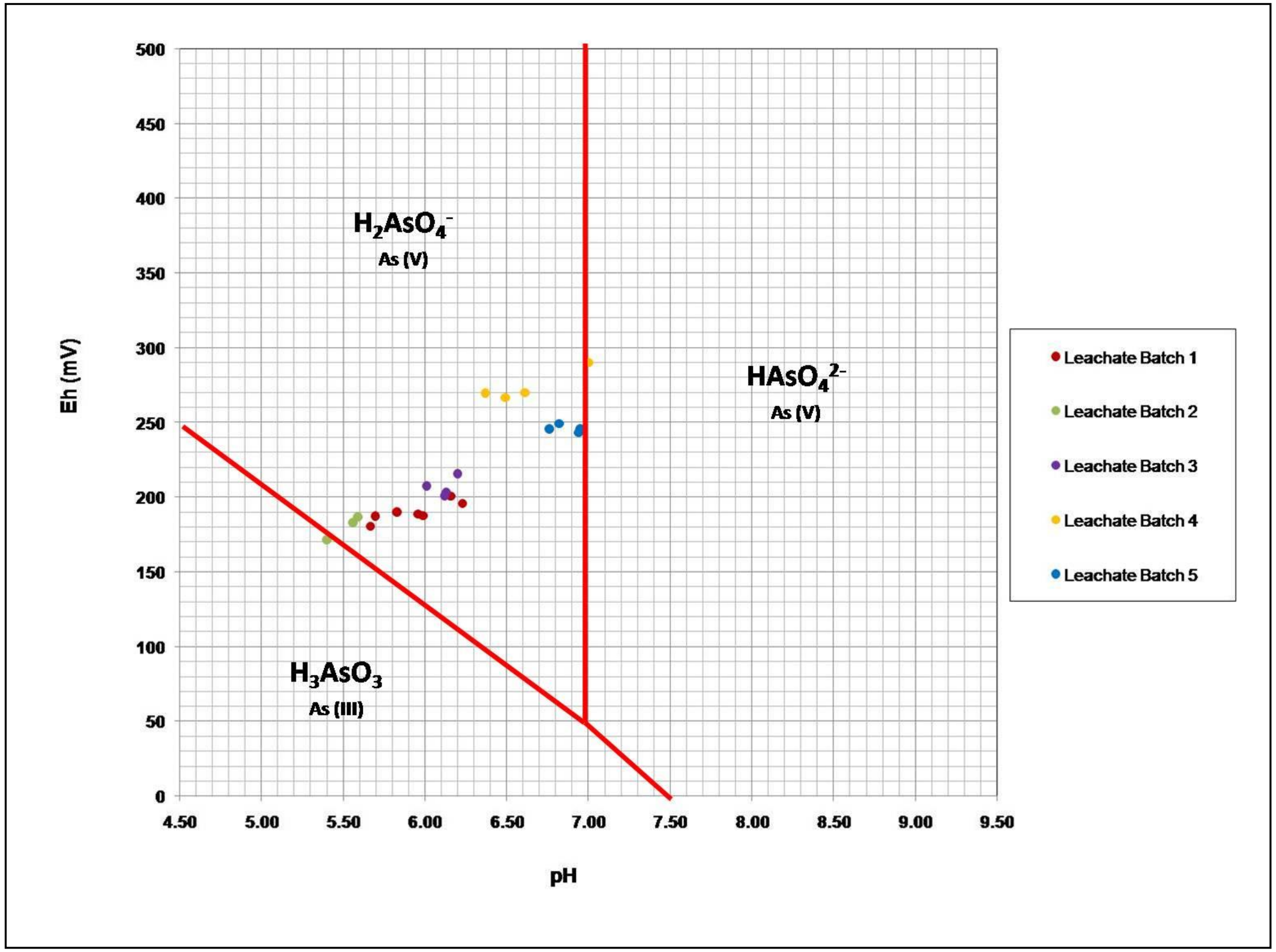


Figure 6-8: Short-Term Study Leachate Arsenic Eh/pH Values (Eh/pH boundaries from Solo-Gabriele et al., 2004b)

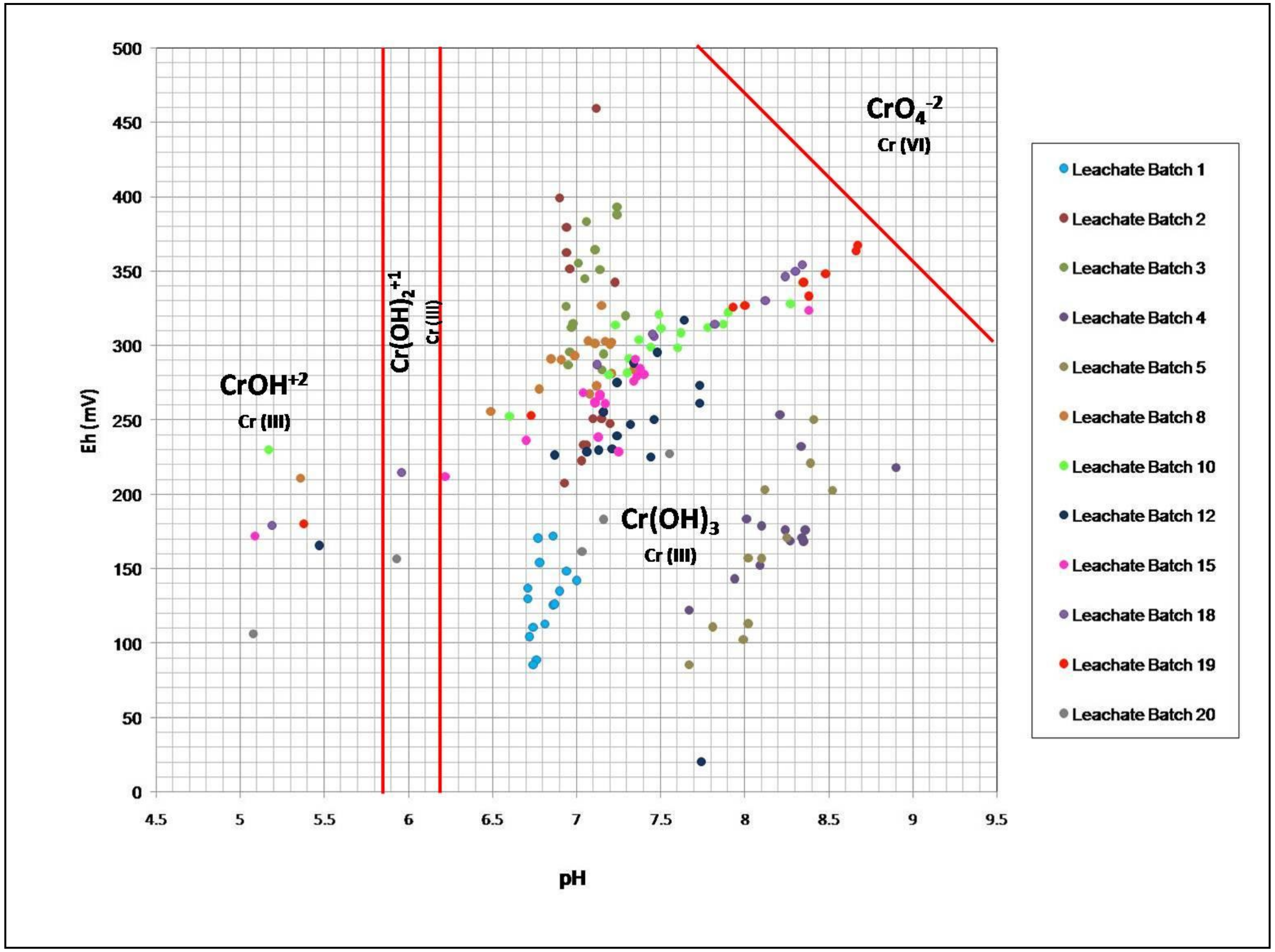


Figure 6-9: Long-Term Study Leachate Chromium Eh/pH Values (Eh/pH boundaries adapted from Solo-Gabriele et al., 2004b)

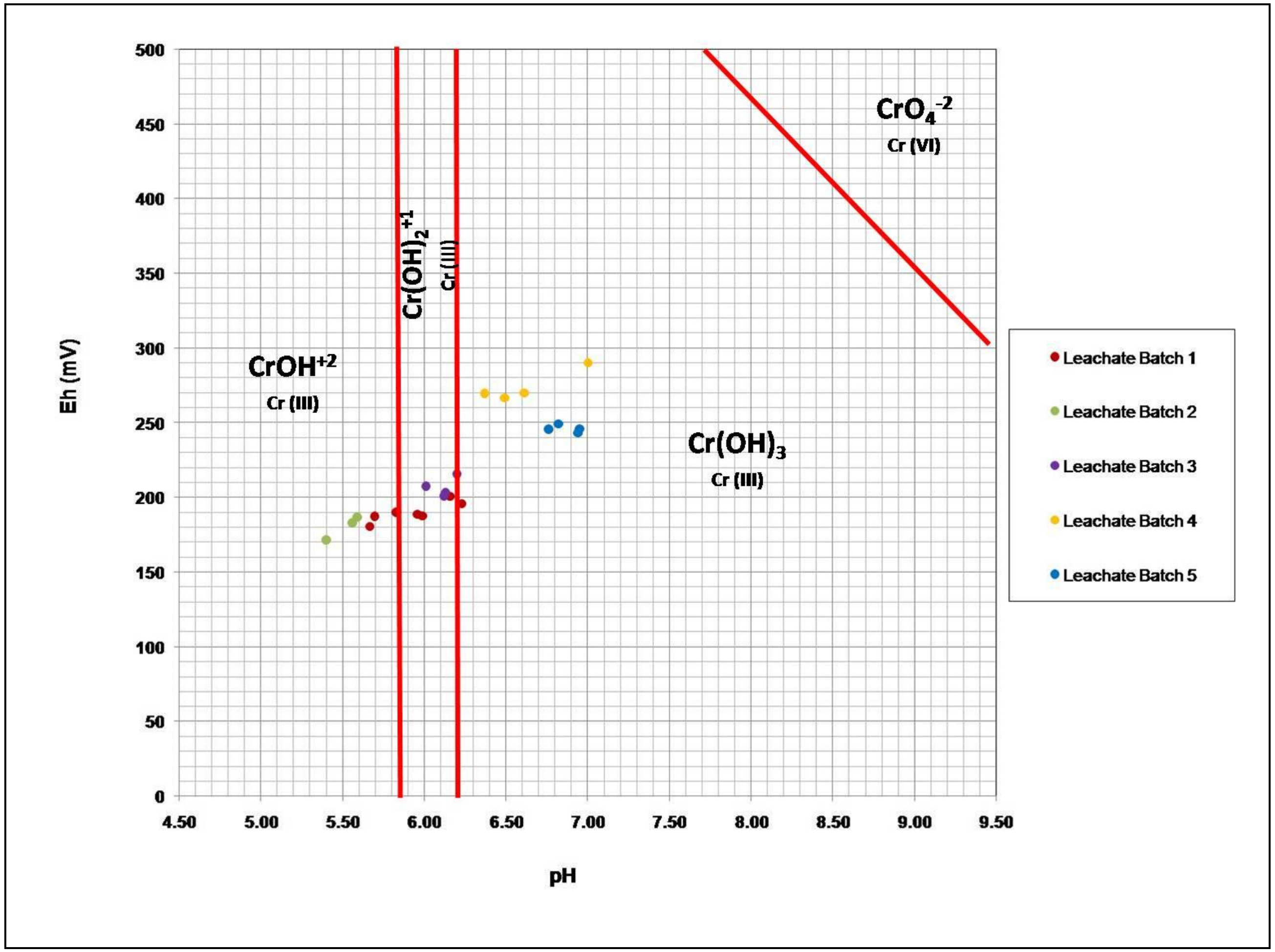


Figure 6-10: Short-Term Study Leachate Chromium Eh/pH Values (Eh/pH boundaries adapted from Solo-Gabriele et al. 2004b)

6.4 Arsenic, Chromium and Copper Inorganic Species in Leachate

Metal(loid) speciation analyses were carried out on representative samples from the first leaching batch of the long-term leaching study using the method outlined in section 3.2.9. The resultant speciation chromatograms of the samples are presented in Figure 6-11 to 6-15. In all the treatments containing soil (Figure 6-11 to 6-13), inorganic species were present as arsenic (III) and chromium as chromium (III).

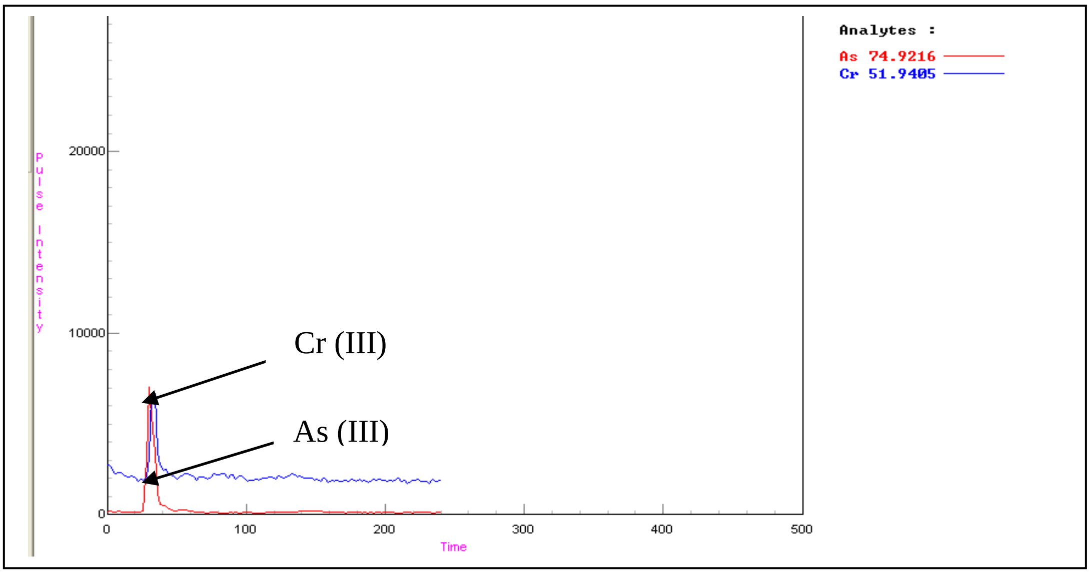


Figure 6-11: Soil Monofill Leachate Chromatogram

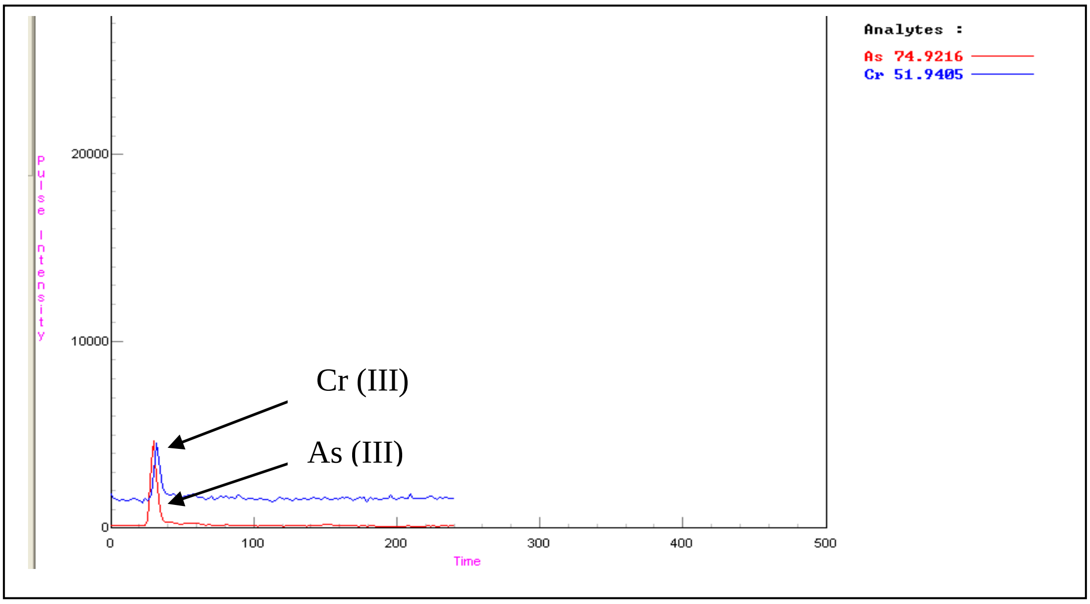


Figure 6-12: Untreated Wood and Soil Lysimeter Leachate Chromatogram

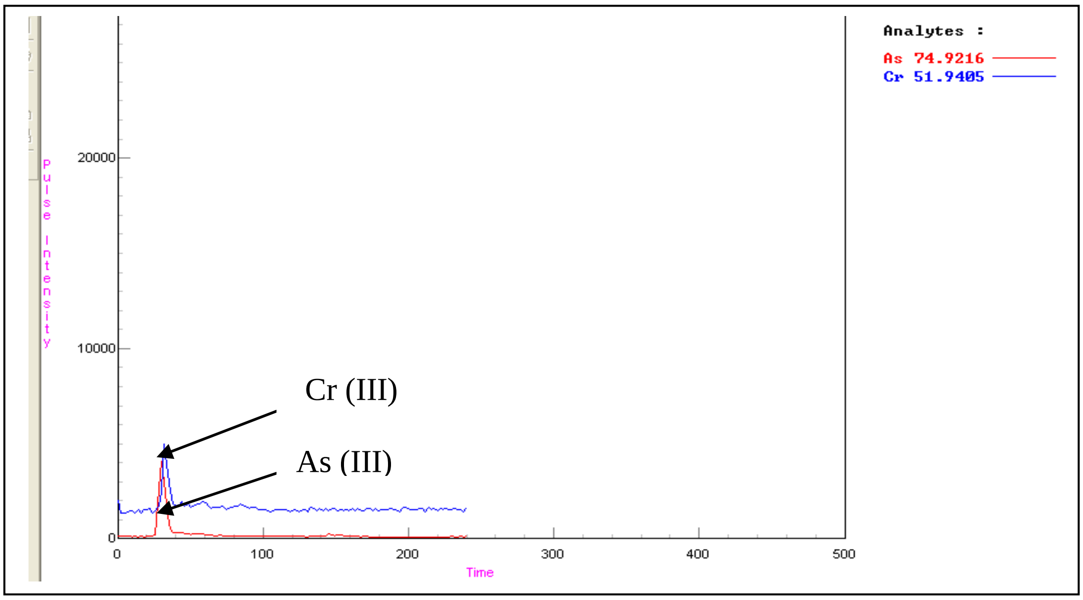


Figure 6-13: CCA-treated Wood and Soil Lysimeter Leachate Chromatogram

These results suggest that the arsenic and chromium in the early-formed leachates are derived from the soil as leachates from the mulch containing lysimeters had similar results to leachate from the soil monofill. However, quantitative results were not available to determine this. Furthermore, the total metal(loid) results at the start of the experiment from all soil-filled lysimeters were not significantly different from each other. This suggests similar results in terms of the species present. This may change over time as the total metal(loid) contents in the leachates, particularly the CCA-treated wood and soil and untreated wood and soil lysimeters varied significantly.

In the leachate from the CCA-treated wood monofill, arsenic is present as both As (III) and As (V) (Figure 6-14), with no evidence of chromium species. The untreated wood monofill leachate did not contain any detectable inorganic arsenic or chromium species (Figure 6-15). This indicates that the wood and leachate was not contaminated during experiment set-up, sample collection or analysis.

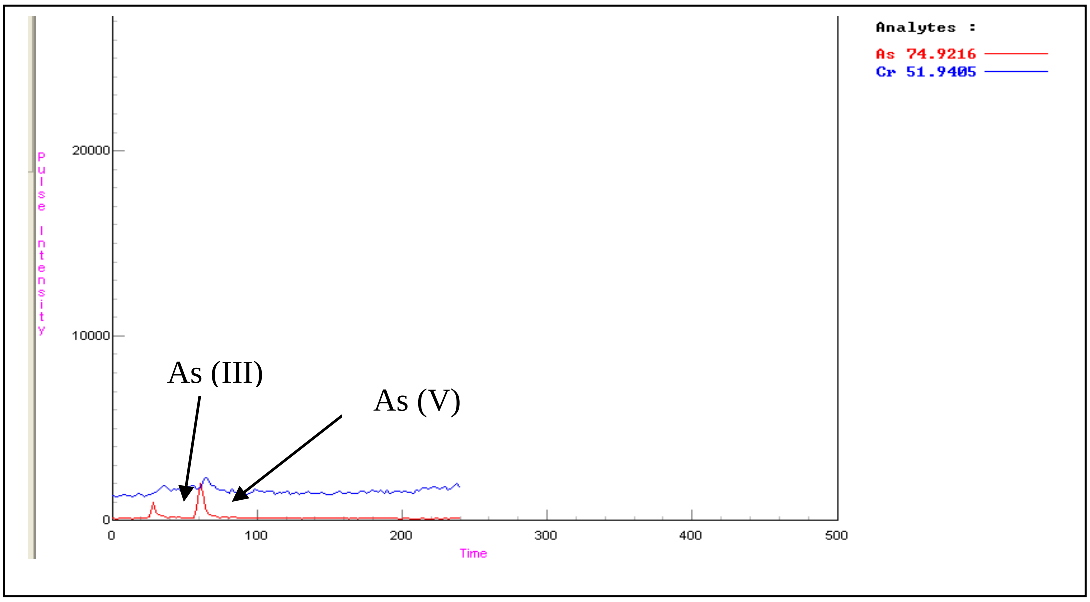


Figure 6-14: CCA-treated Wood Waste Monofill Leachate Chromatogram

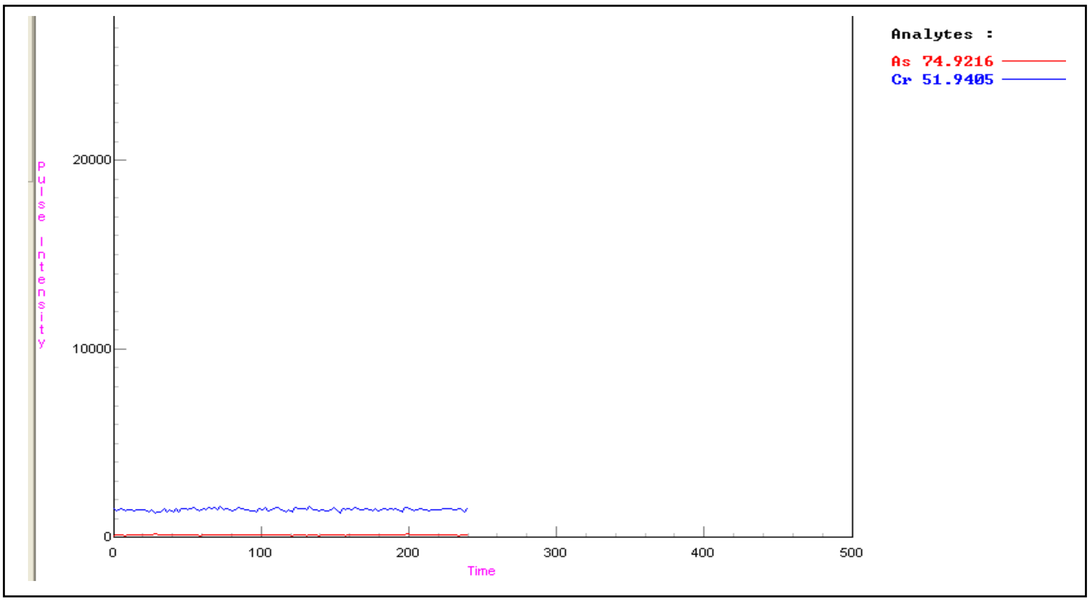


Figure 6-15: Untreated Wood Monofill Leachate Chromatogram

6.5 Discussion of Leachate Metal(loid) Levels

This section will present the discussion of the leachate metal(loid) levels in light of the published literature. Only results from CCA-treated wood will be covered as these were found to exceed EQS in some cases and therefore pose a risk to the environment and human health.

6.5.1 Synthetic Precipitation Leaching Procedure

Results from the SPLP demonstrated that metal(loid)s in freshly treated wood leach out in greater amounts than metal(loid)s in weathered wood (Table 6-1). This may be because freshly treated wood loses CCA rapidly in the initial stages of exposure to a leaching medium compared to weathered wood, due to a freely available surface deposit (Lebow *et al.,* 1999; Khan *et al.*, 2004; Waldron *et al.,* 2005). In addition, the movement of preservatives to the surface of the wood is exacerbated by the steep concentration gradient between the wood and leachant (Cooper, 1994).

The SPLP results suggest that the method is a more severe leaching procedure than exposure to natural conditions. This was confirmed in the long-term leaching study where the CCA wood monofill leachate didn’t reach the same levels as the SPLP extracts until day 21. Many authors argue that this method is not representative of natural conditions due to the severity of the leaching agents used (Yamamoto *et al.,* 1999; Kennedy & Collins, 2001; Lebow *et al.,* 2004; Yoon *et al.,* 2005). The acidification of water with sulphuric acid in the SPLP causes increases in the solubility of arsenic, copper and chromium compared to other possible treatments (Moghaddam & Mulligan, 2008). This may be further exacerbated by the large surface-to-volume ratio from using chipped wood which has been shown to increase extraction rates in laboratory leaching studies (Yamamoto *et al.*, 2000; Hingston *et al.*, 2001). As such, the method can overestimate the loss of metal(loid)s particularly from freshly treated wood (Yoon *et al.*, 2005).

Comparing data from SPLP to regulatory guidelines may not be appropriate as there are many additional factors which must be considered when extrapolating to the direct application of woodchips to soil (Townsend *et al.*, 2003a). In this study, the technique was only used as an indication of possible levels of metal(loid) loss from the wood prior to setting up the lysimeters. It also provided a useful comparison of the leaching characteristics of both freshly-treated and weathered CCA wood and is a useful screening tool to rapidly detect low levels of arsenic in CCA-treated wood mulch (Jacobi *et al.*, 2007).

6.5.2 Exceedance of Environmental Quality Standards and Drinking Water Standards

In the long-term leaching study leachate from both the CCA wood monofill and CCA-treated wood and soil lysimeters exceeded the EQS. This exceedance and the observed increase in leaching over time do not fit in with suggestions that CCA-treated wood waste is comparatively leach resistant and if any metal(loid) release should occur, this would be in the early stages (Cockcroft & Laidlaw, 1978; Van Eetvelde *et al.,* 1995b; Lebow *et al.,* 2003). Rather, the trend suggests that the CCA-treated wood waste is degrading and increasingly releasing the metal(loid)s bound to the wood over time. Hasan *et al.* (2008) actually found that leaching rates for weathered wood were almost double for those of freshly treated wood due to the weathering process.

The exceedance of the maximum EQS has wide-ranging implications. The standards are put in place to ensure that the conditions of surface and/or groundwater can support ecosystems (Environment Agency, 2006). The levels experienced in the leachate from CCA wood demonstrate that contamination of the soil would result in adverse impacts to soil flora and fauna. Furthermore, if the mulch is used in a landscape setting human health may be at risk. This is particularly the case if there is direct contact through ingestion, dermal absorption or inhalation of CCA components from the wood or through indirect contact via contaminated crops or livestock that comes into contact with the wood. The mobility of the metal(loid)s in soil as evident in the leachate taken from the base of the CCA-treated wood and soil lysimeters imply that there are significant risks of contamination of surface and groundwater. The World Health Organisation (WHO) set drinking water standards for arsenic at 10µg/l and chromium at 50µg/l (WHO, 2004). However, the maxima concentrations found in the leachate were 425.62µg/l arsenic and 230.80 µg/l chromium which are much higher than the standards.

6.5.3 Total Metal(loid) Leaching Trends

6.5.3.1 Proportions of Metal(loid)s Leached Out

In the SPLP, the metal(loid)s leached in the following amounts from freshly treated wood: Cr<Cu<As (Table 6-4). In the weathered wood, copper leached in the highest

amounts followed by arsenic and chromium: Cr<As<Cu (Table 6-4). In the long-term leaching study, both the CCA wood monofill, and CCA-treated wood and soil lysimeters leached out arsenic in the highest amounts followed by copper and chromium (Cr<Cu<As). The leaching patterns from both studies do not reflect initial proportions within the preservative (47% CrO_3, 19% CuO and 34% As_2O_5) suggesting preferential leaching for arsenic and copper, although they occur in smaller concentrations than chromium in the wood. This finding has also been confirmed in other CCA leaching studies (Warner & Solomon, 1990; Taylor & Cooper, 2003; Stefanovic & Cooper, 2006).

Table 6-4: As:Cu in Leachate Taken from CCA-Treated Wood

	Unweathered CCA wood	**Weathered CCA wood and In-service Wood**
SPLP (Leaching at pH4.5)		
Current SPLP Study	1.32	0.45
Townsend *et al.* (2004)	2.24	
Warner & Solomon (1990)	0.49	0.74
Leaching with Water		
Lebow, Williams & Lebow (2003)	1.95	
Hasan *et al.* (2008)		4.94
Leaching in Soil		
Current Long-Term Leaching Study		2.11 (CCA + soil) 1.32 (CCA monofill)
Zagury, Samson & Deschênes (2003)		0.28
Townsend *et al.* (2005)		1.19

6.5.3.2 Preferential Leaching of Arsenic and Copper

The preferential leaching of arsenic and copper varied in the long-term study and SPLP. This is also contested in the literature (Townsend *et al.*, 2003b; Taylor & Cooper, 2005). Warner & Solomon (1990) and Zagury *et al.* (2003) report that in their respective studies copper leached the most, followed by arsenic (see Table 6-4). Lebow, *et al.* (2003), Townsend *et al.* (2005) and Hasan *et al.* (2008) found the inverse relationship to be true (see Table 6-4). Stefanovic & Cooper (2006) reported differing leaching proportions of arsenic and copper over time in a single leaching experiment. In the first six months of the experiment, copper leached in the highest quantities followed by arsenic for the remainder of the experimental period. This demonstrates potential problems when interpreting the proportions of the metal(loid)s leached out from CCA-treated wood waste.

The proportion of leachable arsenic depends on the original retention levels of chromium and the ratio of As:Cu in the treatment formulation. Where formulations have been used with high As:Cu ratios, less hexavalent chromium is formed (Moghaddam & Mulligan, 2008). The hexavalent chromium is responsible for the rate of fixation of the arsenic and copper to the lignin of the wood. Therefore lower levels result in a slower fixation rate and release of arsenic. With a low As:Cu ratio, the production of hexavalent chromium is increased therefore accelerating fixation rates of arsenic and copper to the wood during pressure treatment (Moghaddam & Mulligan, 2008). This results in less arsenic release whilst in-service. The CCA formulation used has a higher As:Cu ratio and consequently may well be an influencing factor.

Townsend *et al.* (2004) warn against comparing between leaching studies as there are many different factors involved and leaching rates can vary between studies. Furthermore, variability in retention values and amount of depletion can occur even in the same piece of lumber (Schultz *et al.,* 2002; Townsend *et al.*, 2004). As such, care needs to be taken in the interpretation of the results.

6.5.3.3 Leach Resistance of Chromium

In the SPLP and the long-term study CCA wood monofill and CCA-treated wood and soil leachates, chromium was the most leach resistant metal in the CCA wood. This has also been reported in other leaching studies (Warner & Solomon, 1990; Cooper, 1991; Hingston *et al.,* 2001; Lebow *et al.,* 2003; Taylor & Cooper, 2003; Stefanovic & Cooper, 2006; Shibata *et al.,* 2007). Warner & Solomon (1990) explain that copper mainly binds to the cellulitic portions of the wood whilst chromium binds to the lignin. The bonds with cellulose are weaker than the bonds between chromium and lignin. Furthermore cellulose degrades quicker than lignin, resulting in a higher proportion of copper being leached than chromium. Arsenic binds to all the wood as copper and chrome arsenates. These arsenate bonds with the wood may be disrupted by ion exchange reactions (Warner & Solomon, 1990). The smaller proportions of chromium leached can also be explained by the reduction of hexavalent chromium to the less mobile trivalent chromium during the fixation process (Townsend *et al.*, 2005). As the chromium is in a form that is less mobile, there is a lower probability for it to leach out of the wood.

6.5.3.4 Temporal Trends in Leaching

Temporal trends are evident from the long-term study where leachate was generated throughout. The leaching trends were similar for all three metal(loid)s. The highest levels were observed in the CCA wood monofill. A similar trend was observed by Gifford *et al.* (1997) in a similar lysimeter leaching study where the highest values were observed from lysimeters containing only CCA weathered wood as opposed to lysimeters containing CCA weathered wood with soil.

Levels in the CCA wood monofill leachate were found to increase over time, a similar result to that of Jambeck *et al.* (2006) who reported increasing results for more than a year before concentrations levelled off. In the long-term study it seems likely that as the experiment ran for only five months, the data may be exhibiting the initial stages of the trend. These results differ from those of Gifford *et al.* (1997) who used 'CCA wood waste, no soil' lysimeters. They found copper and chromium levels in the leachate decreased over an 18 month period whereas arsenic decreased for 9 months before increasing substantially. They attributed these trends to seasonal variations in rainfall and temperature. However, in the current leaching studies, temperature was not a significant influence on leaching, whilst rainfall patterns were.

The CCA-treated wood and soil lysimeter results remained at or below EQS for all metal(loid)s until day 19 of the experiment. Beyond this, the levels of leached metal(loid)s exceeded and fluctuate around the EQS thresholds. Although the soil had some buffering effects to the levels leached out of CCA-treated wood. The results suggest that the attenuation of the soil was exceeded following rainfall events resulting in levels of arsenic, chromium and copper in the leachate that exceeded regulatory thresholds.

It has been established that metal(loid)s leach from fresh CCA-treated wood in the early stages of exposure to leachants and then decrease over time. Therefore, it is expected that metal(loid)s in aged and weathered wood should not be readily leachable (Moghaddam & Mulligann, 2008). However, this was not reflected in the study. In previous studies, samples up to 20 years old still leached metal(loid)s (Townsend *et al.*, 2005). This raises concern over the longevity of the risks associated with the management of CCA-treated wood waste.

The higher retentions in the weathered wood observed in this study suggest that most of the preservative remains fixed in the wood whilst in-service and following the SPLP. In freshly treated wood approximated percentage losses of arsenic, chromium and copper were 11.99%, 2.98% and 8.9% respectively. For weathered wood, losses were 0.14%, 0.04% and 0.57% (for arsenic, chromium and copper). It is possible that “even small percentage losses may be environmentally significant due to the toxicity of the components” (Hingston *et al.*, 2001, 58).

The fact that the EQS were exceeded and that there is an increase in leaching over time does not fit in with assertions that CCA-treated wood waste is comparatively stable and that metal(loid) release only occurs in the early stages of exposure (Cockcroft & Laidlaw, 1978; Van Eetvelde *et al.*, 1995b; Lebow *et al.*, 2003). Rather, the trend suggests that the degradation of CCA-treated wood waste is progressively releasing more metal(loid)s bound to the wood. This result is comparable with Hasan *et al.* (2008) who also found that leaching rates for weathered wood were almost double for those of freshly treated wood due to the weathering process.

6.5.3.5 Factors Influencing Increased Leachate Rates

A number of factors may be involved with the temporal trends for metal(loid) leaching from CCA wood. The increased surface area caused by chipping, results in the exposure of new surfaces for rapid leaching and weathering (Cockcroft & Laidlaw, 1978; Hingston *et al.*, 2002; Townsend *et al.*, 2003a; Lebow *et al.*, 2004; Townsend *et al.*, 2004; Yoon *et al.*, 2005). Metal(loid) leachability increases with decreasing particle size (Townsend *et al.*, 2004) and so small shavings and particles resulting from the chipping process may have also added to the higher metal(loid) levels in the leachate. In addition, the effect of grain orientation (which results in higher leaching rates due to the structure of wood cells) may be exaggerated in smaller wood samples (Lebow *et al.*, 2004). This is because CCA is most mobile along the lonigudinal axis of the wood due to the longitudinal orientation of the xylem vessels (Ko *et al.*, 2007).

The waste wood in this study had previously been used in indoor cooling towers and had never been exposed to weathering. Exposure of the weathered wood to UV light causes breakdown of the lignin through radical-induced depolymerisation (Schmalzl *et al.*, 2003). Although CCA has been shown to provide some protection against UV degradation, it still occurs even if coated with applications of water repellents (Lebow *et al.*, 2003). As the lignin depolymerises, the bound metal(loid)s will be released (Cooper, 1994; Lebow *et al.*, 2003; Khan *et al.*, 2006a; Morrell, 2006). Leaching can be further accelerated by loss of wood fibres following lignin degradation (Lebow *et al.,* 2003).

Another cause of temporal changes in the early stages is due to the dissolution of metal(loid)s bound on the surface of the wood in a similar way to leaching from freshly treated wood (Jambeck *et al.,* 2006). This is followed by a slower leaching mechanism involving water penetration into the wood causing hydrolysis and/or dissolution of the fixed or complexed components (Hingston *et al.,* 2001). The preservative will migrate towards the surface of the wood due to the steep concentration gradient between the wood and leachant. Therefore, the first 6 months of leaching should be characterised by a rapid release phase followed by a plateau at a lower level (Lebow *et al.,* 1999). As this study was 5 months long, the leaching patterns are characteristic of the rapid release phase. This mechanism combined with high levels of rainfall and increased contact time of the wood waste with the water resulting from waterlogging, would increase the leaching of the metal(loid)s (Townsend *et al.,* 2004).

This weathering process may be amplified in the presence of oxygen and moisture (Derbyshire & Miller, 1981). The higher leaching rates are caused by changes in the wood structure during the weathering process (Townsend *et al.,* 2005). As CCA-treated wood is not safeguarded from constant moisture and evaporation conditions, associated warping, cracking and splitting caused by weathering can expose metal(loid)s and cause them to release (Khan *et al.,* 2006a; Cooper & Ung, 2009).

The loss of metal(loid)s over time and degradation of the wood could both result in a decreasing resistance to structural breakdown and therefore amplification of the leaching mechanism (Hasan *et al.,* 2008). This paper reported that wood undergoes a rapid release leaching stage followed by slower release leaching. The rates then increase over time as the wood weathers, thereby releasing the metal(loid)s bound to the wood (Figure 6-16). This final stage of leaching can result in leaching rates being higher than leaching from new wood (Hasan *et al.,* 2008).

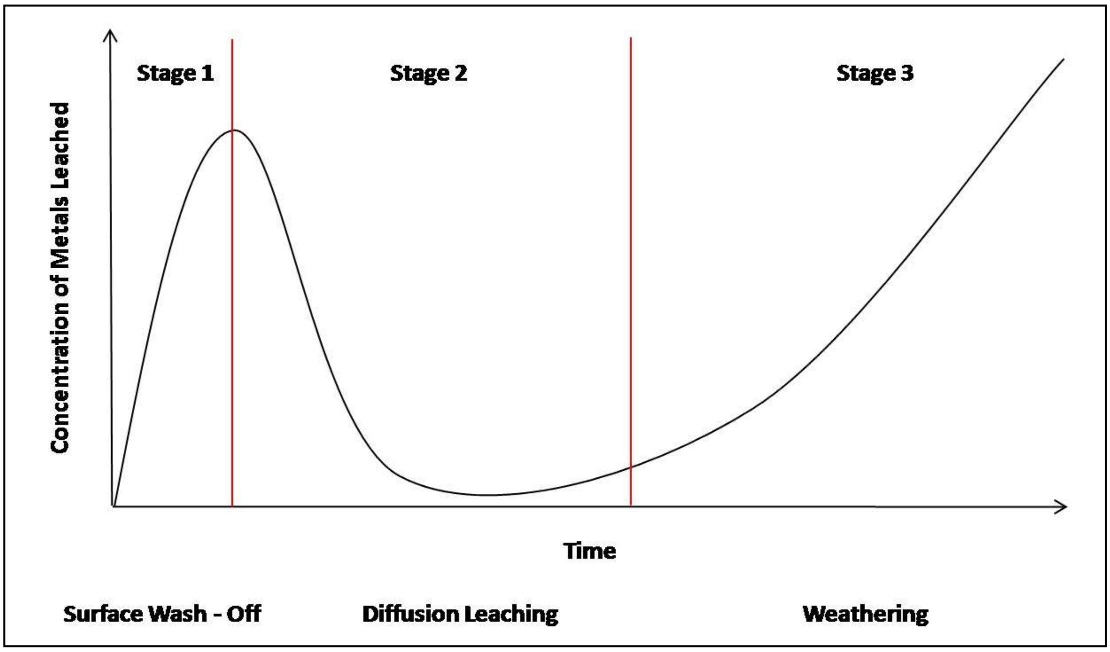


Figure 6-16: Leaching Mechanism from CCA-Treated Wood Over Time from First Exposure to a Leachant

The leaching patterns and influencing factors may account for the variations in leaching observed during the long-term study. Lower levels were associated with heavy rainfall events (day 51). The peaks at day 43 and 64 may be attributed to light continuous rainfall a few days prior. The higher levels observed in day 127 and 148 follow dry spells. Taylor & Cooper (2005) and Khan *et al.* (2006a) found higher levels of leaching from in-service treated wood following long dry spells. They concluded that rainwater penetrates into the inner part of the woodchips and dissolves arsenic. This causes the arsenic to diffuse to the surface/soil during the dry spell and in the next rainfall event this material washes off. The variations in leachate concentration may also be caused by microbiological activity (although this was not covered in the study) and changing soil properties in terms of metal(loid) binding and release.

6.5.4 Short-Term Study Leachate

The lower metal(loid) values in the CCA-treated wood and soil lysimeter leachates are probably due to the short-term nature of this study and absence of UV light, thereby increasing resistance of the wood to weathering (Cooper, 1994; Khan *et al.*, 2006a; Morrell, 2006). Soil temperatures and the amounts of water applied were also lower than those in the long-term study and it is to be expected that the metal(loid)s would tend to bind to the soil rather than being flushed out.

6.5.5 Speciation of Metal(loid)s in Leachate

The leachate Eh/pH data showed that conditions would favour arsenic as As (V) and and chromium as Cr (III). These expected species are the same as those in the soil samples. However, some of the leachate Eh/pH data points sit near the boundaries representing inorganic As (III) and Cr (VI) species. The leachates that were analysed for inorganic metal(loid) species were an example of this.

The presence of As (III) in the analysed leachates of the soil-filled lysimeters is of concern as it is more toxic, soluble and mobile than As (V) (Masscheleyn *et al.,* 1991b; Balasoiu *et al.,* 2001; Hingston *et al.,* 2001; Macur *et al.,* 2001; Jambeck, 2004; Khan *et al.,* 2004; Solo-Gabriele *et al.,* 2004b; Dobran & Zagury, 2006). Furthermore, it is this mobile fraction that causes contamination and health risks (Pantsar-Kallio & Manninen, 1997). As (III) may play a role in the increased leaching of arsenic from the weathered wood due to its greater mobility (Solo-Gabriele *et al.,* 2004b). As such, the faster leaching rates and higher levels of arsenic leached in the long-term leaching study (section 6.3.1) may also be attributed to this leaching characteristic.

It is possible to find As (III) under conditions that theoretically favour As (V) as in the long-term study. In the soil lysimeters, any available As (V) may have adsorbed to the soil whereas the mobile and soluble As (III) passed through the soil column. Soil OM has also been shown to influence the formation of As (III) in aerobic environments by facilitating the reduction of As (V) to As (III). Fulvic and humic acids found in soil OM are important electron donators for the reduction of elements and can increase arsenic mobility (Redman *et al.,* 2002; Dobran & Zagury, 2006). The soil OM content in this study are at the upper end of the range which will increase As (III) mobility (Balasoiu *et al.,* 2001).

The formation of As (III) in aerobic environments may also be due to the reduction of As (V) to As (III) by bacteria, fungi and algae (Cai *et al.,* 2006). It is believed that in microorganisms, the reduction acts as a detoxifying mechanism (Cullen & Reimer, 1989; Cai *et al.,* 2006; Dobran & Zagury, 2006). Those microorganisms that are resistant to high levels of arsenic reduce As (V) to As (III) via intracellular reduction (Macur *et al.,* 2001). The As (III) is then excreted into the surrounding environment and moves down the soil profile. Microbiological measurements were not carried out in this study but it is likely that these may have contributed to the results considering the similarity of this study environment to other leaching studies.

The CCA wood monofill leachate contained both inorganic species of arsenic. These results are similar to those of Hingston *et al.* (2003), Jambeck (2004) and Khan *et al.* (2004). In all of these studies, arsenic (V) was the predominant species. This is also the case in the CCA-treated wood waste monofill leachate. In contrast, some studies have found only As (V) in freshly treated CCA wood extracted leachate (Khan *et al.,* 2004; Nico *et al.,* 2006). Arsenic is present as only As (V) in weathered CCA-treated, therefore the presence of As (III) in weathered wood leachate must be due to the reduction of As (V) biologically and/or chemically whilst the wood is in service (Khan *et al.,* 2004).

The presence of Cr (III) as opposed to Cr (VI) in leachate has also been observed in other CCA leaching studies (Cooper, 1994; Hingston *et al.,* 2003; Solo-Gabriele *et al.,* 2004b; Solo-Gabriele *et al.,* 2005). Cr (III) is the most commonly found species in wood, leachate and soil and occurs naturally in the environment (Nico *et al.,* 2004). Chromium (VI) is usually only found under alkaline (pH>9.0) and highly oxidising conditions (James & Bartlett, 1983; Song *et al.,* 2006). It is also a common component of CCA-treated wood ash (Yoon *et al.,* 2005; Jambeck *et al.,* 2006) and has been found in leachate from soils that had received surface applications of CCA solution (Carey *et al.,* 2002). Cr (III) was only found in the soil-filled containers suggesting that the topsoil is the source. Chromium was not detected in the leachate from the CCA wood monofill and this confirms the finding that chromium is more stable than arsenic.

6.6 Summary

This chapter presented results of leachate sampled from the three sets of experiments. A synthetic precipitation leaching procedure was used to determine the potential for metal(loid)s to leach out from both freshly treated and weathered CCA woodchips. A long-term lysimeter leaching study allowed for exposure to near-natural conditions to examine leaching of CCA-treated wood waste when applied to soil as mulch against a soil control, untreated wood monofill and CCA wood waste monofill. The final experiment, a short-term lysimeter study was set-up to implement a controlled watering regime, comparing CCA-treated wood and soil and untreated wood and soil. The results have been used to characterise the leaching patterns and mechanisms of preservative components from both freshly treated and weathered woodchips. A summary of the main results are outlined below:

1. The proportions of arsenic, chromium and copper leaching out from both freshly and weathered CCA wood were inconsistent. The ratios of all three metal(loid)s were found to differ from the original preservative formulation and initial levels in the wood. Chromium was most stable whilst the preferential leaching of arsenic or copper varied among samples, possibly due to variations in retention values.

2. Levels of all metal(loid)s leached from freshly treated CCA wood were orders of magnitude higher than from the weathered wood in the SPLP due to freely available surface deposits and unfixed portions of the preservative that easily wash off on exposure to a leachant.

3. Leachate concentrations of all three metal(loid)s from both the freshly treated and weathered CCA-treated wood exceeded the maximum Environmental Quality Standards of the Water Framework Directive in the SPLP and long-term lysimeter leaching study. This was due to surface wash-off from the freshly treated samples and a combination of surface wash-off, diffusion leaching and weathering in the wood waste samples. Conversely, concentrations from control lysimeters without CCA wood waste remained at or below the standards.

4. In the long-term study, leaching trends were similar for all three metal(loid)s in the CCA-treated wood lysimeters and CCA wood monofill with high positive correlations observed. Furthermore, significant fluctuations were found to correspond. However, the metal(loid)s leached out in significantly greater amounts from the CCA wood waste monofill due to a buffering effect of the soil in CCA-treated wood and soil lysimeters.

5. Less leachate was generated from the short-term study than from the long-term one. Only two incidents of EQS exceedance were observed from a single CCA-treated lysimeter. These results are predictable from the physico-chemical and background conditions of the study.

6. The Eh/pH conditions in the leachate favoured the inorganic species As (V) and Cr (III). However, in the soil-containing lysimeters, inorganic metal(loid) species were present as As (III) and Cr (III). In the CCA wood monofill, arsenic was present as both As (III) and (V) but there was no

detectable chromium due to its stability in the wood. The unexpected presence of As (III) could be due to its greater mobility, influence of soil OM and microbial mediated reduction.

7. The trends in leaching observed in the SPLP and long-term study could be due to a number of factors in addition to the physico-chemical and background conditions of the experiments. These are listed below:

    - Age of the wood.
    - Duration of contact with leachant.
    - Degree of As:Cu in original preservative formulation.
    - Exposure to UV radiation.
    - Surface area of the wood.
    - Structural breakdown and weathering of the wood.
    - Soil attenuation levels for binding of metal(loid)s.
    - Dry/wet cycles resulting in warping, cracking and splitting of the wood.
    - Resistance to structural breakdown.

8. The freshly treated CCA wood loses the preservative components in a rapid leaching phase in the initial stages of exposure to a leachant. This is due to the presence of a freely available surface material.

9. Metal(loid)s in chipped CCA wood waste leach out in a similar manner to freshly treated wood in the initial stages of contact with a leachant. This is then followed by a slower stage of removal as water penetrates into the wood causing dissolution of the fixed or complexed components. The steep concentration gradient between the wood and leachant causes the preservative to diffuse slowly to the surface of the wood before being washed off. A final leaching phase is characterised by an acceleration of removal caused by the weathering of the wood. The increasing trends observed in the long-term leaching study suggest that leaching may be caused by the first rapid release phase and/or the final leaching phase (refer to Figure 6-16).

The next chapter will give a general discussion of the partitioning and movement of arsenic, chromium and copper in the lysimeters using mass balances. Implications of the results on human health and the environment will also be discussed.

7 Discussion and Mass Balance

7.1 Introduction

This chapter will use the metal concentration data generated in the results chapters to calculate temporal changes in mass balances for arsenic, chromium and copper in the CCA-treated wood and soil lysimeters. These will provide an overview of how the metals migrate in the lysimeters and identify locations where metals are lost, retained and move within the lysimeters. The factors affecting the distribution of metals and fluxes will also be addressed.

The rationale for using mass balances will be presented in section 7.2. The long-term study mass balance will be presented in section 7.3 followed by the short-term study mass balance in section 7.4. A total mass balance for both studies is presented in section 7.5. The loss of metals in the system is discussed in section 7.6. This is followed by the limitations of the mass balances in section 7.7. The fate of the metal(loid)s and implications are covered in section 7.8 and 7.9 respectively. The final section, 7.10, is a summary of the chapter.

7.2 Rationale for Mass Balances

The results concerning the metal(loid)s in the system were reported as concentrations in the wood, soil and leachate. Although some emerging trends were observed (i.e. increased concentration in leachates), the original volumes and weights had not been taken into account and therefore absolute quantities of the elements had not been calculated. This calculation in the form of a mass balance is necessary to understand the processes occurring in the lysimeters. The calculated total quantities for wood, soil and leachate can demonstrate the migration, fluxes and accumulations of the metal(loid)s through time within the lysimeter system. A comparison at the start and end of the experiments can also demonstrate if there were any gains or losses from the system.

A further need for calculating mass balances arose due to difficulties in interpreting the migration and final locations of the leached metal(loid)s. In both lysimeter studies, the elemental concentrations within the wood remained high with little change. However, there was a small loss of arsenic, chromium and copper, resulting in elevated concentrations of the metal(loid)s in the soil. Although some instances existed where concentrations in the soil exceeded SGVs, these remained at orders of magnitude less than those in the CCA wood. The metal(loid)s were also present in the leachate of both studies suggesting that they had passed through the soil column. However, the concentrations were orders of magnitude less than in the soil despite exceeding EQS. Therefore, the trends suggest that some of the leached metal(loid)s must be lost from the system through another mechanism (i.e. not accumulating in soil or lost in leachate).

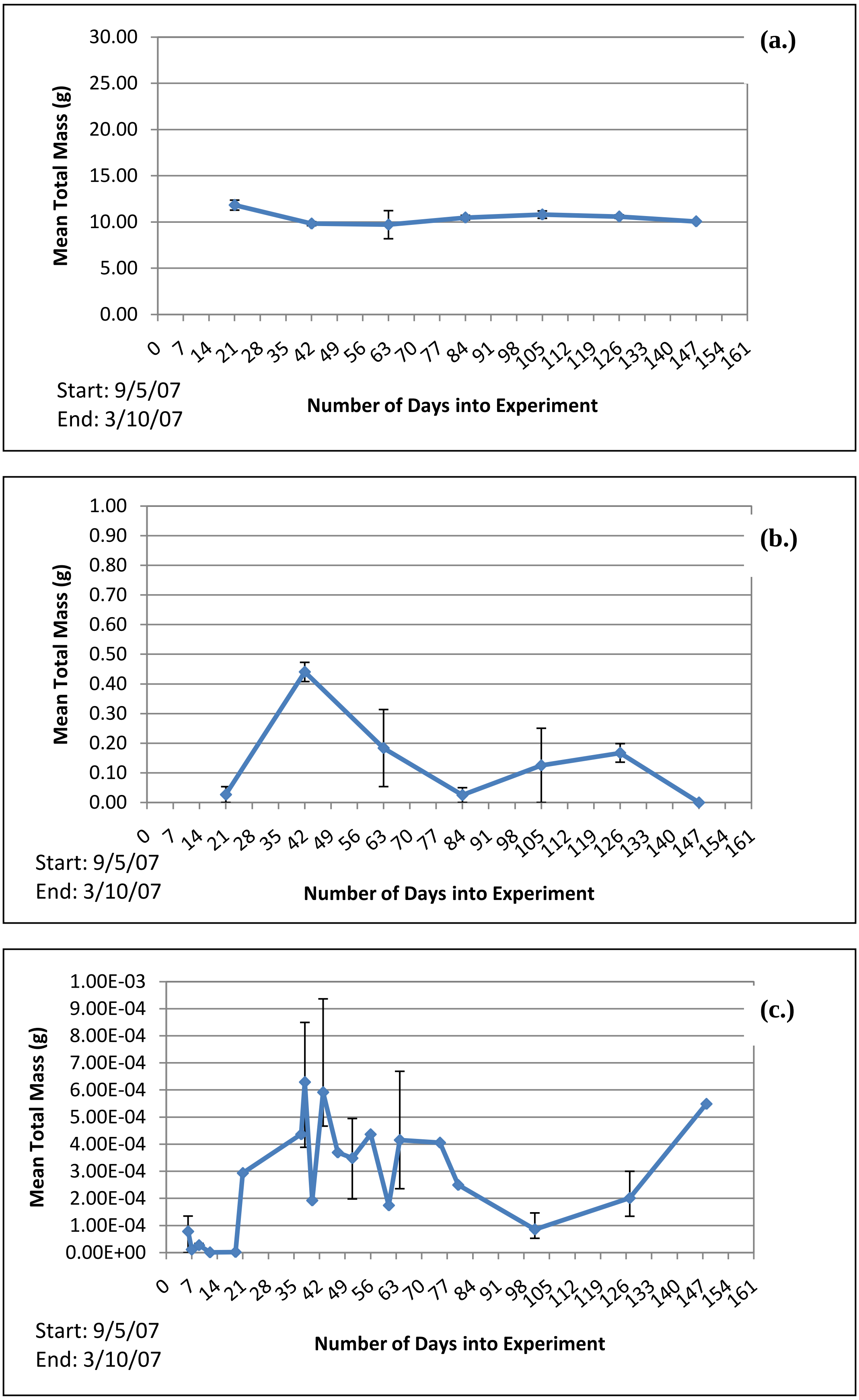
Mass balances were calculated for the CCA wood and soil lysimeters in both the long and short-term studies. In summary, the total arsenic, chromium and copper data for soil, woodchips and leachate were calculated by multiplying the average concentrations by the original quantity of each medium in the lysimeters. These calculations were carried out for each sampling date. Where data was missing (as in the case of the leachate), quantities were inferred from the analysed batches (see section 3.2.8.8 for more details). A mass balance between the start and end of the experiments was also calculated to determine the flux of elements throughout the sampling period.

7.3 Long-Term Study Mass Balance

Mass balances for arsenic, chromium and copper in the long-term leaching study (Figure 7-1 to Figure 7-3) show similar trends for all the metal(loid)s within each environmental medium studied (wood, soil and leachate). There was not much variation in the total mass of metal(loid)s in the wood over time. However, there was an initial decrease around days 21, 42 and 63 after which, the values remained more or less constant. This suggests that the elements are leaching out early in the experiment following exposure to rainfall. This is in line with the results from the SPLP experiments that showed that CCA-treated wood waste leached rapidly at high concentrations on initial exposure to a leachant. In the soil, all three elements increased rapidly around day 42 which appears to coincide with the loss of metal(loid)s from the wood. Concentrations then decreased in July before increasing again in the middle of September during a period of rainfall.

Leachate was monitored more frequently than the soil and woodchips and the resultant graphs give a more detailed trend over time. Initially, the quantities of metal(loid)s in the leachate were low but from day 21 increased and fluctuated at the same time as the wood was losing the elements and there was accumulation in the soil. Quantities remained high even after concentrations in the soil dropped, which could be due to a lag effect from the exceedance of the soil absorption potential and slow percolation from the base of the lysimeters. Quantities in the leachate then decreased from day 77 as levels in the soil increased. This period was characterised by no rainfall and as a result the metals leached from the wood were most likely re-adsorbed to the soil rather than passing through the lysimeter column. The final period of rainfall that occurred around days 98 and 105 resulted in a sharp increase in quantities of metal(loid)s in the leachate and a sharp decrease in quantities within the soil. This second stage of release may be associated with weathering of the wood and exceedance of soil adsorption properties.

When comparing all three elements across wood, soil and leachate (Figure 7-4), differences were found. In the wood, chromium was present in the largest quantities followed by arsenic and copper (Cu<As<Cr). This is a reflection of the preservative formulation. In the soil, copper was generally present in the highest quantities apart from two sample batches near the start of the experiment (day 42 and 63) where chromium was highest. Levels of arsenic were lowest in the soil (As<Cr<Cu). Conversely, in the leachate arsenic was present in the greatest quantities followed closely by chromium and copper (Cu=Cr<As). Arsenic is generally more mobile in the soil profile whilst chromium and copper are more effectively bound to the soil. This would contribute to the results seen in the mass balance.



Start: 9/5/07
End: 3/10/07

Start: 9/5/07
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Figure 7-1: Mean Values for Total Mass of Arsenic in the Long-Term Leaching Study: (a.) Wood, (b.) Soil and (c.) Leachate. Error Bars Represent Min and Max values. N.b. different scales.

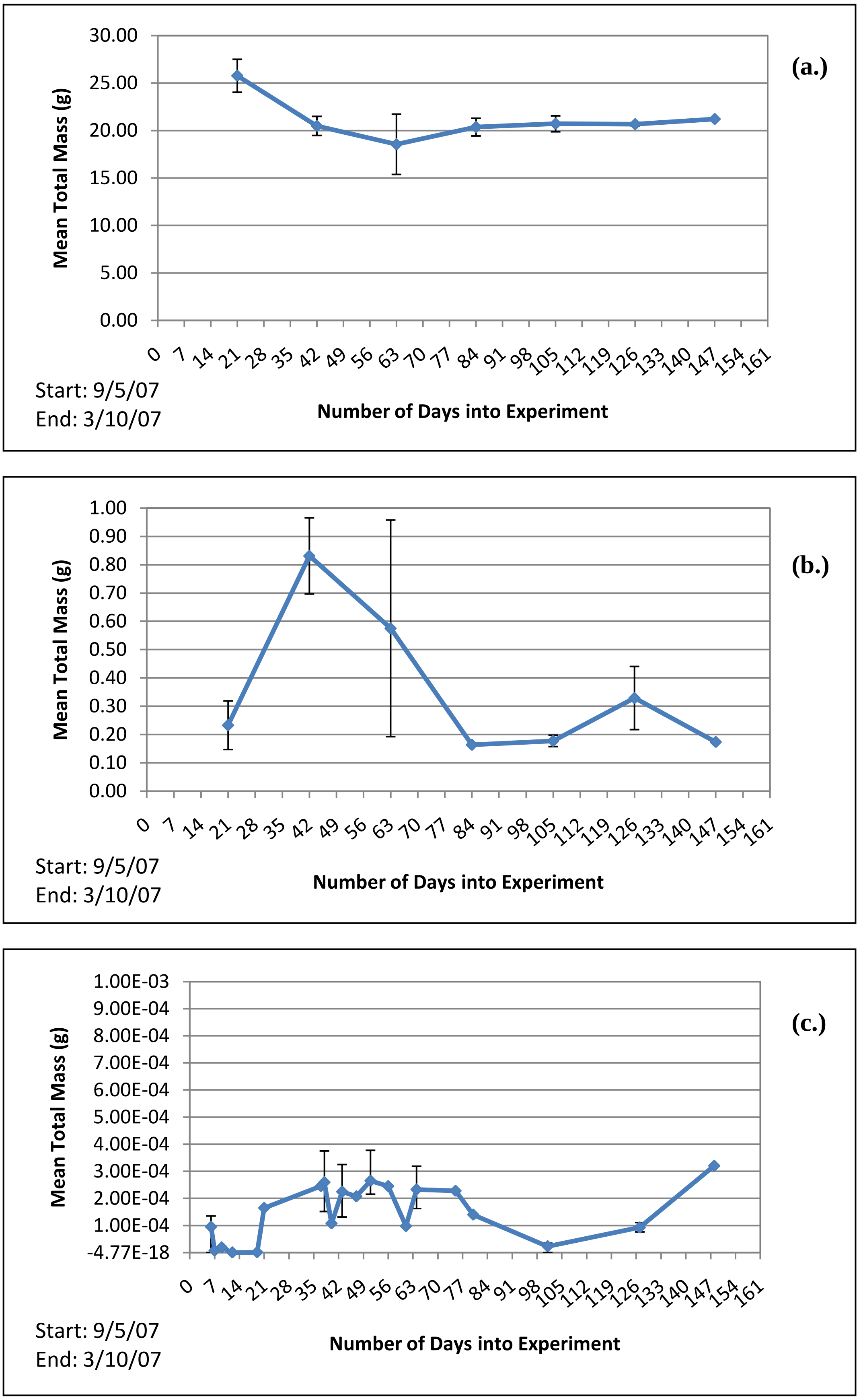

Figure 7-2: Mean Values for Total Mass of Chromium in the Long-Term Leaching Study: (a.) Wood, (b.) Soil and (c.) Leachate. Error Bars Represent Min and Max values. N.b. different scales.

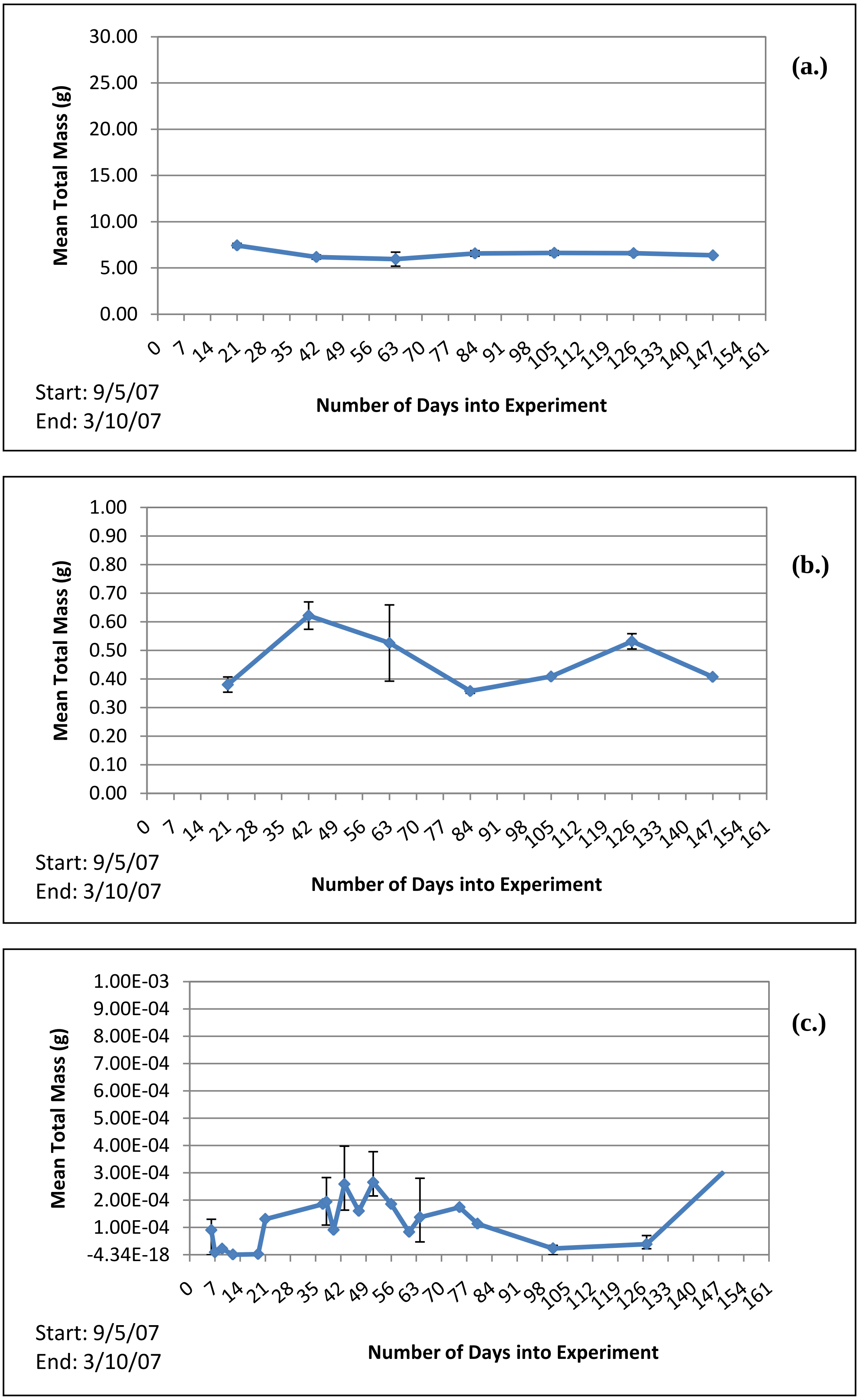

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Figure 7-3: Mean Values for Total Mass of Copper in the Long-Term Leaching Study: (a.) Wood, (b.) Soil and (c.) Leachate. Error Bars Represent Min and Max values. N.b. different scales.

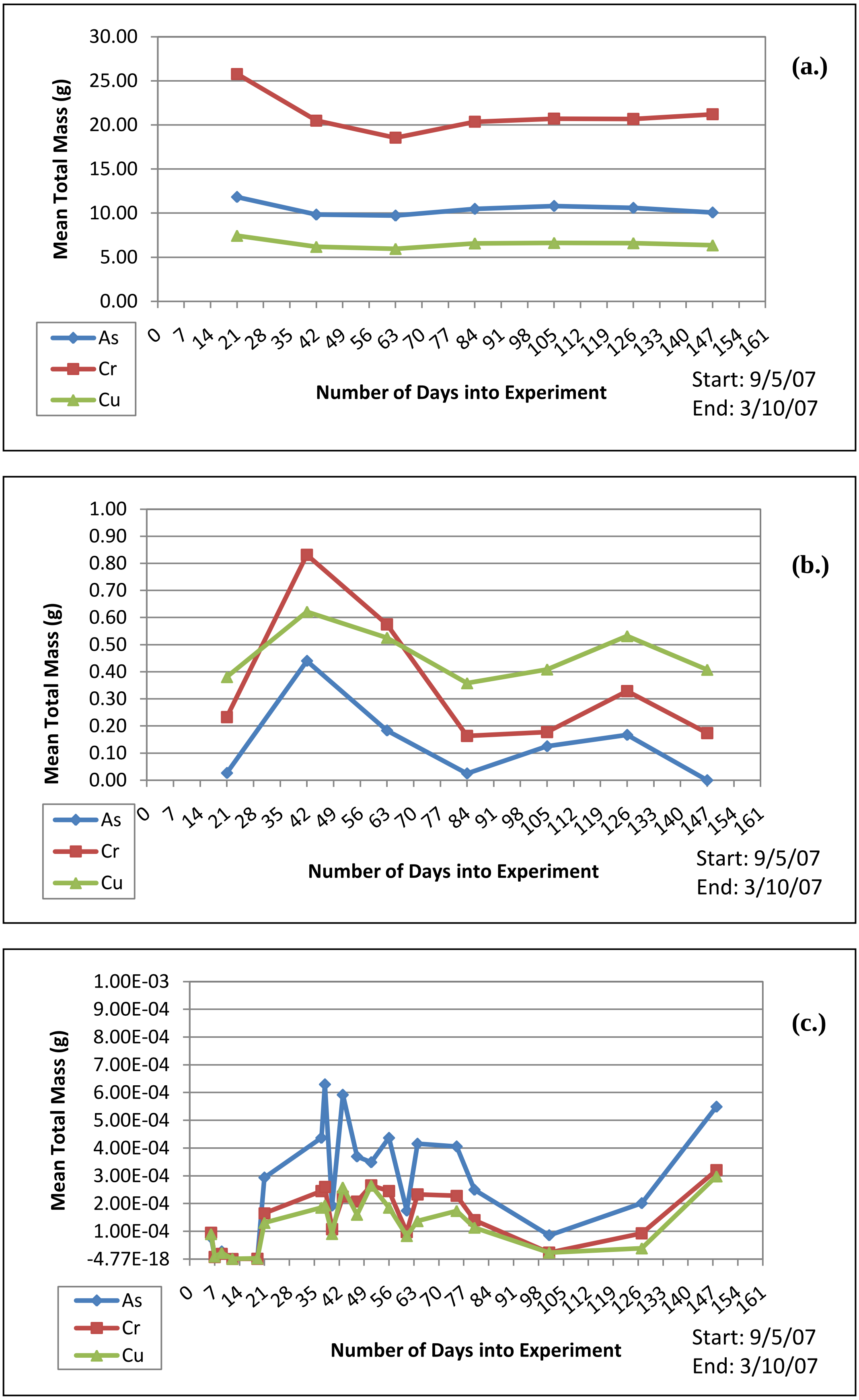

Figure 7-4: Mean Values for Total Mass of Metal(loid)s in the Long-Term Leaching Study: (a.) Wood, (b.) Soil and (c.) Leachate. N.b. different scales.

7.4 Short-Term study Mass Balance

Results for the mass balance calculations over time for arsenic, chromium and copper in the short-term leaching study are shown in Figure 7-5 to Figure 7-7. Quantities of all metal(loid)s in the wood were similar to those in the long-term study. Amounts remained fairly constant with a decrease towards the end of the month. This is similar to the trend observed in the first month of the long-term leaching study and may be due to the surface wash-off stage of leaching. Quantities in the soil and leachate were also within the range of the long-term study with slightly larger amounts at the start and end of the experiment. Again, this may be due to the initial washing-off leaching stage and where the adsorption potential of the soil was exceeded and the metal(loid)s travelled through the soil column into the leachate. The increase in quantities of the elements in the soil and leachate coincide with the leaching from the CCA wood.

When comparing all three elements in the various environmental media (Figure 7-8), there are similar trends to those found in the long-term study. In the wood, chromium levels are highest followed by arsenic and copper (Cu<As<Cr). In the soil, arsenic was least abundant (As<Cr=Cu). In the leachate it appears that copper was present in the greatest amounts followed by arsenic and chromium. However, due to the smaller amount of leachate generated in the lysimeters compared to the long-term study, statistical analysis could not be carried out to determine the significance of these results.

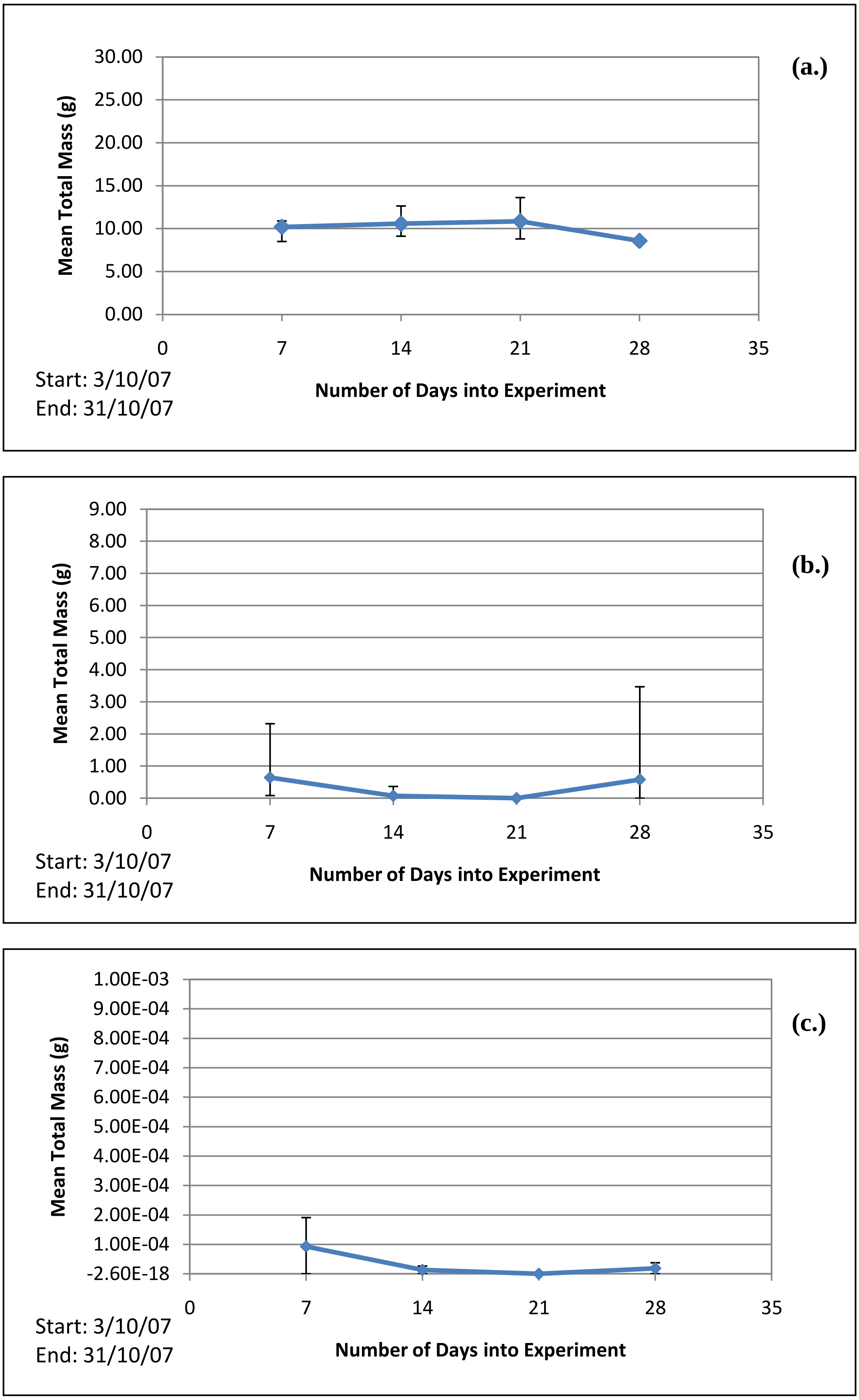

Figure 7-5: Mean Values for Total Mass of Arsenic in the Short-Term Leaching Study: (a.) Wood, (b.) Soil and (c.) Leachate. Error Bars Represent Min and Max values. N.b. different scales.

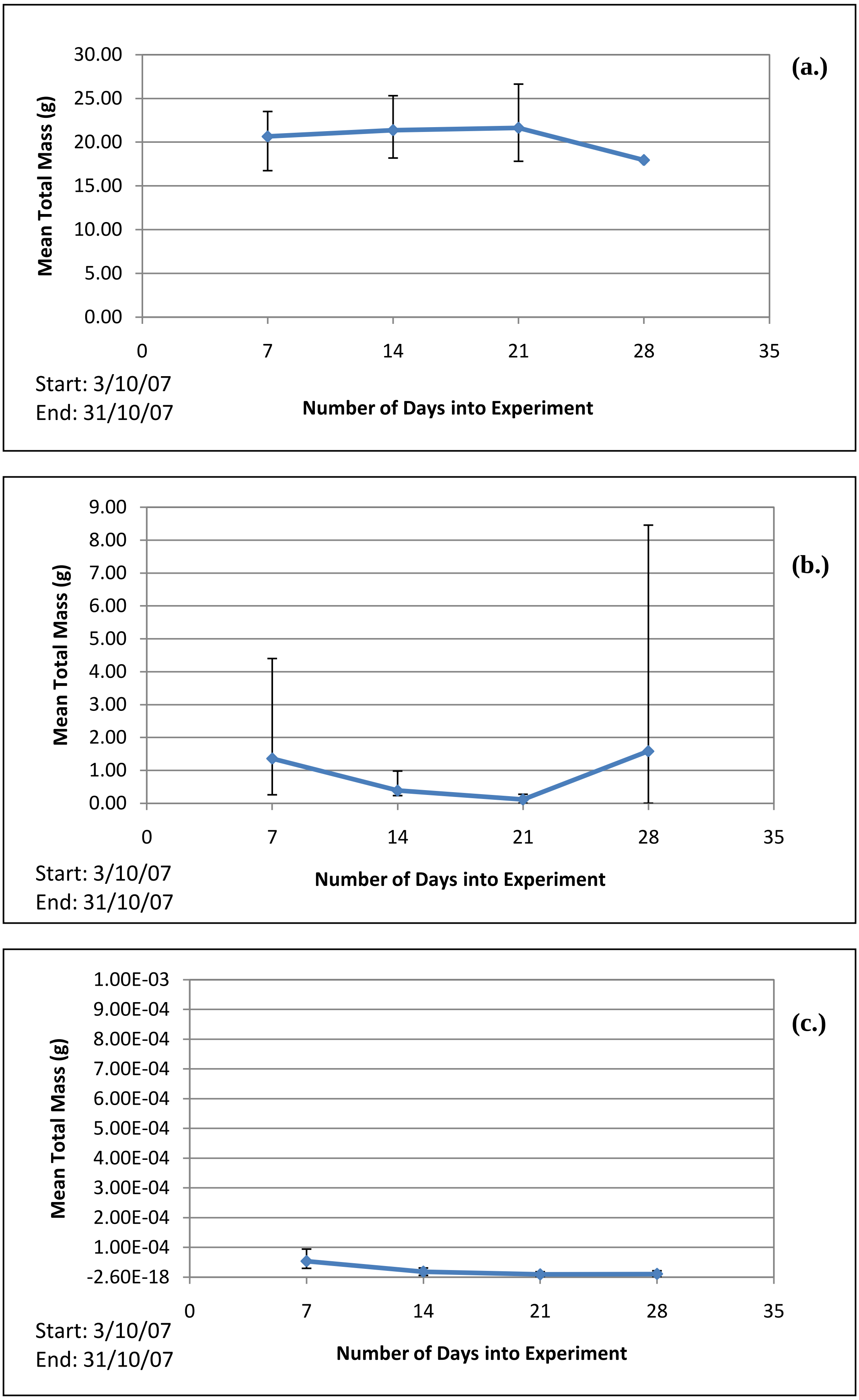

Figure 7-6: Mean Values for Total Mass of Chromium in the Short-Term Leaching Study: (a.) Wood, (b.) Soil and (c.) Leachate. Error Bars Represent Min and Max values. N.b. different scales.

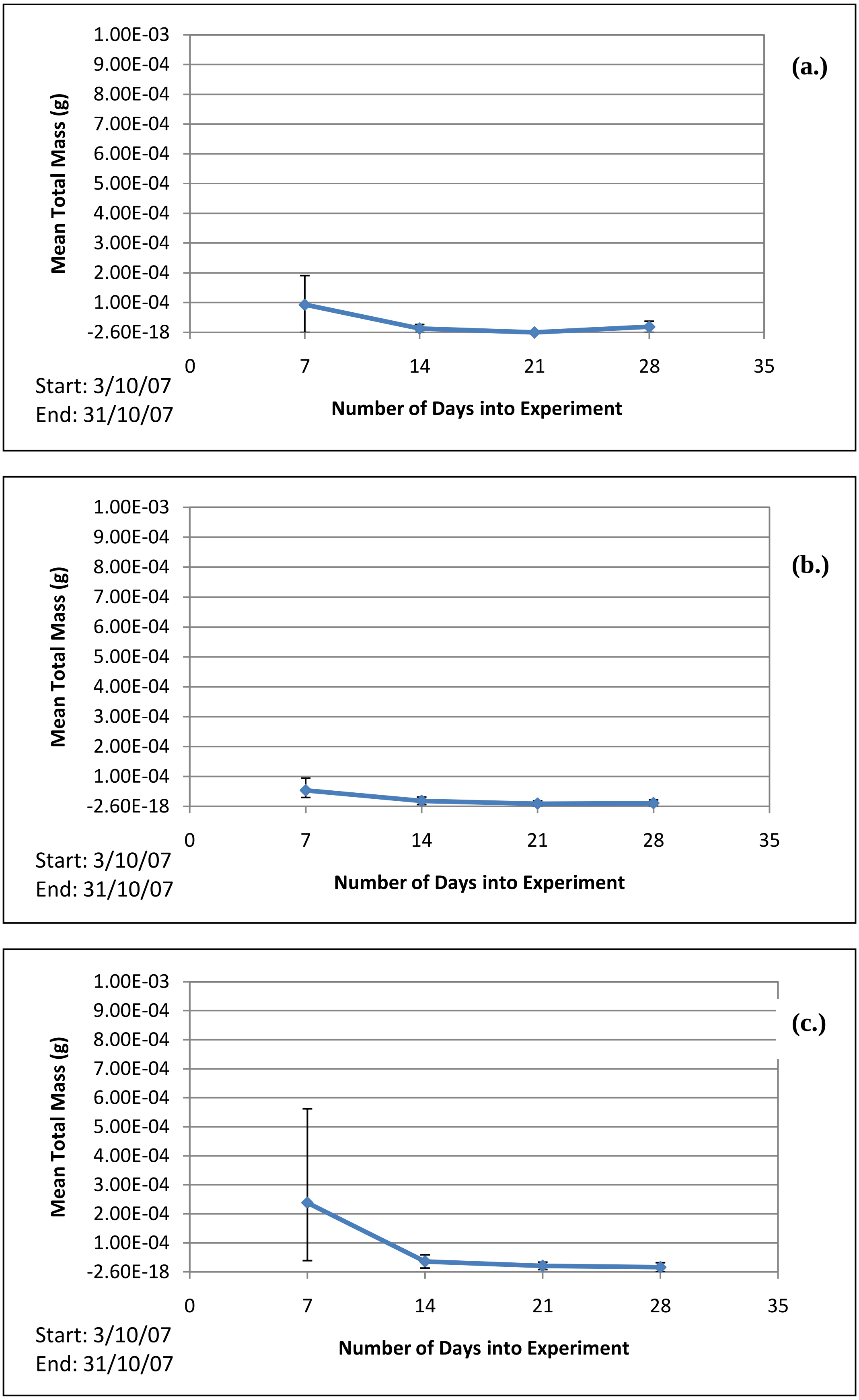

Figure 7-7: Mean Values for Total Mass of Copper in the Short-Term Leaching Study: (a.) Wood, (b.) Soil and (c.) Leachate. Error Bars Represent Min and Max values. N.b. different scales.

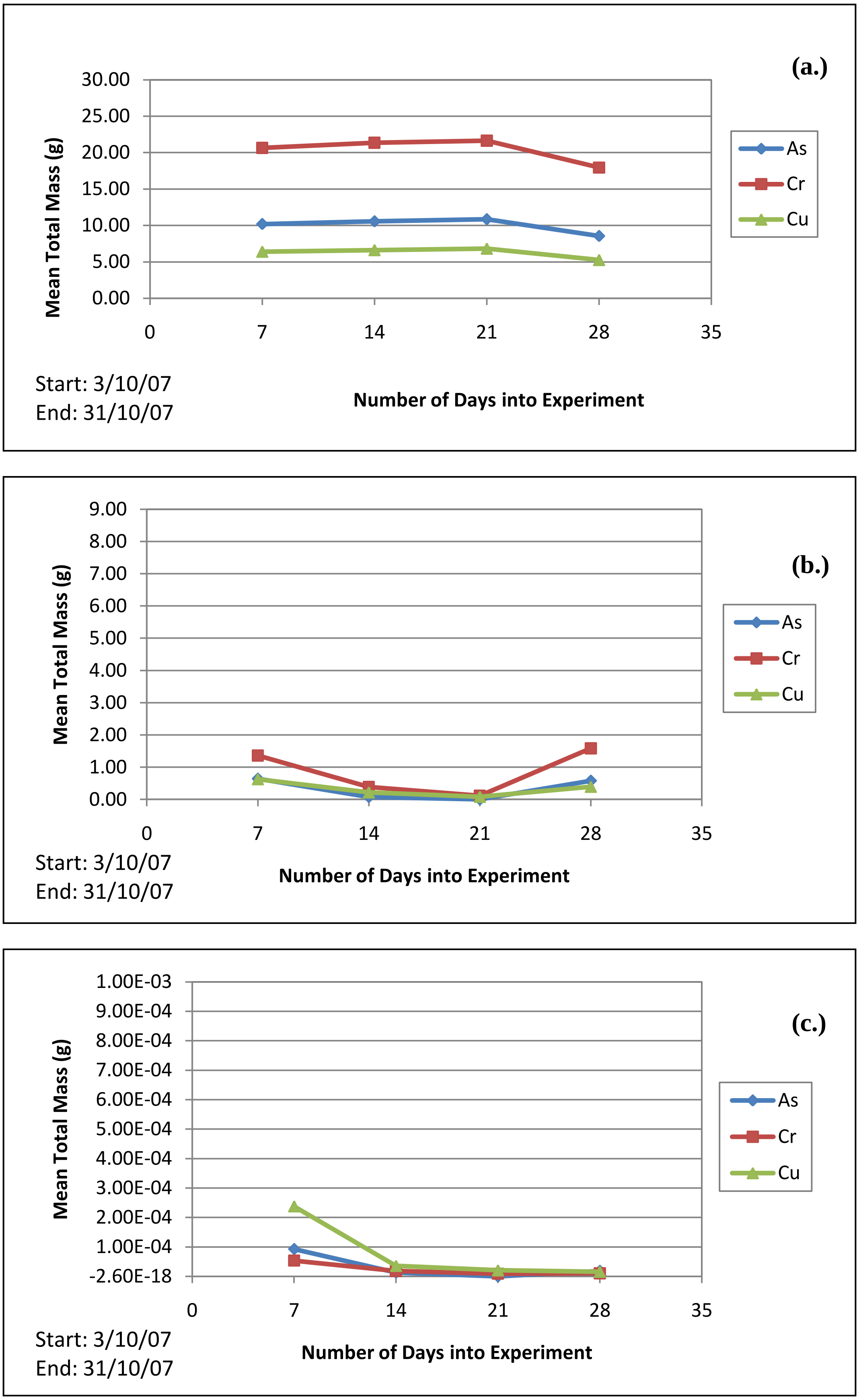

Figure 7-8: Mean Values for Total Mass of Metal(loid)s in the Short-term Leaching Study: (a.) Wood, (b.) Soil and (c.) Leachate. N.b. different scales.

7.5 Total Mass Balance

A total mass balance was calculated to determine changes in partitioning of the metal(loid)s at the start and end of each experiment (Figure 7-9).

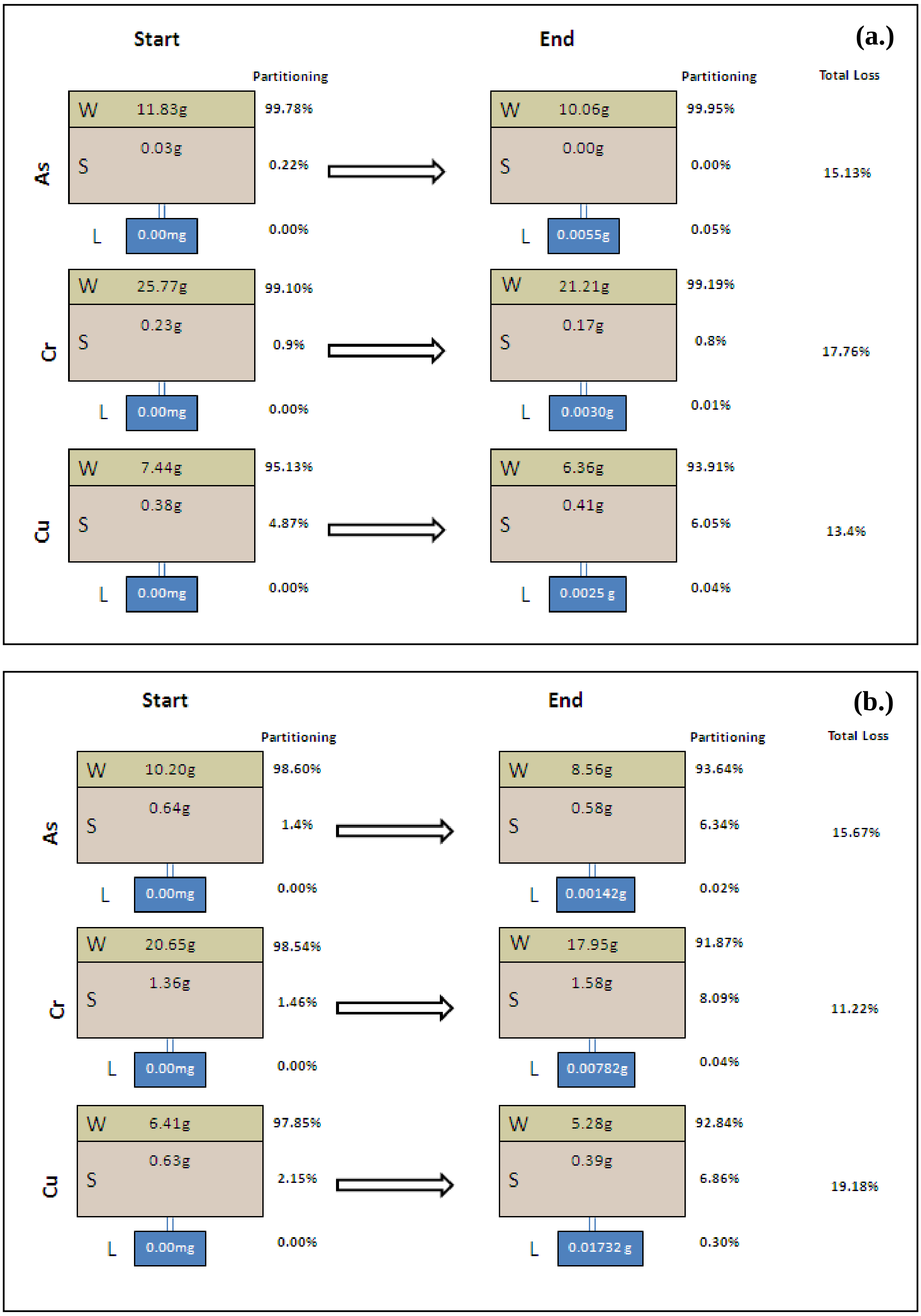

Figure 7-9: Mass Balance at the Start and End of the Long-Term (a.) and Short-Term (b.) Leaching Studies. W = wood, S = soil and L = leachate.

The mass balances showed that a high proportion of the metal(loid)s in the system were contained in the CCA wood (>95%). At the start of the experiments, the soil had less than 5% and there was no leachate. By the end of the experiments, the metals were still heavily partitioned in the wood suggesting limited leaching. This will act as a reservoir for prolonged contamination. Levels in the soil generally decreased or remained about the same, whilst smaller amounts leached through the system to the base. However, in all cases there was a net loss of all metal(loid)s in the system ranging from 13.4% to 19.18%. It is unclear why such a large loss would occur even following correction for missing leachate data (in the long-term study). However, as losses were observed in both studies and the magnitude was similar, it might be inferred that there was a further and unmeasured process taking place resulting in the loss of the metal(loid)s from the system.

7.6 Loss of Metal(loid)s from the System

The mass balances were based on the total metal(loid)s in the wood, soil and leachate. However, the significant loss from the system must have been either to the air or through removal from the surface, as all other potential pathways are accounted for. The lysimeters were weeded during sampling in an attempt to reduce the uptake of the elements by the plants. Arsenic, chromium and copper are reported to accumulate in plants by uptake from the soil (Speir *et al.,* 1992; Vajpayee *et al.,* 1999; Navqi & Rizvi, 2000; Ma *et al.,* 2006; Ko *et al.,* 2007; Rahman & Naidu, 2009), sometimes in toxic amounts (Navqi & Rivzi, 2000; Rahman & Naidu, 2009). Usually, the highest levels are found in the roots of plants (Vajpayee *et al.,* 1999; Navqi & Rizvi, 2000; Ko *et al.,* 2007; Smith *et al.,* 2009). The DGT profile study demonstrated that the metal(loid)s tend to accumulate in the top 5cm of the soil, the location of all the early stage plant roots. Furthermore, the more toxic and mobile of the chromium species was found to concentrate in the topsoil. Unfortunately, the weeds were not kept for analysis and the loss from this route cannot be quantified.

Another possible route through which metals might be lost to the system could be due to environmental processes. The lysimeters were filled quite high with material and it was observed that the surface water in the lysimeters overflowed during heavy rainfall and any metals present would have also been lost from the system through this route. This overflow water was not captured and measured.

Losses of arsenic from the system may have also resulted from volatilisation processes. Arsenic can undergo biotransformation in reducing soils where arsenate is reduced to arsine, then methylated to form methylarsines resulting in volatilisation from the soil to the atmosphere (Frankenberger & Arshad, 2002). In some cases, the loss of arsenic as arsines can be very high (Frankenberger & Arshad, 2002). Microbiological analyses and volatilisation processes were not carried out in this work and again losses from this route cannot be quantified. However, losses of all metal(loid)s were measured. Volatilisation is only likely for arsenic and in the case of the results, there was no preferential loss of arsenic over chromium and copper. Therefore, uptake by plants and/or overflow must be considered to be significant processes in metal(oid) losses.

7.7 Critical Evaluation of Mass Balance Data

Mass balances are useful for gaining an understanding of how elements are partitioned within a system and how they migrate. In this study, they provided an overview of the leaching patterns and interactions between the different environmental media through time. They also show if there were any losses or gains of particular elements in the system. However, their use can be problematic. For example, when calculating the mass balances in this study, average concentrations were used and multiplied by the volume/weight of wood/soil applied to the system. In the long-term study, only two samples of soil and wood were taken at each sampling date. Furthermore, two different lysimeters were selected each time and therefore the data do not necessarily represent the conditions in all the lysimeters. Once the concentrations were multiplied by the quantities of the media present, any discrepancies can result in major differences in the results. On the last sampling date, only one lysimeter was used. The problems of replication were rectified in the short-term study where twelve replicates were sampled each time.

In order to account for leachate batches that had not been analysed or collected, values were estimated from other data. However, this does not allow for unexpected variations within the data over time. This was the only way of producing a full set of leachate data that could be used for calculating the total mass balance of the system. There is only one other study that used a mass balance approach for studying leaching of a CCA in-service structure (Shibata *et al.*, 2007). In their study the authors also had to estimate when water overflowed the collection reservoirs or sampling dates were missed (Shibata *et al.*, 2007).

A further problem for mass balances in this case was a series of analytical problems. The soil, wood and leachate had to be acidified for digestion then diluted for analysis with ICP-OES. However, in the case of soil samples, the dilution resulted in the sample being very close to the limit of detection (LOD) for the instrument. As such, it is likely that in some cases where zero was reported, it may not reflect the true levels of metal(loid)s within the soil. Once the concentrations are used in the mass balance equation, this can result in differences between those results that are reported as zero and those that may just be over the LOD. However, errors from this source are likely to be small given the low concentrations.

Finally, mass balances can be calculated and reported in a variety of ways. The study by Shibata *et al.* (2007) used percentages rather than the mass of the metals measured in the various environmental media. As a result this study does not report the total mass movements within the system but only proportions, ignoring any losses. Complex mass balances can rarely account for 100% of the movement of metals in the system. Therefore it is important to report the results as mass so that any gains or losses in the system can be accounted for.

7.8 Fate of CCA Metal(loid)s Following Application to Land

The leaching of CCA treated wood waste and movement through soil and leachate is very complex and is controlled by a combination of external and physico-chemical factors related to the wood, soil and leachate. The fate of the CCA metal(loid)s within the lysimeter system is also complex (Figure 7-10). Although the bulk of the metal(loid)s remain in the woodchips, all the experiments have shown that these elements leach on exposure to a leachant. The amount leached out is significant in some cases and results in elevated concentrations in both soil and the leachate. In the SPLP, and lysimeter studies, regulatory limits in the soil and leachate were exceeded.

Previous authors have suggested that leaching from the wood occurs in three stages, with initial surface wash-off followed by diffusion leaching and final release as the wood weathers. The weathering wood releases the metal(loid)s due to breakdown caused by radical-induced depolymerisation (UV exposure) (Schmalzl *et al.,* 2003). As the lignin breaks down, the metal(loid)s which are bound to it are released (washed off and dissolved). Release mechanisms resulting from weathering include loss of wood fibres (Lebow *et al.*, 2003) and associated warping, cracking and splitting (Khan *et al.*, 2006a; Cooper & Ung, 2009). During the weathering process the metal(loid)s will therefore be leached by a combination of surface wash-off, diffusion leaching and loss of metal(loid)s still bound to the wood (due to loss of wood fibres). The metal(loid)s migrate into the soil where they are fixed to form various metal/organic compounds. When the adsorption capacity of the soil is exceeded, or if no time is available for fixation, the remainder of the more mobile species are transported through the soil column as leachate. It is likely that there was also a certain degree of uptake of bioavailable species from the soil by weeds. Biologically and physico-chemically remediated transformations of the elements may also result in methylisation of arsenic in particular and release through volatilisation. The metal(loid)s may also be lost by removal from the surface due to overflowing of surface water.

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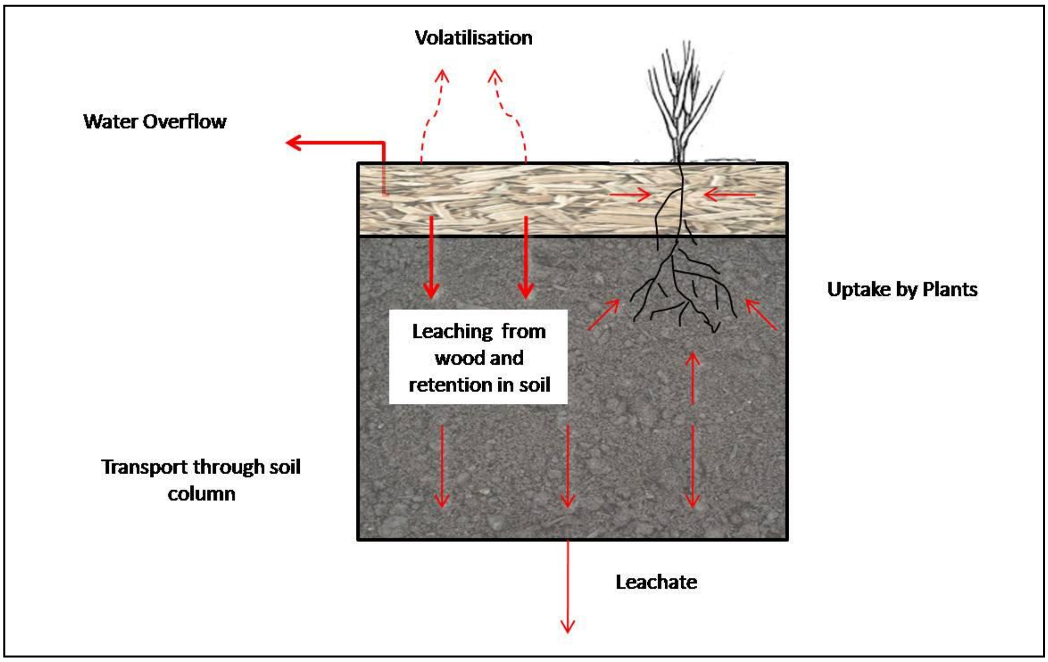

Figure 7-10: Fate of CCA Metal(loid)s Following Application to Land

7.9 Implications of Leaching

There are wide-ranging implications associated with the evidence of leaching from the CCA-treated wood waste used in this study. All of the present UK and WHO regulatory thresholds were exceeded, at times by two to three orders of magnitude. This may impact on the surrounding environment and human health following either direct or indirect exposure.

These limits were put in place to prevent potential impacts on human health and the environment. The Environmental Quality Standards are put in place to ensure that conditions in surface or groundwater are sufficiently good to support ecosystems.

Leaching of the metal(loid)s into surface and groundwater can result in toxic effects including accumulation of the elements in organisms, DNA damage, inhibited growth, altered behaviour and mortality. In terms of human health, the World Health Organisation limits on drinking water and UK soil guideline values were also exceeded with implications for chronic health effects (refer to section 1.5). Furthermore, all the guidelines are based on total concentrations of the metal(loid)s. However, the DGT and leachate speciation work highlights that the more toxic and mobile species of arsenic and chromium can be found in the soil and leachate and therefore pose an increased risk.

The results from the previous chapters have illustrated that the most severe risk of leaching is from CCA wood that is not combined with other soil materials (SPLP and CCA wood monofill results). The application to soil reduces the mobility of the metals through the adsorption and complexation mechanisms which occur in this medium. Copper which is a cationic species tends to bind to the soil by forming strong complexes with organic carbon (Chirenje *et al.,* 2003). This occurs primarily on the salicylate and phthalate ligands in humic acid due to a resulting net negative charge (Livens, 1991). Arsenic and chromium (oxyanions) form co-ordination bonds with Fe and Al oxides. These oxides form cationic bridges between the oxyanions and soil organic carbon and tend to be weaker bonds than the copper (Chirenje *et al.*, 2003). It has been reported that arsenic is incorporated into soils during hydroxide formation rather than by adsorption (Chirenje & Ma, 2006). However, all of these processes will reduce bioavailability.

The high levels of rainfall during the long-term study resulted in water-logging and anaerobic conditions in the soil. This increased the solubility and mobility of the metal(loid)s. In the future, extreme rainfall events like that observed in Hull in 2007 are predicted to increase in the UK due to climate change (Ekström *et al.*, 2005). Furthermore, temperatures are expected to increase in both summer and winter (UKCP09, 2009). Both these external factors have been shown to cause increased leaching of CCA elements from the wood. Added to this is the projected increase in CCA-treated wood waste entering the waste stream in the UK (Murphy *et al.*, 2004). Currently there is no single system that is effective in detecting CCA wood in the waste stream. Therefore removal and remediation is not always possible. This study has highlighted the potential impacts that can result from inadvertent application of CCA-treated wood waste to land and current trends suggest that this may become more of an issue in the future.

7.10 Summary

This chapter has presented the results from mass balances calculated for the CCA-treated wood and soil lysimeters in the long and short-term leaching studies. The mass balances have been used to characterise the leaching patterns and fluxes within the lysimeter systems. A summary of the main results are outlined below:

1. Similar trends were observed in both the leaching studies with quantities falling within the same range for the same components. Relative quantities in the wood were indicative of the preservative formulation. Quantities in the soil and leachate reflected the mobility of arsenic in relation to chromium and copper.

2. The wood tends to leach primarily at the beginning of the experiments following exposure to a leachant and at the end of the long-term study. The initial stage is related to the washing-off of metals from the surface of the wood exposed by the chipping process. In the long-term study, the release at the end of the study could be due to increased weathering of the wood. This was also observed in the CCA wood monofill. During times when quantities do not change, the wood may not be in contact with the leachant or a slower diffusion leaching process may be taking place.

3. Once leached from the wood, metal(loid) amounts build up in the soil, particularly at the surface. As more water is introduced into the system or the adsorption capacity of the soil is exceeded, the metal(loid)s move down in the soil water through the soil profile and accumulate in leachate at the base. There is usually a lag in trends from the soil to the leachate due to the initial adsorption to the soil.

4. The calculation of total mass balances revealed that there were losses of the metal(loid)s in both studies. This may be due to plant uptake, volatilisation and loss of water from the surface. However, given the patterns of loss, the most likely pathway is through plant uptake. This has important implications for the application of wood chips in horticulture.

5. Although the mass balances have limitations, they are useful for understanding the movement of metal(loid)s through the system and therefore the implications of leaching. These include impacts to human health and the environment.

The concluding chapter will revisit the original aims of the research and discuss how these aims have been reached. A summary of the main research findings will be presented and used to identify areas that are in need of future research.

8 Conclusion

8.1 Introduction

This chapter summarises the main findings from the monitoring of the lysimeter experiments carried out during this study to characterise leaching from CCA-treated wood waste. These results are discussed in light of the original aims of the thesis as outlined in the introduction chapter:

1. To quantify the leaching of arsenic, chromium and copper from CCA-treated wood waste mulch using a combination of field and laboratory based experiments.
2. To evaluate the distribution and movement of the elements between the wood mulch, soil and leachate.
3. To determine the inorganic arsenic and chromium species present in soil and leachate.
4. To determine the factors responsible for leaching from CCA-treated wood waste mulch.
5. To compare the levels of arsenic and chromium in the soil and leachate with UK regulatory thresholds.
6. To evaluate the potential implications of the results for environmental and human health.

The second part of the chapter will make suggestions for further work and consider recommendations for wood waste management based on the results from the current study.

8.2 Review of the Main Findings

8.2.1 Quantification of Leaching of Arsenic, Chromium and Copper from CCA-Treated Wood Waste Mulch

In order to quantify leaching from CCA-treated wood waste, a combination of field and laboratory based experiments were used. This holistic approach has proven effective in quantifying leaching in both soil and water. Overall, the wood was found to be fairly resistant to leaching. However, due to the high retention values of the metals in the wood even after prolonged use, small amounts of leaching such as those observed in the experiments resulted in significant pollution of both soil and leachate.

A Synthetic Precipitation Leaching Procedure (SPLP) was carried out to ascertain leaching from fresh and weathered CCA wood. The elements leached out in larger quantities from the freshly treated wood than the weathered wood. In the long-term lysimeter leaching study, a CCA wood monofill was used to replicate the SPLP over a longer time scale. The results indicate that freshly treated wood leaches preservative components very rapidly in an initial phase caused by wash-off of freely available surface deposits. A similar mechanism takes place in chipped weathered wood due to the exposure of new surfaces by the chipping process. This rapid release stage is then followed by a slower and longer period associated with diffusion leaching. As the wood begins to weather over time, metal(loid)s are released causing a second increase in leaching rates.

In the lysimeter studies (long-term, short-term and DGT), the wood was exposed to soil. In all cases, levels of contamination in the soil of CCA-containing lysimeters were elevated compared to the untreated wood-containing lysimeters. The DGT study revealed that most of the mobile constituents are translocated to the top 5cm of the soil profile. The presence of soil results in lower concentrations of the metal(loid)s in the leachate compared to leachate from the CCA wood monofill or SPLP study.

In all studies, arsenic was found to be the most mobile of the elements studied followed by both chromium and copper. As a result, the proportions of each metal leaching out of the wood were not consistent with the original preservative formulation used.

8.2.2 Distribution and Migration of the Elements in the Lysimeters

The distribution and migration of the elements in the lysimeters was evaluated using mass balances. Similar trends were observed in both the long and short-term leaching studies. Once the metal(loid)s leached out of the wood, contamination levels increased in the soil through deposition, adsorption and complexation processes. When large volumes of water were added to the lysimeters (as observed in the long-term study), or if the adsorption capacity of the soil was exceeded, small amounts of metal(loid)s moved through the soil profile and were removed from the system as leachate at the base. The processes in the soil caused a time lag before the metal(loid)s were detected in the leachate.

Overall, there was a loss of metal(loid)s to the system and this may have been caused by plant uptake (with weed removal), volatilisation of arsenic and loss of surface water in the lysimeters due to waterlogging. The most likely cause of the loss is from plant uptake, as levels in leachate were low and therefore not likely to be significant. Furthermore, volatilisation of arsenic would have resulted in preferential losses, however this was not the case.

8.2.3 Speciation of Arsenic and Chromium in Soil and Leachate

Limited work on metal speciation was carried out on selected leachate and soil samples. In order to predict the stable species across all samples, Eh/pH diagrams were used. The Eh/pH conditions for soil samples in both the the long and short-term studies suggested that arsenic would be present in the pentavalent form and chromium in the trivalent form. Both of these species are less mobile and toxic of all the inorganic species. However, when analysing samples of leachate for inorganic arsenic and chromium species, it was found that trivalent arsenic was present in all samples apart from the untreated wood monofill. In the soil, *in situ* measurements of chromium were conducted using DGTs. Both trivalent and hexavalent chromium species were detected. In the top 5cm of the soil profile, hexavalent chromium was present in greater amounts.

The results demonstrate that Eh/pH diagrams are a useful guide for the majority of samples, however, the presence of the more toxic and mobile species of arsenic and chromium in the samples suggest they are not always accurate. This is due to the fact that the diagrams represent certain Eh and pH ranges in aqueous solutions at 25°C and 1 atmosphere. In this case they were applied to soil as well as leachate and therefore may not be as accurate. Furthermore, in both lysimeter experiments, temperatures fluctuated well below the 25°C condition. In addition, the diagrams illustrate conditions in a static system where equilibrium is reached (Stumm & Morgan, 1981, p.441). However, the environment in both the soil and leachate was highly dynamic as can be seen in the physico-chemical and metal(loid) concentration results.

8.2.4 Factors Affecting Leaching

There are many factors which may affect leaching of CCA from the wood and soil and not all of these were covered in this study. In terms of the physico-chemical factors, the following were found to increase leaching:

Weather Conditions

- The intense and long duration of rainfall events experienced in the long-term leaching study.

Conditions in the Soil

- High soil moisture content.
- High levels of soil organic matter.
- Reducing soil redox conditions.

Conditions in the Wood

- High loading value of the elements in the wood and the Cr-rich formulation used to treat the wood.
- Duration of contact with the leachant.
- High Degree of As:Cu in the original preservative formulation.
- Increased surface area of the wood resulting from chipping.
- Structural breakdown and weathering of the wood.
- Decreased resistance to structural breakdown due to weathering.

In addition, other studies have shown that conditions in this study would influence leaching of the metal(loid)s. These include:

- Exposure to UV radiation.
- Dry/wet cycles resulting in warping, cracking and splitting of the wood.
- Sandy loam soil texture.
- Low background levels of arsenic, chromium and copper in the soil.
- Soil attenuation levels for binding of metal(loid)s.
- High concentrations of common elements in the soil such as aluminium, calcium, iron and manganese.

- Age of the wood.

8.2.5 Toxicity of Soil and Leachate in Relation to Regulatory Guidelines

In the leaching studies, most of the UK and WHO regulatory guidelines for soil and leachate were exceeded. In the long-term leaching study, the soil guideline values (SGV) were not exceeded. This was probably due to the high levels of rainfall entering the system, flushing the metal(loid)s out of the soil. In the short-term study the SGVs were exceeded by up to 8.7 times for arsenic and 3.3 times for chromium. The leachate collected from the SPLP, CCA-treated wood and soil lysimeters and CCA wood monofill exceeded Environmental Quality Standards (EQS) and World Health Organisation (WHO) Drinking standards by up to three orders of magnitude.

8.2.6 Potential Implications for Human Health and the Environment

There are wide-ranging implications associated with the levels of leaching observed in the studies. The toxicity of the metal(loid)s can result in adverse environmental effects including contamination of soil and surface/groundwater. Biological effects may also be seen at the community, population and organism level. There are many human health effects associated with chronic exposure to arsenic and chromium. With regards to this study, the major pathways are likely to be ingestion of contaminated soil/chips if children are in close vicinity of the wood mulch (i.e. woodchips used in children's playgrounds). Potential ingestion via contaminated soil/groundwater may also be possible as regulatory threshold values in leachate were exceeded. Consumption of crops/plants grown in soil contaminated with CCA leached metal(loid)s is also a risk considering the translocation of the leachate to the top 5cm of the soil, bioavailability of the species present and loss of metal(loid)s by plant uptake. This risk may also extend to livestock that have consumed the contaminated media/plants.

Dermal absorption is another pathway, particularly for arsenic. As the wood is completely exposed, it is likely that if it is used in a residential setting, there will be human contact. Inhalation may also be a significant route particularly during size reduction of CCA-treated wood.

The health effects resulting from exposure are numerous. Arsenic and hexavalent chromium are known carcinogens and arsenic exposure can also manifest in various health problems around the body. Hexavalent chromium exposure can cause irritation and sensitisation of the skin as well as corrosion of mucous membranes of the respiratory system and cancer of the lungs.

The risks associated with leaching from CCA-treated wood waste are predicted to increase in the future due to the projected increase in the wood waste stream and inadequate detection methods. Climate change models predict increases in temperatures and extreme rainfall events in the UK such as those observed in the long-term leaching study.

8.3 Recommendations for Future Research

The findings of this thesis have highlighted areas that are in need of future research in order to further understand the leaching processes and the factors involved.

8.3.1 Experimental Design

The lysimeter designs used in the study were quite simplistic and relied on the use of cheap components. Changes in lysimeter design should be trialled based on the requirements of the study and to improve sampling. For example, pumps can be added to the base of the lysimeters to aid the draining of leachate. This would have been particularly useful in the long-term leaching study where pooling and loss of leachate was noted in the lysimeters, particularly following periods of heavy rainfall. Cylindrical leaching columns or closed systems could also be trialled. Furthermore, various probes to measure pH and redox can be utilised to provide *in situ* readings with a higher temporal resolution than using portable probes. An additional weakness of the long-term study was the limited number of replicate lysimeters. In future studies, a greater number of lysimeters need to be incorporated into experiments.

The longest leaching experiment lasted five months. Although this was adequate time to observe the leaching processes, a study over a longer timescale (i.e. 2-3 years) would be beneficial in order to see the trends in more detail and assess the impact of leaching arising from wood weathering. In order to measure this, samples of the wood need to be kept and analysed with a scanning electron microscope (SEM) to see how the surface of the wood is degrading over time.

All of the fieldwork has concentrated on using lysimeters. A field plot study using naturally occurring soil would be more indicative of real world conditions and would allow for the natural movement of the metal(loid)s to be studied both radially and with depth.

A finding of the mass balances was that there was a significant loss of metal(loid)s in the lysimeters system. This may be through volatilisation, plant uptake processes and loss of surface water. As these losses were not entirely accounted for, any future work should attempt to identify and quantify the losses through experimental re-design, plant uptake studies and measurement of arsenic volatilisation.

8.3.2 DGT Study

The DGT studies proved very useful for understanding heavy metal transport. These studies could be extended and enhanced by measuring at higher spatial resolutions in the soil profile. Arsenic and copper speciation can also be studied using DGTs, as some results indicate potential speciation occurring in the gels. Finally, a DGT capable of measuring both anions and cations by combining ferrihydrite and Chelex-100 gel in the binding layer (Mason *et al.* 2005) could be used in future studies and compared to the DGT studies in this work that use separate binding layers. This can be used to determine if the combined hydrogel is an effective and time saving technique for measuring arsenic and chromium in this setting.

The results from the DGT profile study could also be strengthened by accompanying them with measurements of total metal(loid)s in the profile. This would allow the partitioning of metal species in the soil to be quantified.

8.3.3 Factors Affecting Leaching

This study investigated the main factors affecting leaching of CCA into and through soils. However, not all factors were examined and their role in the leaching processes observed in the study is therefore not proven. For example in the soil, Fe and Al exchangeable cations, cation exchange capacity and inorganic C can all influence retention of metal(loid)s in the soil (Zagury *et al.*, 2003). However, these were not analysed and future work should address this.

The effects of microbiology in the transformation of the metal(loid)s was unaccounted for and may play a significant role in the leaching trends observed. Some microbes can be resistant to CCA and may affect leaching by changing the local environment. For example, Jambeck *et al.* (2006) found that in a lysimeter environment, micro-organisms reduced the pH, thereby accelerating leaching from the wood. Some bacteria also consume fatty acids and resin acids in the wood affecting release of preservative compounds. Future work could concentrate on microbial diversity, community structure and activity (enzyme activity). The role of CCA resistant microbes could also be explored alongside isolation of the genes in bacteria that can reduce/oxidise arsenic and chromium species.

The individual contribution of leaching factors was assessed in this work. Only the relationship of pH and redox on leaching was assessed in the soil and leachate of the lysimeter studies. Further work is required in order to understand how the factors may interrelate and either promote or hinder leaching.

8.3.4 Speciation Study

The speciation work undertaken in this study was very limited but identified some interesting results. Future studies should concentrate on the quantitative speciation of arsenic chromium and copper in soil and leachate using the techniques employed briefly in this study. The simultaneous arsenic and chromium method used on the leachate is quick and easy and could be used in future studies. For speciation in soils, the DGT method could be used alongside more established methods such as chemical extraction.

8.4 Recommendations for Management of CCA-Treated Wood Waste

CCA-treated wood waste needs to be carefully managed in the future to reduce the potential for contamination of the environment. The first step is to be able to identify whether wood waste has been treated with CCA and to what extent (Peylo & Peek, 1998). In the current study it was found that the common techniques for identifying CCA wood by observation and chemical stains were not effective due to different initial retention quantities of the preservatives, inhomogeneous distribution of the preservative and variations in environmental and biological conditions for each particular wood component (Peylo & Peek, 1998; Peylo & Peek, 1999; Khan *et al.*, 2004; WRAP, 2004). Furthermore, the use of laboratory techniques such as ICP-OES and ICP-MS were very time consuming and costly to run. Therefore, they are not applicable for the detection and sorting of wood at waste/recycling plants. Various studies on analytical techniques for rapid sorting and identification have been undertaken (Homan & Militz, 1994; Jacobi *et al.*, 2007; Solo-Gabriele *et al.*, 2004a). Further research and development is required for the most promising techniques to ensure their applicability for large volume of wastes, operating capabilities and costs. These include hand-held XRF units and/or mounted automatic XRF units that can be used on conveyor belts

(Jacobi *et al.,* 2007) and laser induced breakdown spectroscopy units (Solo-Gabriele *et al.,* 2004a).

Once the wood has been detected, the harmful components must be remediated to reduce the risk. There are numerous studies outlining emerging technologies with the potential to remediate the harmful chemicals in CCA. This can be through biological (Cole & Clausen, 1996; Clausen 1997; Yang & Illman, 1999; Clausen, 2000; Kartal & Imamura, 2004; Son & Lee, 2005), chemical (Honda *et al.,* 1991, Kristensen *et al.,* 2001; Velizarova *et al.,* 2002; Kartal, 2005; Tarakanadha *et al.*, 2005; Christensen *et al.,* 2006; Kakitani *et al.,* 2006) and mechanical processing or a combination of all three (Clausen & Smith, 1998). As with sorting and identification technologies, many of these developments are still in their infancy and have not been proven to be economically viable (WRAP, 2005). On the technical front, none have demonstrated 100% removal of the treatment chemicals. According to WRAP (2005), even a 90% removal of CCA components from wood waste may still leave it unsuitable for re-use. Further research and development is required in this area.

Due to the risks associated with CCA and the introduction of the partial ban, attempts have been made to reduce the use of CCA by developing more environmentally friendly alternatives such as copper based biocides including copper azole and biodegradable organic biocides (Enviros Consulting Ltd and Biocomposites Centre, 2004; Solo-Gabriele & Townsend, 2000). Although these alternatives leach less arsenic, they leach more copper than CCA-treated wood (Solo-Gabriele *et al.,* 2003). Again this is a positive trend in reducing the use of CCA and needs to be continued. However this does not combat the high proportion of CCA treated wood that is still in service and will eventually end up as waste.

The option of reusing CCA-treated wood waste is highly restricted and governed by the Marketing and Use Directive (SI 2003 No. 3274) Regulations, 2003. Recycling options are also limited though there is potential for its use in exterior flakeboard products, wood-cement composites, and wood-plastic composites (Solo-Gabriele & Townsend, 2005; WRAP, 2005). Recycling options that are excluded from using CCA treated wood waste include composting, mulching and animal bedding (WRAP, 2005).

Incineration of CCA treated wood waste is not a favourable option as there are associated issues with the control of arsenic emissions (Khan *et al.,* 2004; Solo-Gabriele & Townsend, 2005; WRAP, 2005). The CCA components in the wood are oxidised and released, with the arsenic converting to toxic arsenic trioxide. The ash produced from burning is also toxic (Comfort, 1993). If the other waste management routes are not appropriate the wood waste should be disposed in hazardous waste landfills without any reuse, recycling or energy recovery (TRADA & Enviros Consulting, 2005).

The current study has demonstrated that inadvertent application of CCA wood waste as mulch can contaminate underlying soil and surface/groundwater. In situations where this is suspected and confirmed, the wood should be removed, and followed by remediation of the surrounding area. This can include immobilisation methods such as containment, soil washing, electrokinetic remediation, bioremediation, phytoremediation and permeable barriers (Ramussen *et al.*, 1999; Blaylock *et al.*, 2004).

8.5 Summary

This thesis has presented the data collected from laboratory and lysimeter-based leaching studies used to determine leaching from CCA-treated wood. The distribution and behaviour of the leached elements was also determined in soil and leachate. The main factors involved in the leaching process were also examined. A range of physico-chemical measurements, elemental analysis and speciation were carried out on the samples. The results have been used to determine the toxicity of the leached components and potential for environmental and human health impacts.

It is hoped that the findings of this study will encourage future research in leaching of CCA-treated wood waste with emphasis on the influencing factors, speciation and loss of metals from the system. General recommendations for management of the wood waste in the future include development of sorting and identification methods to detect the contaminated wood in the stream to ensure that it does not inadvertently end up as mulch and remediating soils/surface water that have been contaminated with this mulch.

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